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Reduction of heavy metal contents in liquid effluents by vermicomposts and the use of the metal-enriched vermicomposts in lettuce cultivation

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Abstract

The removal of Cu, Ni and Zn from electroplating effluents by adsorption in cattle manure vermicompost has been discussed. A glass column 38 cm long and 7 cm i.d. was loaded with cattle manure vermicompost and effluents were passed through it. The metal concentrations were measured in the elutant. The experiments on adding effluent aliquots into the columns were continued until the metal concentrations in the elutant reached the maximum values established for effluent discharges in water courses by the Brazilian quality criteria, i.e., $Cu = 1.0$ mg L^{-1}, $Ni = 2.0$ mg L^{-1}, and $Zn = 5.0$ mg L^{-1}. The amount of Cu retention by the vermicompost was determined at the natural effluent pH (2.0). The Zn and Ni retentions were evaluated at the natural effluent pH (6.9 and 7.4, respectively) as well pH 2.0. Vermicompost residues obtained from this process were used for lettuce cultivation. The vermicompost was found to be efficient in removing metals from the electroplating wastes, as well as in the increase of its pH values. Metal retention values were close to 100%. The Cu concentrations in lettuce leaves from the treatment with vermicompost enriched with this metal were below the range of critical toxicity level to plants, i.e., from 20 to 100 mg L^{-1}. However, the estimated Cu concentrations in the roots from the treatment with vermicompost enriched with Cu were much larger than that of the treatment with the natural vermicompost, reaching 246.3 mg L^{-1}. The Ni and Zn concentrations in lettuce leaves from the treatments, with vermicomposts enriched with the respective metals, were above the range of critical toxicity levels to plants, i.e., from 10 to 50 mg kg^{-1} and from 15 to 30 mg kg^{-1}, respectively. However, no symptom of toxicity was found visually. Larger accumulations of Cu, Ni and Zn were found in the lettuce leaves than in the roots after the treatments with the uncontaminated vermicompost. A greater absorption of Cu and Ni by roots was found in treatments with vermicompost enriched with these elements, whereas Zn was found preferentially in the leaves. The statistical analysis was done by analyses of variance and regression.
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1. Introduction

One of the most important sources of pollution is the discharge of industrial effluents into soil and surface waters. Electrochemical methods are employed in metal finishing for protection and/or decoration of a variety of metal surfaces (Förstner and Wittmann, 1981). In the electroplating process, the rinsing operation to remove excess chemicals from the treated surfaces produces effluents containing high metal concentrations. Currently, most of the electroplating wastes in Brazil are discharged into water courses without a suitable treatment. The presence of heavy metals such as Cu, Ni and Zn in waste materials dis-

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charged into water courses may be toxic to the flora and fauna (Gigliotti et al., 1996). This requires controlled discharge of effluents to avoid hazardous situations. Significant reductions of metal concentrations in liquid effluents can be achieved by the humic substances in vermicomposts (Jordão et al., 2002; Pereira and Arruda, 2003). These materials contain a great number of sorption sites that interact with the metals. The organic fraction of vermicompost represents about 50% of its weight (Senesi et al., 1989).

Different organic wastes can be used in vermicompost production, such as urban solid waste (Alves and Passoni, 1997), swine manure (Atiyeh et al., 1999), residues of plant decomposition (Kamergam et al., 1999), sewage sludge and sugarcane pulp (da Silva et al., 2002), among others. The vermicompost can also be produced from cattle manure (Kiehl, 2001). Animal manures contain significant quantities of plant-available nutrients which could increase crop yields (Eneji et al., 2001). Waste reduction by recycling is an important part of any integrated liquid waste-management system.

The use of vermicompost seems to be a good alternative for reducing heavy metal contents in liquid effluents. The vermicompost residues obtained after the purification of effluents might be used in agriculture. Lettuce is a vegetable that accumulates relatively large amounts of heavy metals such as Cu, Zn and Pb (Hue et al., 1988; Boon and Soltanpour, 1972). This characteristic allows the use of lettuce as an indicator of soil metal contamination.

This paper reports the use of vermicomposts for purifying effluents containing Cu, Ni and Zn collected from an electroplating plant. The effluents were passed through a glass column containing vermicompost and the metal concentrations in the elutant were measured to verify if they were within the guidelines for effluent discharges into water courses by the Brazilian legislation. For the purpose of using vermicompost residues for lettuce nutrition, vermicompost was used together with lettuce in pots for metal evaluation in leaves and roots.

2. Methods

2.1. Sample collection and pre-treatment

Five kg of commercial cattle manure vermicompost (Super Húmus), produced in the Vista Alegre farm in the city of Ubá (State of Minas Gerais, Brazil) was used as the sorptive material of Cu, Ni and Zn from electroplating effluents. The raw vermicompost was air-dried for 72 h and passed through a 2 mm sieve. Samples of 10 L of electroplating effluents containing Cu, Ni or Zn were obtained from a factory located in Ubá. The zinc effluents were collected twice, the second collection being 6 months latter the first one. Two hundred kg of an oxisol were collected from the soil surface (0–20 cm depth) in Viçosa, State of Minas Gerais, Brazil. Subsamples of the oxisol were air-dried, ground to pass through a 4 mm sieve and used in the determination of the oxisol characteristics as well as in the let-

Table 1
Soil characteristics[a]

pH in H_2O (1:2.5)	4.15
Organic matter (%, w/w)	1.25
CEC ($cmol_c \, dm^{-3}$)	11.60
Available P ($mg \, dm^{-3}$)	1.60
Available K ($mg \, dm^{-3}$)	14.00
Exchangeable Al ($cmol_c \, dm^{-3}$)	2.3
Exchangeable Ca ($cmol_c \, dm^{-3}$)	0.12
Exchangeable Mg ($cmol_c \, dm^{-3}$)	0.03
H + Al ($cmol_c \, dm^{-3}$)	11.4
Total metal ($mg \, kg^{-1}$)	
Cu	17.4
Ni	33.9
Zn	34.5
Al	72,700
Fe	49,400
Ca	37.1
Cd	3.4
Pb	<1
Mg	76.1
Na	93.7
K	15.2
Mn	65.1
Clay (%, w/w)	60
Silt (%, w/w)	12
Sand (%, w/w)	28
Textural class	Clay

[a] Value preceded by < symbol indicate detection limit.

tuce cultivation experiments in soil amended with vermicompost enriched with Cu, Ni or Zn. The oxisol characteristics are summarized in Table 1.

2.2. Natural vermicompost characterization

The vermicompost pH was measured in deionised water (solid/solution ratio = 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 (Kiehl, 1985). 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 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 (Stevenson, 1994). To obtain titration curve, 1 g of the vermicompost, previously sieved to a particle size of less than 0.177 mm, was titrated potentiometrically with NaOH solution. A nonlinear regression equation was adjusted to the titration data to differentiate the acid groups. This allowed the determination of the pK_a values. The total concentrations of Cu, Ni, Zn, Mn, Fe, Pb, Cd, Ca, Mg, Na, and K were determined in the 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. Five mL of concentrated $HClO_4$ (70% w/v) and 5 mL 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 deionised water to 25 mL (Jordão et al., 2002).

The particle size distribution was evaluated by a pipette method, using 1 mol L^{-1} NaOH solution as a dispersant agent (Embrapa, 1979). The sample was subjected to XRD analysis to evaluate the mineral components and was done at angles of 2θ, from 5 to 45°, using radiation tube Co-kα ($\lambda = 1.78897$ Å), at 40 kV and 20 mA. Infrared spectroscopy of the vermicompost, previously dried at 65 °C for 4 h, was done from a 100 mg of the sample in KBr.

2.3. Effluent characterization

The effluents were filtered through a 0.45 μm membrane filter to collect suspended particles. The effluent pH was determined by immersing electrodes into the solutions. From the precipitate formation in the effluents following the collection, the Cu, Ni and Zn concentrations remaining in the resultant solutions after filtration were evaluated. The solutions were then used for experiments in metal retention by the vermicompost. The filtration of Ni and Zn effluents were done twice. Concentrations of Cu, Ni, Zn, Al, Fe, Ca, Mg, Cd, Pb, Na, and K were determined in effluent samples acidified previously to pH 2 with HNO_3, by atomic absorption spectrophotometry (Jordão et al., 2002).

2.4. Metal retention by the vermicompost

The metal sorption experiments were in borosilicate glass columns 38 cm long and 7 cm i.d. The columns were loaded with 50 or 100 g of the vermicompost over a bed of glass wool. Those amounts were chosen based on the expected metal concentrations in the effluents. For the effluent that was less concentrated in Zn from the first collection (230 mg kg^{-1}), aliquots of 50 mL each were passed through a column containing 50 g of vermicompost, with 6 repetitions. For the more concentrated Zn effluent (2400 mg kg^{-1}) as well as for the Cu and Ni effluents (700 mg kg^{-1} and 1600 mg kg^{-1}, respectively), effluent aliquots of 25 mL each were passed through the columns containing 100 g of vermicompost, with 6 repetitions for Zn and 9 repetitions for Cu or Ni. Each column was introduced into a plastic tray containing 15 mL of deionised water to allow the saturation of the sample via capillarity, before passing the effluents through the columns. Thus, the air in the pores of the vermicompost was eliminated, which avoided the formation of air bubbles in the columns. The columns were kept in water for 24 h to obtain suitably compacted material.

The Cu retention by the vermicompost was determined at the pH of the effluent (2.0). The increase in Zn and Ni concentrations of the vermicompost were evaluated at the effluent pH (6.9 and 7.4, respectively) as well as pH 2.0. Successive aliquots of 25 mL of effluents containing Cu, Ni or Zn were passed through the column, containing the vermicompost, at a rate of 10 mL min^{-1}. The flow rate was controlled by the column stopcock. Deionised water (175 mL) was poured into the column after the passage of each aliquot of the effluent. The elutant was collected in a 200 mL volumetric flask. The Cu, Ni and Zn concentrations were then determined by atomic absorption spectrophotometry.

Experiments of adding effluent aliquots into the columns were conducted until the Cu, Ni and Zn concentrations in the elutant reached the maximum values established for effluent discharges in water courses by the Brazilian legislation (Cu = 1 mg kg^{-1}; Ni = 2 mg kg^{-1}; and Zn = 5 mg kg^{-1} (Brasil, 2005).

The 25 mL aliquots of the Ni effluent were collected into a 200 mL volumetric flask. If Ni concentration in the resultant solution was above the value allowed by the Brazilian legislation, 190 mL of the elutant were passed through the column again and the solution collected into a 500 mL volumetric flask. There was also an experiment in which 190 mL of the solution were poured through a new column containing vermicompost. This procedure had the objective of treating the effluent by using the maximum retention capacity of the substrate.

Equations were adjusted from the data obtained from the columns to evaluate the amount of metal retention capacity by the vermicompost. The regression equations were adjusted for the metal concentrations in the elutant (in mg L^{-1}) in relation to the masses of the metal retained (in mg) by each gram of the substrate.

2.5. Metal absorption by lettuce

The procedure of adding lime to the soil has been described elsewhere (Embrapa, 1979). The moisture content of the limed soil was kept close to field capacity. The soil sample was incubated for 20 days before applying the vermicompost to the soil. Individual soil subsamples were amended with vermicompost at four different doses as follows: 25, 50, 65, and 80 t ha^{-1}. The vermicompost samples include the vermicompost as well as enriched vermicomposts containing Cu, Ni or Zn from the experiment described above.

The mixture of vermicompost with soil was done by hand to obtain better homogeneity. The plastic pots were filled out with 1.8 dm^3 of soil, which correspond to 2.04 kg. The amount of air-dried vermicompost applied to the pots was 224.4 g as follows: 25.5 g (25 t ha^{-1}), 51.0 (50 t ha^{-1}), 66.3 g (65 t ha^{-1}), and 81.6 g (80 t ha^{-1}). The value of 50 t ha^{-1} is recommended by Comissão de Fertilidade do Solo do Estado de Minas Gerais (1989). During the incubation period (16 days), distilled water was added to the pots to keep the moisture content close to field capacity.

Lettuce (*Lactuca sativa* L cv. Regina de Verão) seedlings were cultivated in plastic trays 40 cm long and 20 cm width. The plants were watered with distilled water for 24 days and transplanted into 2L pots. To all pots, the inorganic fertilizer treatments in the day of transplanting included the addition of a solution containing 0.16 g of $(NH_4)_2SO_4$, 0.9 g of $CaH_4(PO_4) \cdot H_2O$ and 0.06 g of KCl for each pot. After 10 days, one application of 0.16 g of $(NH_4)_2SO_4$ and 0.06 g of KCl were made for each pot. Additionally, two applications of 0.24 g of $(NH_4)_2SO_4$ and 0.09 g of KCl at each 10 days were also added. A solution containing the micronutrients Mn, B and Mo were added to each pot 20 days after transplanting. The amounts of micronutrients added were 10 mg of $MnSO_4$, 10 mg of $Na_2B_4O_7$, and 0.5 mg of NH_4MoO_4.

Thirty nine days after sowing, the roots were separated from the adhering soil and the roots were with deionised water. The leaves and the roots of the plants were cut, the clippings were dried at 70 °C for 72 h and the leaves were macerated. Roots provided only sufficient material for the determination of the metal concentrations in the total mass of each plant. The leaves and roots were digested with a mixture of 14.4 mol L^{-1} HNO_3 and 30% (w/v) H_2O_2 (Huang and Schulte, 1985). A colorimetric method with the formation of the molybdophosphate complex in a H_2SO_4 matrix and reduction with ascorbic acid was used for the determination of *P* content in the leaves of lettuce.

For the characteristics in this study, a statistical analysis of a completely randomized design $(4 \times 4) + 1$ was used. The treatments included 4 vermicomposts (natural vermicompost and vermicomposts enriched with Cu, Ni or Zn), produced as described above in experiment of metal retention by vermicompost, and 1 soil in which was applied only inorganic fertilizer), with 4 replications.

Analyses of variance and regression were used. The averages of the qualitative factor (vermicompost type: natural, enriched with Cu, Ni or Zn) within each dose of vermicompost were compared by Tukey's test at the 5% level of probability. For the quantitative factors (dose of vermicompost), the models were chosen according to the significance of the regression coefficients (*t*-test at the level of probability up to 10%), as well as to the determination coefficients (R^2).

2.6. Instrumentation and some relevant information

The concentrations of Cu, Ni, Zn, Al, Fe, Ca, Mg, Cd, Pb, Na, and K were determined by atomic absorption spectrophotometry. The concentrations of these metals were measured with a Varian atomic absorption spectrophotomemter (model SpectrAA 200), by direct aspiration of the solutions into an air–acetylene or nitrous oxide–acetylene flame. Background correction was used for Pb, Zn, Co, Cd, and Ni determinations. For pH measurement a TEC-NOW pH meter, model Iris 7, was used. The titration was accomplished with an Orion pH meter, model 901.

The C, H and N measurements were performed in a CHNS/O analyzer of Perkin Elmer, Series II 2400. The IR spectroscopy was conducted in a Perkin Elmer spectrophotometer, model Ft Spectrum 1000. The XRD measurement was performed in a Rigaku Radiation Shield (Geigerslex) instrument.

All glassware and materials were cleaned for metal analysis and certified analytical grade reagents were used throughout. Nitric acid (65% wt/v) and $HClO_4$ (70% wt/v) were used for digestion, with maximum heavy metal contents reported by the supplier Cd < 0.01, Pb < 0.02 and Ni < 0.02 (in µg mL^{-1}). Blanks were run through all experiments. A midpoint check standard and calibration blank at the beginning end and periodically was analyzed with each group of samples to certify that the instrument calibration had not drifted. Concurrent analyses of samples of Standard Sediments (National Institute of Standard & Technology no. 2704) gave the following values which were within the range of certified values: Zn = 447, Ni = 44.2, and Cu = 94.5 (mg kg^{-1}); Al = 61.0 and Mg = 12.2 (g kg^{-1}).

3. Results and discussion

3.1. Vermicompost characterization

The vermicompost characteristics are summarized in Table 2. The moisture content of the vermicompost reached $47.4 \pm 0.41\%$, above the maximum limit (44%) allowed by the Brazilian legislation for composted solid wastes used as fertilizer (Brasil, 1983). The high capacity for water retention of vermicompost allows its application for soil conditioning.

The vermicompost had a high organic matter content ($42.0 \pm 0.34\%$), a value above the minimum limit established by the Brazilian legislation, i.e., 40% of total organic matter (Brasil, 1983). Organic matter contents of vermicomposts in the range of 27–53% have been reported (Lamim et al., 1998; Pereira and Arruda, 2003).

The ash content was above the values reported by Lamim et al. (1996) and Jordão et al. (2002) for cattle manure vermicompost, 47.3% and 45.0%, respectively. However, the value in the present work, $57.9 \pm 0.31\%$, is within the range (41.2–68.8%) reported by Pereira and Arruda (2003). 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 the composting process.

The contents (%) of C (19.61), H (3.13) and N (1.93) are in good agreement with the values reported by Pereira and Arruda (2003) 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).

Among the improvements in soil conditions due to the compost additions to soil, the most significant alteration was the increases in the organic matter content (He et al., 1992). The initial C/N ratio of the materials used in

Table 2
Vermicompost characteristics[a]

Characteristic[a]	Mean ± standard deviation[b]
pH in H_2O	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
Metal ($mg \ kg^{-1}$)	
Cu	31.0 ± 6.7
Ni	21.7 ± 2.1
Zn	108 ± 4.4
Al	16,300 ± 490
Fe	20,100 ± 35
Ca	6330 ± 1100
Cd	1.7 ± 0.1
Pb	2.6 ± 0,7
Mg	2670 ± 230
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).

vermicomposting processes varies according to its composition. Initial C/N values of 17, 15, and 181 for cattle manure (Farias, 2001), sewage sludge and sugarcane pulp (da Silva et al., 2002), respectively, have been reported. 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 (Kiehl, 1985), and value found in this research study (11.85) was within this range (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 (Lamim et al., 1996; Kiehl, 2001; Pereira and Arruda, 2003). The pH provides valuable information about the decomposition stage of organic matter during the humification process. The raw organic matter, vegetable or animal, is naturally acidic unless amended with lime or ash. Independently of the use of corrective, the process of aerobic composting leads to the formation of humic substances with alkaline characteristics. Values of vermicompost pH close to neutrality indicate there was biological stabilization of the material (Kiehl, 1985).

The metal concentrations in the vermicompost agree with values reported by Lamim et al. (1996) and Jordão et al. (2002) for cattle manure vermicompost and by da Silva et al. (2002) for sewage sludge and cane-thrash vermicomposts.
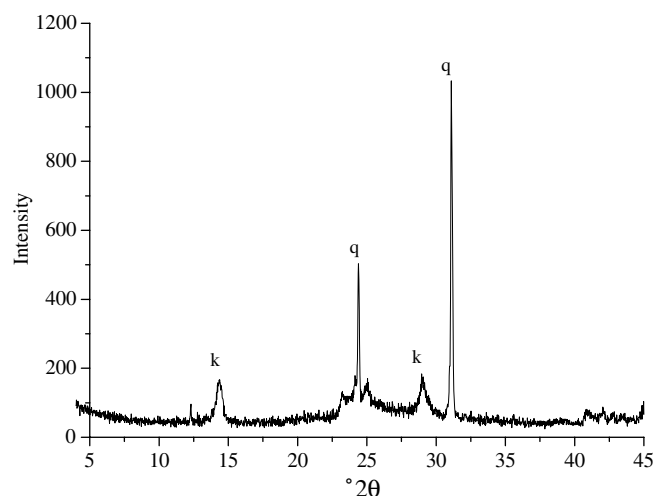

Fig. 1. X-ray diffraction spectrum for the vermicompost sample.

Implementation of stringent regulations is generally required in many countries. Countries in Europe such as Germany and The Netherlands are at the forefront of legislation pertaining to composting. Other countries such as Spain and Italy are producing low quality, low value compost (Choi, 1996). In Brazil, no regulations address the land application of compost. However, taking into account the moisture contents and ash contents in this research study, it is recommended as a quality control of compost in the market.

Fig. 1 shows the X-ray diffraction spectrum of the vermicompost revealed kaolinite (angles 2θ of 14.5° and 29.2°) and quartz (angles 2θ of 24.40 and 31.1°) as the two major components. The high Al concentration (16,300 $mg \ kg^{-1}$) of the vermicompost (Table 2) was attributed to kaolinite present in the vermicompost sample, since composting process using earthworms are commonly conducted on soil. Kaolinite and quartz are clay minerals commonly present in tropical soils and have low chemical activities. Thus, they not exert a major influence on the cation retention capacity of the vermicompost.

The titration curve (Fig. 2) includes 300 experimental points, and end points may not be evident because the titration of one point begins before that of the other is complete. It is not possible to observe inflection points due to the very close pK_a values of the acidic groups. The use of nonlinear regression allowed five classes of titrated groups to be determined. The first three pK_a values are in the region of the typical pH for carboxylic groups, while the last two values are typical of phenols and amines. The volumes of the NaOH solution used, were also determined, being the first volume ($V_0 = 2.58$ mL) corresponding to the titration of the excess of HCl, and the other five volumes ($V_1 = 5.02$, $V_2 = 7.36$, $V_3 = 9.35$, $V_4 = 12.04$, and $V_5 = 19.63$) corresponding to the volumes of the equivalence point of each group titrated. The experimental curve was similar to that using regression data.

From the volume of base consumed during titration (3.37 mL), it was possible to evaluate the charge of the
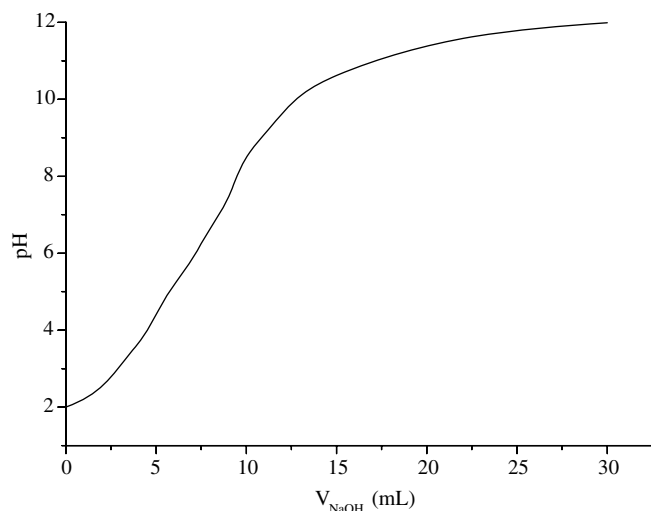
Fig. 2. Adjusted titration curve of the vermicompost with NaOH.

Fig. 3. Infrared absorption spectrum of the vermicompost sample: (a) natural; (b) enriched with Ni; (c) enriched with Cu; (d) enriched with Zn.

material (32.7 cmol kg^{-1}) at the original pH of the vermicompost (7.1). 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 3).

The IR spectrum of the vermicompost sample is summarized in Fig. 3 and the presence of characteristic groups of organic matter is evident. Due to the complexity of the mixture of constituent substances of the material, broad bands are observed. These are due to the superimposed absorption signals. The IR spectrum was similar to those obtained by Pereira and Arruda (2003) for three vermicompost samples from different areas.

The bands from 3695 to 3620 cm^{-1} are due to the N–H stretching of amine and or amino acids. The broad band centered at 3431 cm^{-1} can be assigned to the stretching vibration of O–H, which corresponds to several groups containing hydroxyl. The bands in 2919 and 2850 cm^{-1} can be attributed to aliphatic C–H stretching. The intense absorption band in 1636 cm^{-1} is characteristic of the C–O asymmetrical stretching of carboxylate ions and also of aromatic C=C stretching vibrations (Silverstein et al., 1994). Low intensity absorption band in 1400 cm^{-1} can also be attributed to symmetrical stretching of carboxylate
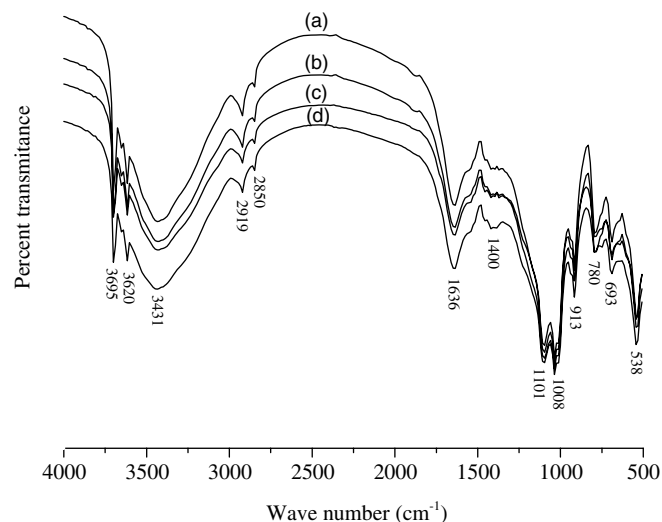
ions. The intense absorption bands in region of 1008 and 1101 cm^{-1} are characteristic of the C–O stretching in polysaccharide or polysaccharide-like substances or even Si–O of silicate present in the sample (Stevenson, 1994).

The absence of bands in 1720 and 1250 cm^{-1} could be attributed to the C=O stretching of carboxylic acid and keto groups (Stevenson, 1994). Low intensity absorption bands in 1508, 1560 and 1654 cm^{-1} are due to the aromatic C=C stretching vibrations (Silverstein et al., 1994). The absence of characteristics bands of COOH stretching in 1720 and 1250 cm^{-1} could be due to its low content in the sample. This agrees with results for the carboxylic groups shown in Table 2. The bands in the area below 900 cm^{-1} are due to contamination. Interactions between metals and humic acids of soil take place with the displacement, decrease or disappearance of some bands (Stevenson, 1994).

The comparison of IR spectra of vermicompost enriched with Cu, Ni or Zn with the spectrum of the natural vermicompost shows that significant alterations were not found in the bands (Fig. 3). This suggests that the formation of complexes was relatively weak and that the interactions of the metals with the vermicompost were preferentially electrostatic (Sposito, 1989).

3.2. Effluent characterization

No suspended particles were found in the effluents. The pH values of Cu, Zn and Ni effluents were 2.0, 6.9 and 7.4, respectively. The metal concentrations in the effluents are presented in Table 4. The Cu and Ni concentrations reached up to 700 and 1600 mg L^{-1}, respectively, while the highest Zn concentrations were 230 mg L^{-1} (first collection) and 2400 mg L^{-1} (second collection). These values are high as compared with the maximum limits established by Brazilian legislation for effluent emissions into water

Table 3
Values of pK_a obtained from the nonlinear regression adjustment of the potentiometric 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 (2000) for humic acids extracted from cattle manure vermicompost.
[c] Values from Masini et al. (1998).

Table 4
Total metal concentrations (mean of three replicates ± standard deviation, in mg kg^{-1}) in the natural vermicompost, enriched vermicomposts and effluents

Metal	Vermicompost				Effluent			
	Natural	Enriched with Cu	Enriched with Ni	Enriched with Zn	Cu	Ni	Zn (1^{rs} collection)	Zn (2^{sd} collection)
Cu	31.0 ± 3.7	3720 ± 290	28.3 ± 2.8	26.4 ± 1.8	700 ± 8	0.03 ± 0.001	0.1 ± 0.01	0.1 ± 0.01
Ni	21.7 ± 2.1	39.3 ± 1.9	4070 ± 370	20.8 ± 2.2	1.2 ± 0.03	1600 ± 15	0.2 ± 0.004	0.3 ± 0.004
Zn	108 ± 4.4	161 ± 8.5	117 ± 11.7	4840 ± 460	8.0 ± 0.02	0.07 ± 0.01	230 ± 13	2400 ± 26
Al	16300 ± 490	16900 ± 1610	17400 ± 550	10400 ± 320	1.4 ± 0.02	0.2 ± 0.02	0.3 ± 0.01	0.4 ± 0.01
Fe	20100 ± 35	21100 ± 550	17700 ± 1660	18700 ± 1710	2.3 ± 0.02	0.02 ± 0.002	0.5 ± 0.01	0.7 ± 0.01
Ca	6330 ± 1100	4120 ± 410	6130 ± 640	3880 ± 400	3.6 ± 0.05	5.6 ± 0.06	5.0 ± 0.3	9.7 ± 0.2
Cd	1.7 ± 0.1	3.8 ± 0.5	2.1 ± 0.3	1.7 ± 0.2	0.3 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.06 ± 0.004
Pb	2.6 ± 0.7	2.7 ± 0.3	1.2 ± 0.3	2.0 ± 0.5	0.06 ± 0.01	<0.004[a]	0.08 ± 0.001	0.2 ± 0.001
Mg	2670 ± 230	613 ± 110	1740 ± 160	950 ± 90	2.2 ± 0.03	97.3 ± 0.6	2.5 ± 0.1	4.3 ± 0.1
Na	475 ± 46	220 ± 24	237 ± 23	270 ± 15	57.2 ± 3.0	68.2 ± 1.4	98.1 ± 3.0	680 ± 17
K	6110 ± 460	463 ± 54	346 ± 35	3470 ± 290	9.9 ± 0.3	10.4 ± 0.8	1100 ± 13	9480 ± 193

[a] Value preceded by < symbol indicate detection limit.

courses (1, 2, and 5 mg L^{-1} of Cu, Ni, and Zn, respectively) (Brasil, 2005).

The Zn effluent from the second collection has relatively high Na and K concentrations due to the presence of salts in the plating solution. The local electroplating plant uses $CuSO_4$ and H_2SO_4 in the Cu plating solution. For Ni, the saline and acidic solutions where plating process take place are $NiSO_4$, $NiCl_2$ and H_3BO_4. Zinc chloride, KCl and H_3BO_4 constitute the Zn plating solutions.

3.3. Metal retention by the vermicompost

Table 4 demonstrates the metal concentrations in the natural vermicompost and in the vermicomposts enriched with Cu, Ni, or Zn. In the process of enrichment of the vermicompost with metals, the greatest changes in concentrations were due to the passage of the effluents containing Cu or Ni. The increments in Cd concentration should be attributed to the presence of this metal in the effluents.

With the passage of the effluents of Cu or Zn through the vermicompost, a reduction in Ca concentration was observed. The reductions of Mg, Na, and K concentrations in the enriched vermicomposts can be attributed to the cation exchange.

The Cu and Ni concentrations in the elutant and the respective percentages of retention of the metals by the vermicompost according to the masses accumulated in the column are shown in Fig. 4, while the values for Zn are shown in Fig. 5.

The initial Cu and Ni concentrations in the effluents were 700 and 1600 mg L^{-1}, respectively, while Zn concentration was 2400 mg L^{-1} (second collection). However, due to the need of filtration of some effluents, the final Cu, Ni and Zn concentrations that were used in the metal retention by vermicomposts were Cu = 690, Ni = 800 and 840, and Zn = 1800 and 1790 (in mg L^{-1}).

The Cu retention in the first aliquots was close to 100% (Fig. 4). The retention was above 98% even after reaching the maximum allowed concentration in the elutant (1 mg L^{-1}).

Besides the metal retention from the effluents, another valuable characteristic of the vermicompost was the pH increase. The Cu effluents at the natural pH (2.0) as well as the Zn effluent at pH 2.0 had the pH enhanced from 6.5 to 7.3. These values are within the range (from 5 to 9) established by the Brazilian legislation for effluent emission into water courses (Brasil, 2005). The pH values of the effluents containing Ni or Zn (natural pH of 7.4 and 6.9, respectively) were not changed significantly after their passage through vermicompost.

From the maximum amount of Cu allowed in effluents that can be discharge in water courses (Brasil, 2005) and using the equation showed in Fig. 4, it was possible to calculate the accumulation capacity of the vermicompost as 3.0 g Cu kg^{-1} of the vermicompost.

It is possible to quantify the possible consumption of vermicompost for Cu recovery from the effluents of the local electroplating plant. The industry discharges about 250 liters of liquid effluent daily containing this metal into the Ubá Stream that runs in its vicinities. This information, together with the value found for Cu concentration in the effluent (690 mg L^{-1}) and the value of metal retention (3.0 g kg^{-1}) as mentioned above, points to a daily need of 57.5 kg of vermicompost.

Fig. 4 shows that the Ni retention was more than 99.5% for the first aliquots. However, even with this high retention, the Ni concentration in all aliquots was above the value allowed by the Brazilian quality criteria, i.e., 2 mg L^{-1} (Brasil, 2005). Thus, a test was conducted where 200 mL of the elutant was passed through the column again. The elutant became a new aliquot (190 mL) that was collected in a volumetric flask of 500 mL. No metal accumulation was observed. However, the passage of a 190 mL aliquot through a column containing natural vermicompost, led to retention above 95%.

Since the pH of the vermicompost + effluent in the column was about 7 and the initial Ni concentration in the effluent was 1.36×10^{-2} mol L^{-1}, the calculations based on the Kps of the Ni(OH)$_2$, 8.7×10^{-19} (mol L^{-1})^3, point to be the precipitation of Ni as hydroxide. This suggests
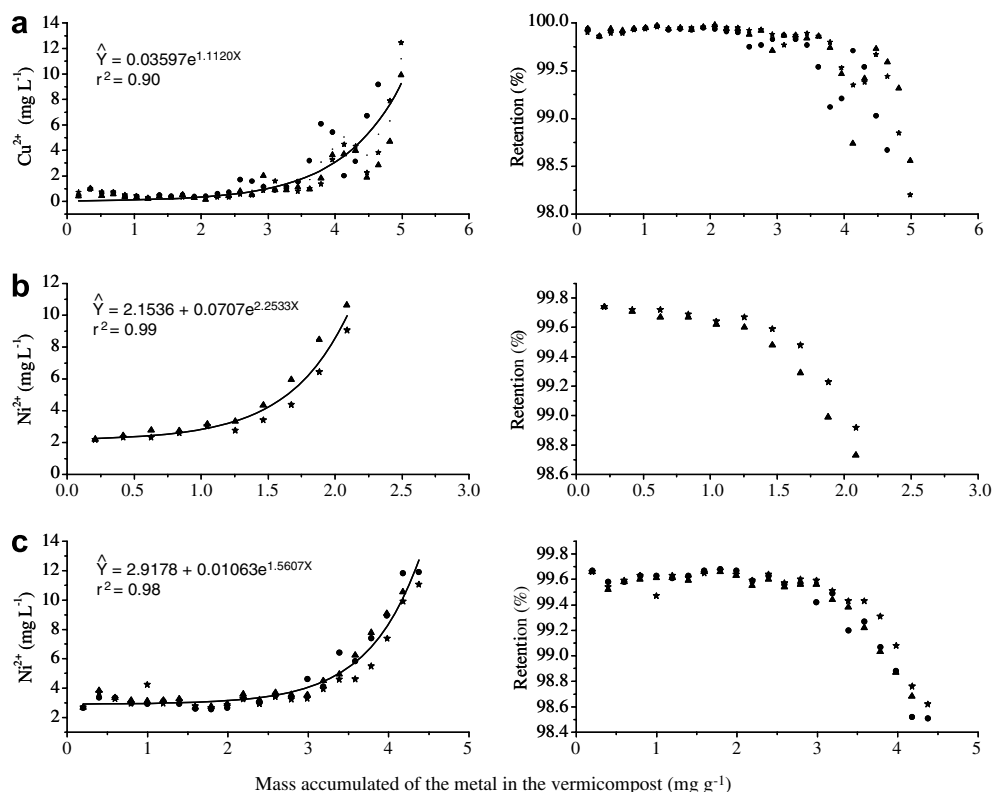
Fig. 4. Copper and Ni concentrations in the elutant and the respective percentages of metal retention by the vermicompost according to the masses accumulated in the column; (★) column 1; (▲) column 2; (●) column 3; (—) estimated; (a) $[Cu^{2+}]_{initial} = 690\ mg\ L^{-1}$ and pH 2.0; (b) $[Ni^{2+}]_{initial} = 840\ mg\ L^{-1}$ and pH 2.0; (c) $[Ni^{2+}]_{initial} = 800\ mg\ L^{-1}$ and pH 7.4. Columns 1, 2 and 3 – mean of three repetitions each. No data are available for column 3 in (b).

that metal retention by the vermicompost could occur by formation of complexes, electrostatic interaction and precipitation as hydroxide. In the first aliquot, Ni might be retained by these three processes. However, by the passage of a new aliquot (190 mL) through the vermicompost, in spite of the pH becomes favorable to the precipitation (around 7), the metal concentration was insufficient to be precipitated as nickel hydroxide. In the absence of precipitation, and taking into account that part of the sites had already been occupied by the metal from the first aliquot, no accumulations were to be expected during the new passage of the elutant through the vermicompost. On the other hand, Ni retention was observed in the column containing the natural vermicompost due to the availability of sites.

The precipitation of Cu and Zn hydroxides has also to be considered in the retention process (Figs. 4 and 5) since the metal concentrations and the pH values were favorable.

To obtain Ni concentrations in the treated effluent according to limits established by the Brazilian legislation, it is recommended to increase the mass of vermicompost/ volume of the aliquot ratio or to use a system of columns in series.

Fig. 4 shows that Ni retention by the vermicompost was affected by the initial pH of the effluent. The average of Ni concentration in the aliquots of the effluent at the initial pH (7.4) was not significant to about 2.5 mg of Ni per gram of

vermicompost. On the other hand, the reproducibility of the data of the columns was also better in relation to the effluent at the initial pH (2.0).

In the evaluation of Ni retention in pH 2.0 (Fig. 4), only the data from 6 replications were used, because the results from the other three columns varied too much. In regard to the evaluation of Zn retention in pH 2.0 (Fig. 5), only the data of 3 replications were used as compared with 6 replications used in pH 6. The variations in some columns were attributed to the occurrence of preferential flow of aliquots inside the column caused by the heterogeneity of the vermicompost sample. The process of adding the vermicompost to the column as well as the action of obtaining compacted material should also be taken into account.

The influence of pH can be explained by competition in an acid environment between metals and H^+ ions and the metal retention in such condition was not significant.

The Zn concentration in all aliquots of the elutant was above the values allowed by the Brazilian legislation. Thus, it was not possible to evaluate the mass of vermicompost necessary for the treatment of the effluent. The Zn retention in the first aliquots was close to 100% (Fig. 5). The retention rate was above 95% even after reaching the maximum allowed concentration in the elutant (1 mg L^{-1}). Similar results were also found for Cu and Ni retentions. The use of vermicompost as a filter for Cu, Ni and Zn
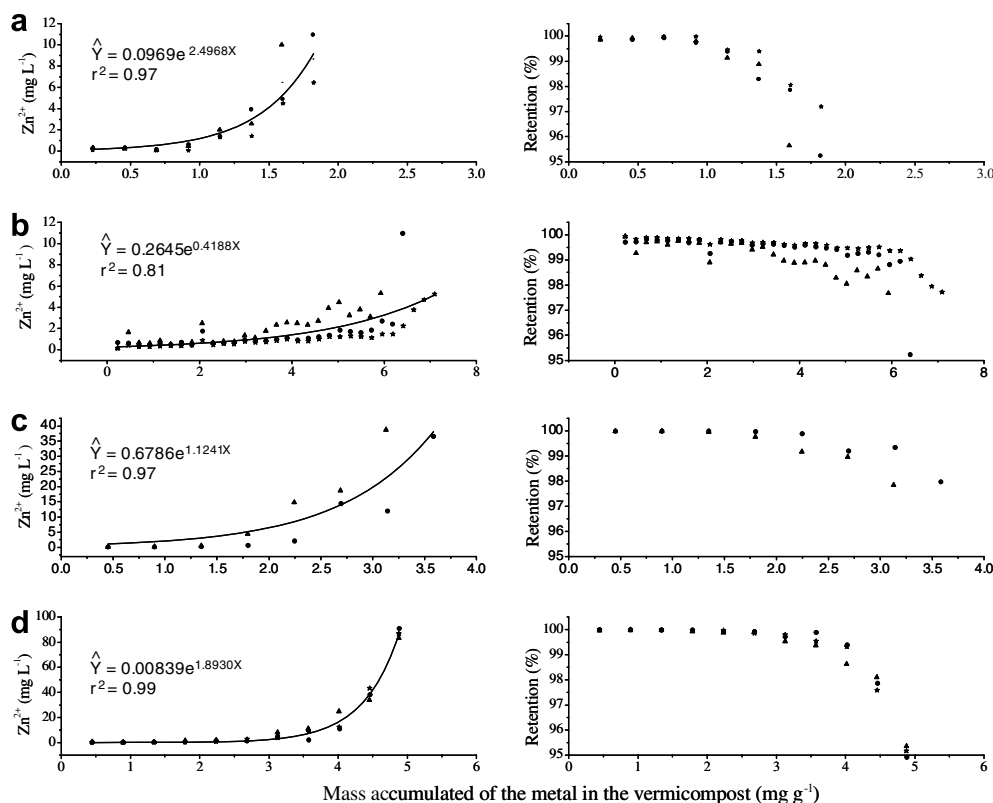
Fig. 5. Zinc concentrations in the elutant and the respective percentages of metal retention by the vermicompost according to the mass accumulated in the column; (★) column 1; (▲) column 2; (●) column 3; (—) estimated; (a) $[Zn^{2+}]_{initial} = 230$ mg L^{-1} and pH 2.0; (b) $[Zn^{2+}]_{initial} = 230$ mg L^{-1} and pH 6.9; (c) $[Zn^{2+}]_{initial} = 1800$ mg L^{-1} and pH 2.0; (d) $[Zn^{2+}]_{initial} = 1790$ mg L^{-1} and pH 6.9. Columns 1, 2 and 3 – mean of three repetitions each. No data are available for column 3 in (a) and (c).

retention did not lead to saturation of the material under the experimental conditions described in this study.

Fig. 5a and b summarize the effect of the pH in the retention capacity of Zn by the vermicompost. In the natural pH (6.9) of the effluent, the retention was greater than in pH 2.0. Fig. 5b and d demonstrate that Zn retention from the effluent containing 230 mg L^{-1} at pH 6.9 was much greater than that of the most concentrated effluent (1790 mg L^{-1}). Different metal concentrations led to different retention values because the interactions depend on the time of contact between the metal ion and the reactive sites of the vermicompost. Since the flow of the collections of the aliquots was 10 mL min^{-1}, it is possible that, for the most concentrated effluent, the time of contact of the metal with the substrate has not been enough to allow interactions between metals and sites of retention.

Although metal retention varied in terms of both effluent pH and metal concentration, the vermicompost was efficient in the treatment of the Zn waste.

Lamim et al. (1998) reported the effects of the time of agitation on Cu and Zn adsorption by vermicomposts. They found that the maximum adsorptions of Cu^{2+} and Zn^{2+} ions were obtained after 16 and 20 h, respectively.

The sorption capacity of the vermicompost to retain Zn was calculated from the data of Fig. 5 as well as from the value of the maximum Zn concentration allowed by Brazil-

ian legislation that can be released in water-courses (Brasil, 2005). Taking into account this capacity as well as the volume of the effluent discharged daily in the water-course by the industry (250 L), it is possible to estimate the daily mass of vermicompost needed to treat the effluent under different conditions (Table 5).

Besides the effect of time, the retention process was also influenced by competition with other ions present in the solution. Zinc retention by vermicompost was greater from synthetic solutions than from effluents collected in an electroplating plant. This was attributed to other substances that might affect the adsorption of the ionic species of interest (Jordão et al., 2002).

Table 5
Capacity of Zn retention by the vermicompost and estimated mass of the vermicompost for removing Zn from the effluent at different pH values and metal concentrations

pH	Zn concentration (mg L^{-1})	Retention (mg L^{-1})	Vermicompost consumption (kg)[a]
2.00	230	1.58	36.4
	1800	1.78	258.2
6.90	230	7.02	8.2
	1790	3.38	132.4

[a] Corresponding to the volume (250 L) of the effluent discharged daily in the water course by the local industry.

The adsorption of Zn and Cd by peat was affected by Na^+, Ca^{2+}, Fe^{3+}, and Al^{3+} ions (Petroni et al., 2000). However, interference of the H^+ ion was more significant, because it began at much lower concentration than the other ions.

The Zn effluent had high Na and K concentrations (Table 4). However, the Na and K levels in the vermicompost enriched with Zn did not increased. This suggests that the metals in the effluents were not present in amounts enough to cause interference.

In the evaluation of Cu retention 29 aliquots of the effluent with the concentration of 690 mg L^{-1} were passed through the column. The correspondent charge of the metal related to its mass added in the columns was 1.58 cmol$_c$. The total charge of the vermicompost was 32.7 cmol kg^{-1} at its original pH (7.1). The charge of the material correspondent to 100 g of the vermicompost was 3.27 cmol$_c$. One may conclude that around 1.69 cmol$_c$ of the material was available to interact with Cu. It means that 51.7% of the retention sites of the vermicompost were not completely occupied.

Similar calculations can be made for the total charge determination corresponding to the Ni and Zn masses added in the columns. The total charges that correspond to the masses of Ni added to the column were 0.72 and 1.50 cmol$_c$, with respect to 10 and 22 aliquots passed through the columns for the concentrations of 800 and 840 mg L^{-1}, respectively. In the evaluation of Zn retention with concentrations of 230 mg L^{-1} at pH 2.0 and pH 6.9, were passed through the columns 8 and 31 aliquots of the effluent, respectively, that correspond to 0.29 and 1.11 cmol$_c$. In Zn retention with concentrations of 1800 and 1790 mg L^{-1} 8 and 11 aliquots were passed through the column, with the values obtained 1.12 and 1.53 cmol$_c$,

respectively. Although the Cu, Ni and Zn concentrations in the elutant were above the maximum values established for effluent discharges in water courses by the Brazilian legislation, the vermicompost enriched with metals still presented available charges for metal retention.

Besides the effects of pH and concentration in metal retention by the vermicompost, another factor affecting the adsorption process is the time that the column remained undisturbed (the column containing the vermicompost and the deionised water poured into the column after the passage of each aliquot of the effluent). If the column stayed undisturbed for several hours, a greater metal retention by the vermicompost was obtained when passing the next aliquot. This could be attributed to the equilibrium among the metallic ions retained in the material and the ions in solution. Due to the release of ions faintly retained by the vermicompost while the columns were undisturbed, a greater number of sites were available for metal retention during the passage of other aliquot.

3.4. Metal absorption by lettuce

The Cu, Ni and Zn concentrations in the leaves and roots of the plants were not affected by the increases in the doses of the natural vermicompost. However, they varied according to the doses of the vermicomposts enriched with the respective metals (Table 6). The Cu concentrations in the leaves of lettuce were affected by the doses of the vermicomposts enriched with both Ni and Zn. The estimated maximum Cu concentrations were 3.5 mg kg^{-1} (for 80 t ha^{-1} of vermicompost enriched with Ni) and 4.4 mg kg^{-1} (for the dose of 46.5 t ha^{-1} of vermicompost enriched with Zn, which is the estimated dose for the maximum Zn concentration in the leaves).

Table 6
Regression equations and coefficients of determination (R^2) related to Cu, Ni and Zn concentrations (Y, in mg kg^{-1}) in the leaves and roots of lettuce as a function of compost doses (X, in t ha^{-1}) for the natural and enriched vermicomposts

Vermicompost[a]	Leaves		Roots	
	Equations	R^2	Equations	R^2
Cu				
1	$\widehat{Y} = 2.8$		$\widehat{Y} = 10.9$	
2	$\widehat{Y} = 2.6 + 0.1253^{**}X - 0.000716^{**}X^2$	0.801	$\widehat{Y} = 14.1 + 2.9027^{**}X$	0.928
3	$\widehat{Y} = 2.2 + 0.0165^{**}X$	0.902	$\widehat{Y} = 10.5$	
4	$\widehat{Y} = 2.2 + 0.0967^{*}X - 0.00104^{**}X^2$	0.889	$\widehat{Y} = 12.9$	
Ni				
1	$\widehat{Y} = 2.1$		$\widehat{Y} = 5.8$	
2	$\widehat{Y} = 1.3$		$\widehat{Y} = 8.3$	
3	$\widehat{Y} = 1.2 + 0.7168^{**}X - 0.00377^{**}X^2$	0.991	$\widehat{Y} = 53.8 + 17.3756^{**}X - 0.14137^{**}X^2$	0.911
4	$\widehat{Y} = 2.0$		$\widehat{Y} = 10.9$	
Zn				
1	$\widehat{Y} = 47.79$		$\widehat{Y} = 60.6$	
2	$\widehat{Y} = 49.26$		$\widehat{Y} = 58.8$	
3	$\widehat{Y} = 42.93$		$\widehat{Y} = 60.88$	
4	$\widehat{Y} = -24.0 + 29.4827^{**}X - 0.2068^{*}X^2$	0.939	$\widehat{Y} = 162.93 + 6.9758^{**}X + 0.09659^{***}X^2$	0.974

*,**,***Significant at 5%, 1% and 10% of probability, respectively (*t*-test).
[a] 1 – Natural; 2 – enriched with Cu; 3 – enriched with Ni; 4 – enriched with Zn.

One may figure from Table 6 that the estimated doses of the vermicomposts enriched with Cu, Ni or Zn for the maximum concentrations of these metals in the leaves were 87.5 t ha^{-1}, 95.1 t ha^{-1} and 71.3 t ha^{-1}, respectively. The respective estimated maximum concentrations in the leaves were 8.1 for Cu, 35.3 for Ni, and 1074.8 for Zn (in mg kg^{-1}).

In the roots, it can be estimated the following concentrations of micronutrients: Cu = 246.3 mg kg^{-1} (for the dose of 80 t ha^{-1} of vermicompost enriched with Cu), Ni = 587.7 mg kg^{-1} (for the dose of 61.5 t ha^{-1} of vermicompost enriched with Ni, which is the estimated dose for the maximum Ni concentration in the roots), and Zn = 1339.2 mg kg^{-1} (for the dose of 80 t ha^{-1}). In spite of high Cu, Ni and Zn concentrations in the roots, no toxicity symptom was observed visually on lettuce leaves.

The critical concentrations for Cu deficiency in vegetables range from 1.0 to 3.5 mg kg^{-1} dry matter (d. m.), while critical concentrations of Cu toxicity in the leaves of most of plant species range from 15 to 30 mg kg^{-1} (Robson and Reuter, 1981). According to Kabata-Pendias and Pendias (1984), the critical toxicity level is the range of values above which toxicity is considered to be possible. In the case of Cu, it varied from 20 to 100 mg kg^{-1}. Toxicity to plants by Cu occurred at concentrations above 20 mg kg^{-1} d.m. (Smith, 1992). Copper concentration in lettuce dry matter varies from 5.9 to 13.9 mg kg^{-1} (Furlani et al., 1978). Santos et al. (1998) reported Cu concentrations in the dry matter of lettuce leaves ranging from 3.19 to 13.61 mg g^{-1}. They also reported increased Cu concentrations with the elevation of the doses of urban solid waste compost, with the greatest dose becomes 52.5 t ha^{-1}.

The estimated Cu concentrations in the leaves of lettuce from the treatments with the natural vermicompost, as well as with the enriched vermicomposts containing Ni or Zn, were below the normal values for well-nurtured cultivars (Table 6) (Furlani et al., 1978). The treatment with vermicompost enriched with Cu produced concentrations of Cu in the leaves of lettuce below the critical toxicity level. However, the estimated Cu concentrations in the roots were much larger than those from the treatment with natural vermicompost.

The Ni concentrations in plants varied from 1 to 10 mg kg^{-1} d. m. Critical toxicity levels in plant leaves were in the range from 10 to 50 mg kg^{-1} of dry matter (Marschner, 1995) and from 10 to 100 mg kg^{-1} (Kabata-Pendias and Pendias, 1984). According to Smith (1992), phytotoxic effects can occur above a critical concentration of 11 mg kg^{-1}.

The Ni concentrations in the leaves of lettuce after treatments with vermicompost, as well as with vermicomposts containing Cu or Zn, were within the common range found in plants (Table 6). The Ni concentrations were lower than those reported by Silva (2000), who reported that the application of five different kinds of vermicomposts to soil in amounts varying from 11.3 to 16.4 t ha^{-1} resulted in a mean of 4.16 mg kg^{-1} of Ni in the leaves of lettuce. The

Ni concentrations in the lettuce leaves from the treatment with vermicompost enriched with Ni were in the range of critical toxicity levels for plants. In the roots, the Ni concentrations were much larger than those from the treatment with the natural vermicompost.

The critical concentrations of Zn deficiency in vegetables range from 1.0 to 3.5 mg kg^{-1} d. m., while critical concentrations of Cu toxicity in most of plant species range from 15 to 30 mg kg^{-1} (Robson and Reuter, 1981).

The critical level of deficiency of Zn in leaves range from 15 to 20 mg kg^{-1} d. m. (Marschner, 1995), while the critical toxicity level ranges from 200 and 500 mg kg^{-1} d. m., depending on the species and the age of the plant (Mortvedt et al., 1991). According to Kabata-Pendias and Pendias (1984), the critical level of Zn toxicity varied from 100 to 400 mg kg^{-1}. Well-nurtured cultivars of lettuce accumulated from 94 to 116 mg kg^{-1} of Zn in the dry matter of leaves (Furlani et al., 1978). Costa et al. (1994) reported that at a dose of 20 t ha^{-1} of composted urban waste applied to soil, lettuce accumulated up to 81.47 mg kg^{-1} of Zn in the dry matter.

The Zn concentrations in the leaves of lettuce from the treatments with vermicompost, as well as from vermicomposts containing Cu or Ni, were higher than the critical levels of deficiency for plants, but were lower than the common values of well-nurtured cultivars (Table 6). The Zn concentrations in the leaves from the treatment with the vermicompost enriched with Zn were above the critical toxicity level for plants. The Zn concentrations in the roots were greater than those of the treatment with the natural vermicompost.

In a pot experiment in which vermicompost enriched with Cd, Cu, Cr, Ni, and Zn was applied to soil, Jordão et al. (2002) reported that plants such as *S. aterrimum* and *C. cajan* showed toxicity symptoms due only to Cd. However, these metals were presented together in the sample of the vermicompost at concentrations below the values that were used in the present work.

The Ni and Zn amounts in lettuce leaves and roots from the treatments with the vermicomposts containing these elements were greater than those in the other treatments at all the evaluated doses (Table 7). However, the amounts of Zn in the roots at a dose of 25 t ha^{-1} did not differ statistically. Increases the doses of vermicompost did not affect Cu amounts in the roots or the Ni and Zn amounts in the leaves and roots of the plants. On the contrary, the amounts of the metals in the leaves and roots varied with the dose of the vermicomposts enriched with the respective metal. The amounts of Cu in the leaves also varied according to the doses of vermicompost, as well as according to the doses containing Ni or Zn, in a linear manner.

In general, larger accumulations of Cu, Ni and Zn were found in the leaves than in the roots in the treatments with the natural vermicompost (Table 8). Larger accumulations of Cu in the leaves also occurred in the treatments with the vermicomposts enriched with Ni or Zn, compared with the roots. In the treatments with the vermicomposts containing

Table 7
Regression equations and coefficients of determination (R^2) related to Cu, Ni and Zn amounts (Y, in µg plant^{-1}) in the leaves and roots of lettuce as a function of compost doses (X, in t ha^{-1}) for the natural and enriched vermicomposts

Vermicompost[a]	Leaves		Roots	
	Equations	R^2	Equations	R^2
Cu				
1	$\widehat{Y} = 2.3 + 0.1675^{**}X$	0.993	$\widehat{Y} = 4.8$	
2	$\widehat{Y} = 2.0 + 0.2470^{**}X$	0.876	$\widehat{Y} = 2.8 + 0.0988^{**}X + 0.01949^{*}X^2$	0.976
3	$\widehat{Y} = 2.7 + 0.0998^{**}X$	0.743	$\widehat{Y} = 2.7$	
4	$\widehat{Y} = 3.8 + 0.0859^{*}X$	0.614	$\widehat{Y} = 2.3$	
Ni				
1	$\widehat{Y} = 9.9$		$\widehat{Y} = 1.4$	
2	$\widehat{Y} = 2.7$		$\widehat{Y} = 1.6$	
3	$\widehat{Y} = 1.7 + 1.2980^{**}X$	0.887	$\widehat{Y} = 17.8 + 1.4487^{**}X + 0.033406^{*}X^2$	0.831
4	$\widehat{Y} = 5.7$		$\widehat{Y} = 1.0$	
Zn				
1	$\widehat{Y} = 182.5$		$\widehat{Y} = 22.3$	
2	$\widehat{Y} = 101.3$		$\widehat{Y} = 12.1$	
3	$\widehat{Y} = 101.4$		$\widehat{Y} = 13.0$	
4	$\widehat{Y} = -64.4 + 33.19^{**}X$	0.826	$\widehat{Y} = -33.0 + 5.9294^{**}X$	0.941

*,**Significant at 5% and 1% of probability, respectively (t-test).
 [a] 1 – Natural; 2 – enriched with Cu; 3 – enriched with Ni; 4 – enriched with Zn.

Table 8
Partition of Cu, Ni and Zn amounts in the leaves and roots of lettuce plants cultivated in soil samples amended with natural and enriched vermicomposts, at different vermicompost doses

Dose (t ha^{-1})	Leaves				Roots			
	Natural	Enriched with Cu	Enriched with Ni	Enriched with Zn	Natural	Enriched with Cu	Enriched with Ni	Enriched with Zn
Partition of Cu (%)								
0	51.7				48.3			
25	63.1 a	32.0 b	76.9 a	68.8 a	36.9 b	68.0 a	23.1 b	31.2 b
50	61.7 b	17.0 c	79.5 a	80.9 a	38.3 b	83.0 a	20.5 c	19.1 c
65	69.6 a	17.7 b	80.4 a	83.7 a	30.4 b	82.3 a	19.6 b	16.3 b
80	78.3 a	16.2 b	70.3 a	73.3 a	21.7 b	83.8 a	29.7 b	26.7 b
Partition of Ni (%)								
0	39.3				60.7			
25	49.1 a	51.8 a	24.8 a	43.6 a	50.9 a	48.2 a	75.2 a	56.4 a
50	86.3 a	64.6 ab	24.5 b	79.3 a	13.7 b	35.4 ab	75.5 a	20.7 b
65	77.9 a	68.8 ab	30.4 b	83.2 a	22.1 b	31.2 ab	69.6 a	16.8 b
80	74.0 a	75.5 a	23.5 b	58.1 ab	26.0 b	24.5 b	76.5 a	41.9 ab
Partition of Zn (%)								
0	76.3				23.7			
25	81.4 a	89.2 a	89.0 a	88.2 a	18.6 a	10.8 a	11.0 a	11.8 a
50	84.2 a	91.4 a	91.6 a	85.1 a	15.8 a	8.6 a	8.4 a	14.9 a
65	88.9 a	92.8 a	92.4 a	88.0 a	11.1 a	7.2 a	7.6 a	12.0 a
80	95.1 a	84.0 a	85.5 a	83.7 a	4.9 a	16.0 a	14.5 a	16.3 a

Mean values followed by same letters in the line for each variable are not different at the 5% level according to Tukey's test.

Cu or Zn, the amounts of Ni were greater in the leaves than in the roots. Zinc accumulated more in the leaves in all treatments.

A greater retention of metals by the roots in treatments with the vermicomposts containing Cu or Ni was found, because roots are sites of preferential metal accumulation. Thus, high concentrations of available Cu commonly inhibit the development of roots before affecting leaf growth (Marschner, 1995).

The translocation of both Cu and Ni to the leaves was affected by concentrations of the elements in the substrate. At relatively higher concentrations, there was greater accumulation in the roots and less translocation. However, even with high concentrations in the substrate, the Zn distribution was not affected and remained in the leaves. It has been reported that the application of growing doses of Zn result in greater accumulations of Zn in the leaves of lettuce (Pereira, 2001).

According to Morishita et al. (1983), there is a strong relationship between the translocation of elements in plants and their chemical properties. The authors suggest that the electrochemical series of Cu, Ni, Co, Zn, and Mn follows the order of toxicity, as well as the order of the distribution ratio of the elements in the roots in plants of rice.

The amounts of P in the leaves of lettuce ranged from 0.41 to 4.35 mg plant^{-1} at the dose 0 and 80 t ha^{-1}, respectively (values not shown in the tables).

4. Conclusions

This investigation aimed to evaluate the use of cattle manure vermicompost for purifying effluents containing heavy metals and the effects of application of the vermicomposts in lettuce cultivation. Under batch conditions, vermicompost was efficient in removing Cu, Zn and Ni from electroplating wastes. Metal retention values were close to 100%. The Cu retention by the vermicompost was determined at the original pH of the effluent. The Zn and Ni retentions were evaluated at the original effluent pH (6.9 and 7.4, respectively) as well as a pH of 2.0. The greatest metal retentions occurred at the original effluent pH values.

Besides the great capacity for retention of Cu, Zn and Ni, the vermicompost also enhanced pH values of the effluents after the passage through the columns. It was not necessary to correct the effluent pH during the treatment process to reach the levels recommended by the Brazilian legislation for discharge into water courses (Brasil, 2005).

The Cu concentrations in the leaves of lettuce from the treatment with vermicompost enriched with this metal were less than the value that can cause significant plant damage. However, the Cu concentrations in the roots were relatively high. The Ni and Zn concentrations in the leaves from the treatments with vermicomposts enriched with the respective metals were above the critical toxicity levels for plants.

Larger accumulations of Cu, Ni and Zn were found in the lettuce leaves than in the roots in the treatments with vermicompost. The plants grown in soil amended with vermicompost containing Cu and Ni had greater amounts of these metals in the roots, whereas the plants cultivated with vermicompost containing Zn had greater amounts of this metal in the leaves.

In the evaluation of soil contamination for heavy metals, analyses of leaves as well as roots of the plants are recommended, because some metals are retained preferentially in the roots. Results of plant analysis including only levels of metal concentrations in leaves can lead to a false diagnosis of the absorption capacity of metals for the plants.

The application of vermicomposts containing Cu, Ni and Zn to agricultural lands can be recommended. However, before application to soil it is necessary to evaluate the metal concentrations in the vermicomposts. We suggest mixing the vermicomposts containing elevated concentrations of these metals with uncontaminated vermicompost to avoid plant damage.

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