

Vermicompost as a Natural Adsorbent Material: Characterization and Potentialities for Cadmium Adsorption

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Amostras de vermicomposto (material húmico) foram submetidas à caracterização por espectroscopia de infravermelho, difractometria de raios-X, termogravimetria, microscopia eletrônica, entre outras; adicionalmente, foi determinada a capacidade de troca catiônica (CTC). Empregou-se planejamento fatorial para estudar os mecanismos de interação da espécie Cd^{2+} com os sítios adsorptivos do vermicomposto e, posteriormente, foi avaliada a máxima capacidade adsorptiva de cádmio empregando isoterma de Langmuir. A caracterização revelou que o vermicomposto exibe CTC tão elevada quanto 72,9 meq por 100 g, grande área superficial (substância porosa), grupos quelantes e máxima capacidade adsorptiva para Cd ($38,6 \text{ mg g}^{-1}$) em pH 5,0. Esta potencialidade foi explorada em análises de amostras sintéticas e reais (água mineral) apresentando concentrações de cádmio próximas a $5 \mu\text{g L}^{-1}$ e requerendo etapas de pré-concentração. Um fator de enriquecimento de 100 foi obtido.

Vermicompost (humic material) samples were submitted to characterization by infrared spectroscopy, X-ray diffractometry, thermogravimetric analysis, electron microscopy etc. In addition, its cation exchange capacity (CEC) was determined. Factorial experiments were designed in order to elucidate the interaction mechanisms between Cd^{2+} and the adsorptive sites of vermicompost. The maximum adsorptive capacity for cadmium was evaluated by a Langmuir isotherm. The characterization revealed that vermicompost exhibits high CEC values (ca. 72.9 meq per 100 g), high surface area (porous material), chelating groups and a maximum adsorptive capacity for Cd (38.6 mg g^{-1}) at pH 5.0. This potential application was exploited in the analysis of synthetic and real (mineral water) samples with Cd concentrations of ca $5 \mu\text{g L}^{-1}$, requiring a preconcentration step. An enrichment factor of 100 was attained.

Keywords: vermicompost, characterization, cadmium adsorption

Introduction

Humic substances comprise a number of organic compounds with complex molecular structure (aromatic rings, carbonyl groups, phenolic and alcoholic hydroxyl, among others). These substances are formed by chemical and microbial decomposition of animal and plant materials.¹ The humification process occurs naturally in different environments such as soils, sediments, aquatic ecosystems (oceans, rivers and lakes) as well as in the upper plants.² It should be noted that humification depends on several parameters, such as acidity, microbial population, nutrient concentrations, aeration and temperature.³

Due to its structural complexity, it is difficult to establish a classification of the humic substances and acceptable classification criteria are usually based on

solubility properties. Thus, humic acids precipitate in acidic medium, humines are insoluble under both acidic and alkaline conditions and fulvic acids are soluble under both these conditions.⁴

Degradation of organic residues is usually a slow process, however other humification mechanisms may speed up it. Composting is frequently exploited, when conversion of fresh organic matter to substrates with a high degree of degradation is accomplished in a relatively short (usually a few months) period of time.¹ During composting, the organic substrates are decomposed by microorganisms and the main products are CO_2 , H_2O , mineral ions and stabilized organic matter.³

Vermicomposting constitutes a special form of composting. It is accomplished when earthworms (mainly *Lumbricus rubellus*) metabolize and excrete a mixture of soil and organic matter (from agricultural, industrial and urban sources). In the digestive system of these worms, microorganisms are responsible for transforming some

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organic species (proteins, nucleic acids, fats, carbohydrates) into a more stable product (vermicompost). This product presents a high CEC, high humidity content, wide particle size distribution, high concentration of nutrients (Ca, Mg, Na, K, P, S, N) and a characteristic black colour due to the presence of humic substances.^{1,2}

Despite the high CEC values, there are only a few studies about the characterization of vermicompost and about its application as a metal adsorbent. Thus, a characterization was performed to elucidate the interaction mechanisms between cadmium and vermicompost. After the characterization, the potentiality of cadmium adsorption was confirmed by carrying out analyses of Cd requiring a preconcentration step.

Experimental

Instruments and apparatus

For vermicompost characterization, a Shimadzu XRD 6000 X-ray diffractometer (Kyoto, Japan), a Perkin-Elmer FT-IR 1605 infrared spectrometer (Überlingen, Germany), a Perkin-Elmer PE 2400 elemental analyzer (Norwalk, USA), a TA Instruments TGA 2950 thermogravimetric analyzer (New Castle, USA) and a JEOL JMT-300 electron microscope (Tokyo, Japan) were used.

In order to establish the total cadmium concentration, as well as the extractable calcium and magnesium in the vermicompost, a Perkin-Elmer Analyst 300 flame atomic absorption spectrometer (Norwalk, USA), equipped with a deuterium lamp background correction system, was used. This instrument was also used for Cd determinations in the experiments involving factorial design and Langmuir isotherm. In addition, the instrument was used in the emission mode for the determination of extractable sodium and potassium in vermicompost, as well as potassium in mineral water samples.

In the preconcentration experiments, a Perkin-Elmer Analyst 600 graphite furnace atomic absorption spectrometer (Überlingen, Germany), equipped with a Zeeman-effect background correction system, was used to determine the cadmium content in synthetic aqueous solutions and in mineral water samples (after the enrichment process). The operating conditions were those recommended by the manufacturer for maximum sensitivity.

Hollow cathode lamps were employed as the radiation source for calcium ($\lambda = 422.7$ nm) and magnesium ($\lambda = 285.2$ nm) determinations, whereas an electrodeless discharge lamp was used for cadmium ($\lambda = 228.8$ nm).

Decomposition of the vermicompost was carried out using a QCI QW-3000 microwave oven (Mississauga,

Canada), equipped with temperature and pressure sensors and with a magnetron of 2450 ± 13 MHz.

For pH measurements, a Digimed DM20 pH-meter (São Paulo, Brazil) was used.

Ultra-pure nitric acid employed in preconcentration procedures was obtained using a quartz sub-boiling still (Marconi, Piracicaba, Brazil).

A 3.4 x 25 cm glass column was employed in the preconcentration experiments.

Standards, reagents and samples

All solutions were prepared with analytical reagent-grade chemicals (Merck, Darmstadt, Germany) and distilled/deionised water (Millipore, Mosheim, France). For adsorption experiments, a 1000 mg L⁻¹ Cd reference stock solution (in 1.6 mol L⁻¹ HNO₃) based on CdCl₂.H₂O was prepared. Working reference solutions (for FAAS calibrating purposes) with 0.5 – 2.0 mg L⁻¹ Cd were prepared daily by serial dilutions of the reference solution with 0.014 mol L⁻¹ HNO₃.

Calcium, magnesium, sodium and potassium single-analyte stock reference solutions (1000 mg L⁻¹) were prepared using Ca(NO₃)₂.4H₂O, Mg(NO₃)₂.6H₂O, NaCl and KNO₃, respectively. Working reference solutions with 1.0 – 5.0 mg L⁻¹ Ca, 0.1 – 0.5 mg L⁻¹ Mg and 1.0 – 10.0 mg L⁻¹ Na or K were prepared daily by serial dilutions with 0.014 mol L⁻¹ HNO₃.

Vermicompost samples were obtained from different regions of Minas Gerais and São Paulo States (Brazil). Two samples were collected in Tabuleiro do Pomba (MH) and Coimbra (SM), Minas Gerais. Sample XA was collected in Campinas, São Paulo.

For all experiments, except for those involving humidity evaluation, the vermicompost samples were dried in an oven (60 °C) for 24 h and the analyses were performed using particle sizes ranging from 75 to 150 μ m.

For extractable calcium and magnesium determinations, a 10% (w/v) La₂O₃ solution was used as releasing agent.

Procedure

For characterization of the three vermicompost samples (MH, SM and XA), different parameters, such as humidity, ash and total organic matter content (by thermogravimetric analysis), infrared spectroscopy, X-ray diffractometry, elemental composition, electron microscopy, pH, exchangeable Ca, Mg, Na and K, exchangeable and potential acidity, effective and potential cation exchange capacity (CEC) and total Cd content were evaluated.

Thereafter, the XA sample was chosen for the experiments focusing on adsorption studies for Cd (factorial design, Langmuir isotherm and preconcentration). All experiments were made in triplicate, except those involving thermogravimetric analysis.

Humidity

The water content was determined by difference of vermicompost masses before and after submitting 10.0 g of fresh sample to 60 °C for 24 h.

Ash and total organic matter content

The ash and total organic matter content were obtained by heating the vermicompost samples from 20 to 980 °C (10 °C min⁻¹ heating rate), respectively.

Infrared spectroscopy, X-ray diffraction, elemental composition and electron microscopy

The functional groups present in the vermicompost were characterized by Fourier-transform IR spectroscopy, using KBr discs to prepare the vermicompost samples. The spectral range varied from 4000 to 400 cm⁻¹.

For X-ray diffraction, the samples were exposed to X-rays ($\lambda = 1.54060 \text{ \AA}$) with the 2θ angle varying within 5 and 50°. The applied voltage and current were 40 kV and 30 mA, respectively.

Carbon, nitrogen and hydrogen determinations used an elemental analyzer while for electron microscopy, vermicompost samples were covered with a thin layer of gold and an electron acceleration voltage of 20 kV was applied.

pH measurement

The procedures described in this section as well as those indicated in several subsequent sections were adopted or modified from Pace *et al.*⁵

For pH determination, 10.0 g of the vermicompost were shaken with 25 mL of a 1.0 mol L⁻¹ KCl solution for 1 min. The samples were then allowed to rest for 1.0 h. After that, the samples were shaken during 1.0 min and the pH of the resulting suspension was potentiometrically determined.

*Exchangeable Ca, Mg, Na and K*⁵

The vermicompost (3.0 g) was shaken for 1.0 h with 75 mL of a 1.0 mol L⁻¹ KCl solution for Ca and Mg extraction or with 75 mL of 0.05 mol L⁻¹ HCl for Na and K extraction. After shaking, a period of 16 h for sedimentation was

needed to complete both extractions. Ca and Mg concentrations in the liquid phase were then determined by FAAS. For exchangeable Na and K, the FAAS spectrometer was operated in the emission mode.

*Exchangeable or potential acidity*⁵

The species related to exchangeable or potential acidity were extracted by shaking 3.0 g of vermicompost with 75 mL of either a 1.0 mol L⁻¹ KCl solution (for exchangeable acidity studies), or an acetate buffer solution, pH 7 (potential acidity studies), for 1 h. Thereafter, a period of 16 h for sedimentation was needed. In the experiments related to exchangeable acidity, 25 mL of the supernatant were selected and titrated with a 0.025 mol L⁻¹ NaOH solution; bromothymol blue was used as indicator. For potential acidity evaluation, with the same titrant, the end point was determined using phenolphthalein.

*Effective and potential CEC*⁵

The effective CEC value (CEC_{eff}) was calculated as the sum of the exchangeable acidity plus the exchangeable Ca, Mg, K, and Na contents. In addition, the potential CEC value (CEC_{pot}) was calculated as the sum of the exchangeable Ca, Mg, K, and Na contents plus the results obtained for potential acidity.

Total Cd content

In this experiment 600 mg of vermicompost samples were decomposed through an acidic microwave-assisted decomposition procedure⁶ using concentrated HCl, HNO₃ and HF acids (3:1:2 volumetric ratio, 15 mL total volume). After that, the digests were dried almost to dryness and the volume made up to 25 mL with 0.014 mol L⁻¹ HNO₃. For HF elimination, *ca.* 300 mg H₃BO₃ were added to the samples.

After sample decomposition, cadmium concentrations were determined by FAAS.

Factorial design for cadmium adsorption

These experiments were carried out for optimizing the pH and the shaking time interval for cadmium adsorption by the vermicompost. A factorial design⁷ was chosen because this chemometric approach may consider simultaneously both investigated variables (factors): pH and shaking time. Thus, interaction effects are considered, and a more reliable interpretation of results is possible. It is important to note that factorial design was also necessary to construct the Langmuir isotherm.

For factorial design, a 60 mg L⁻¹ cadmium solution was prepared from the 1000 mg L⁻¹ stock reference cadmium solution. The pH of these solutions were adjusted at 2.0, 4.0 or 6.0 by adding 0.1 mol L⁻¹ HNO₃ or NaOH whenever necessary. The shaking times (5.0, 32.5 or 60 min) were tested for each pH condition. According to the factorial design employed (3²), nine combinations were made (Table 1). Twenty-seven assays were carried out (3 replicates for each combination). According to adaptations from Slavek *et al.*,⁸ for each assay, 20 mg of vermicompost were shaken by a magnetic stirrer with 40 mL of 60 mg L⁻¹ cadmium solution. After this step, the samples were centrifuged at 3000 rpm for 20 min. Suitable liquid phase volumes (according to the required dilution) were transferred to 25 mL volumetric flasks and the volume was completed with 0.014 mol L⁻¹ HNO₃ solution. The cadmium concentrations were determined by FAAS.

Table 1. Combinations used in the factorial design (3²) for Cd adsorption studies in vermicompost^a

Combination	pH	Shaking time
1	- 1	- 1
2	0	- 1
3	1	- 1
4	- 1	0
5	0	0
6	1	0
7	- 1	1
8	0	1
9	1	1

^aNumbers -1, 0 and 1 correspond to pH levels of 2, 4, 6 and shaking times of 5, 32.5, 60 min, respectively.

Langmuir isotherm for cadmium

Cadmium saturation in the vermicompost was established by a Langmuir isotherm. To this end, 40 mg of vermicompost were mixed with 40 mL of different cadmium solutions (10, 50, 200, 600, 800, and 1000 mg L⁻¹). The acidity and shaking time were defined as pH 5.0 and 5.0 min, respectively, from experiments performed in the *Factorial design* section. After shaking, samples were centrifuged at 3000 rpm for 20 min and suitable supernatant volumes were transferred to 50 mL volumetric flasks and diluted with 0.014 mol L⁻¹ HNO₃ solution. Cadmium concentrations were determined for these solutions.

Cadmium preconcentration in vermicompost columns

This experiment was made by passing 1000 mL of synthetic or real samples (10 mL min⁻¹) at pH 5.0 through the vermicompost columns. For the synthetic aqueous sample (5.0 μg Cd L⁻¹), 60 mg vermicompost were used whereas for

the real sample (mineral water spiked with cadmium up to 5.0 μg L⁻¹), 120 mg of vermicompost were needed. The mineral water employed in this experiment (Genuína brand, Lindóia SP, Brazil) was obtained at a local market.

After preconcentration, the cadmium retained was desorbed by adding 10 mL of a 1.0 mol L⁻¹ HNO₃ solution. In the elution step, the flow-rate was maintained at 10 mL min⁻¹. Cadmium in the eluent solutions was determined by FAAS.

After preparing synthetic samples and enriched mineral water, the cadmium concentration in these samples was also measured by graphite furnace atomic absorption spectrometry (GFAAS).

Results and Discussion

The X-ray diffractograms (Figures 1a-c) revealed the presence of SiO₂ in the vermicomposts. This mineral was predominant in this material, whereas other minerals occurred only at trace levels, thus making identification difficult. It should be emphasized that other peaks were also associated to SiO₂ but with different inter-planar distances. The material in Figure 1b presents an amorphous characteristic. The main peak of SiO₂ is shown in Figures 1 a-c.

The initial thermal decompositions of organic matter (see thermogravimetric curves, Figures 2a-c) were similar for the different samples: 245 °C (MH), 239 °C (SM) and 243 °C (XA). Otherwise, the final decomposition temperature of organic matter, presented a pronounced difference between XA and the other vermicomposts: 500 °C (MH), 479 °C (SM) and 645 °C (XA), indicating a possible differentiation in the structure of the organic matter in these samples.

The results for total organic matter (TOM) were established by considering the differences of the masses at the initial and final decomposition temperatures. The results obtained matched the literature information.^{9,10} According to these literature, samples collected in Juiz de Fora and São Carlos, presented results of TOM as 47.7 and 31.5 % m/m, respectively. Results for humidity, ash, total organic matter and elemental composition of vermicompost samples are presented in Table 2.

According to the literature,⁹ similar values for ash contents were observed for bovine manure vermicompost. The ash content for the sample collected in Juiz de Fora was 47.3 % m/m. This value reveals the complexity of the raw material employed in vermicompost production.

Products obtained by the vermicomposting process present high humidity levels.¹ In this way, results obtained in the humidity tests (from 56.2 to 59.8 %) are in agreement with this affirmation.

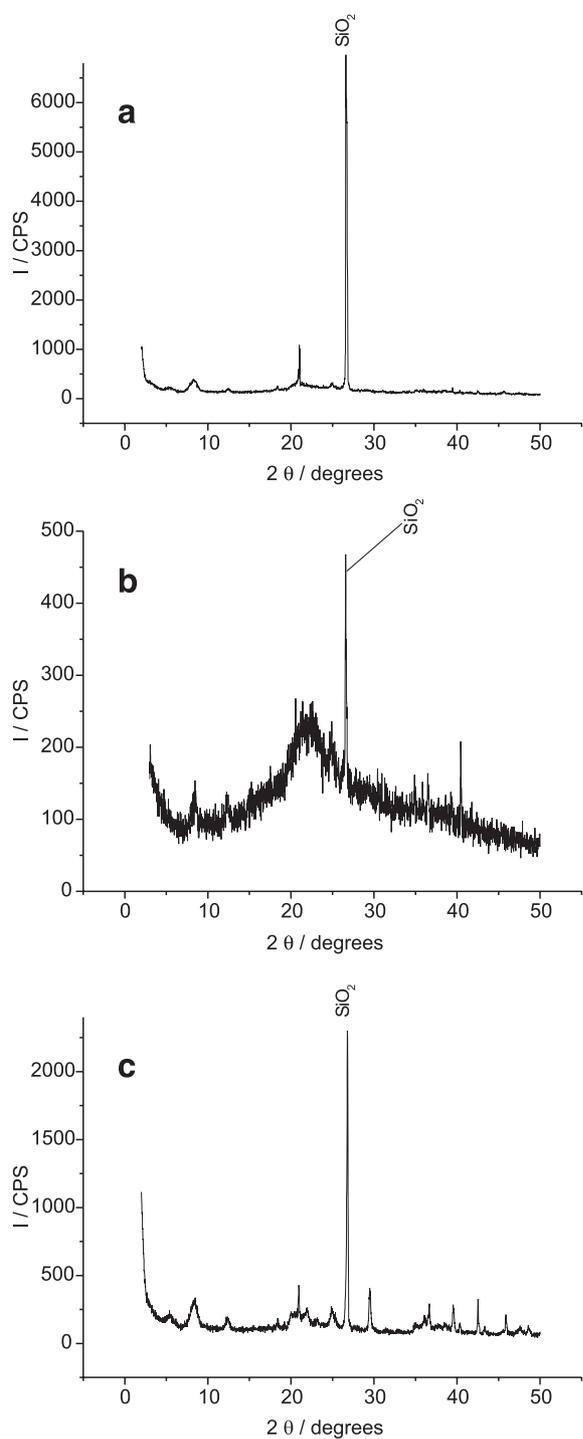


Figure 1. X-ray diffractograms of (a) MH, (b) SM and (c) XA vermicompost samples. For details, see text.

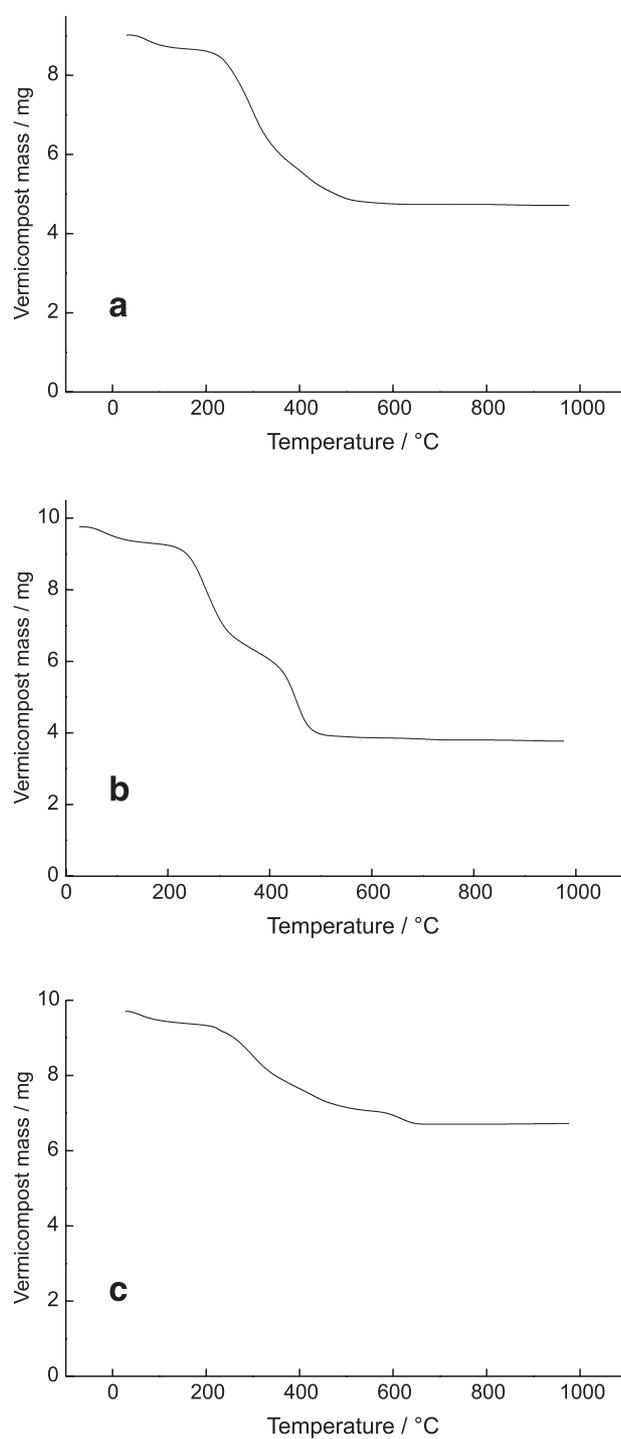


Figure 2. Thermogravimetric graphics of (a) MH, (b) SM and (c) XA vermicompost samples.

Table 2. Humidity, ash, total organic matter (TOM) and elemental composition (C, N and H); n = 3. For sample identification, see text

Sample	Humidity (%)	Ash ^a (%)	TOM ^a (%)	C (%)	N (%)	H (%)
MH	59.8 ± 0.3	53.7	41.2	17.1 ± 0.1	2.0 ± 0.1	3.0 ± 0.1
SM	56.2 ± 0.1	41.1	53.5	33.2 ± 1.0	2.3 ± 0.1	5.0 ± 0.2
XA	57.9 ± 1.3	68.8	27.0	10.4 ± 0.2	0.7 ± 0.1	1.8 ± 0.1

^awithout replicates.

For all vermicompost samples, the potential acidity results were higher than those related to exchangeable acidity (Table 3). This can be explained in view of the organic matter present in vermicompost, whereas at pH 7 (the best pH for potential acidity), several acidic groups of organic matter are dissociated and the titrated acidity comprises the sum of exchangeable acidity (due to Al^{3+} hydrolysis) plus the hydrogen concentration originating from organic matter dissociation. This is an interesting behavior related to the adsorption phenomena of metallic species at higher pH values.

Table 3. Exchangeable acidity (EA), potential acidity (PA) and pH values (n=3). For sample identification, see text

Sample	PA ^a	EA ^a	pH
MH	4.4 ± 0.2	0.9 ± 0.1	5.8 ± 0.2
SM	4.1 ± 0.1	0.0	7.8 ± 0.3
XA	3.2 ± 0.1	1.1 ± 0.1	5.7 ± 0.1

^aValues expressed in meq per 100 g

The exchangeable cation values (Table 4) reveal the differences among the three investigated vermicompost samples, which are probably due to the origin of these samples.

Table 4. Ca, Mg, K and Na exchangeable concentrations (n = 3), expressed in meq per 100 g. For sample identification, see text

Sample	Ca	Mg	K	Na
MH	32.4 ± 2.0	9.2 ± 0.7	1.5 ± 0.1	1.6 ± 0.1
SM	20.9 ± 1.0	18.4 ± 0.6	4.7 ± 0.2	6.4 ± 0.1
XA	52.2 ± 3.3	1.5 ± 0.1	6.7 ± 0.4	9.3 ± 0.3

The vermicompost samples presented CEC values higher than those related to soil materials (Table 5). This can be confirmed comparing CEC results (from 45.6 to 72.9 meq per 100 g) with those already obtained (24.1 meq per 100 g) from Philippine agricultural soils.¹¹ It is important to stress that higher CEC values of vermicompost correspond to a higher capacity to retain metals by adsorption processes. In this way, the XA vermicompost was selected for the adsorption experiments due to the highest CEC values obtained (Table 5).

Table 5. Effective cationic exchange capacity (CEC_{eff}) and potential cationic exchange capacity (CEC_{pot}). Values expressed in meq per 100 g. For sample identification, see text

Sample	CEC_{eff}	CEC_{pot}
MH	45.6 ± 2.1	49.1 ± 2.1
SM	50.4 ± 1.2	54.5 ± 1.2
XA	70.8 ± 3.3	72.9 ± 3.3

The infrared spectra (Figures 3a-c) reveal the presence of groups associated with organic matter, which can be considered as potential sites for binding with metallic species. The bands observed between 3500 to 3000 cm^{-1} indicate the occurrence of the characteristic absorption of N-H from amines and amides as well as alcoholic and phenolic hydroxyls and carboxylic acids (Figure 3a: 3445.7 cm^{-1} ; Figure 3b: 3433.9 cm^{-1} ; Figure 3c: 3527.0 cm^{-1}). In the 3000 to 2800 cm^{-1} region, the absorption was mainly

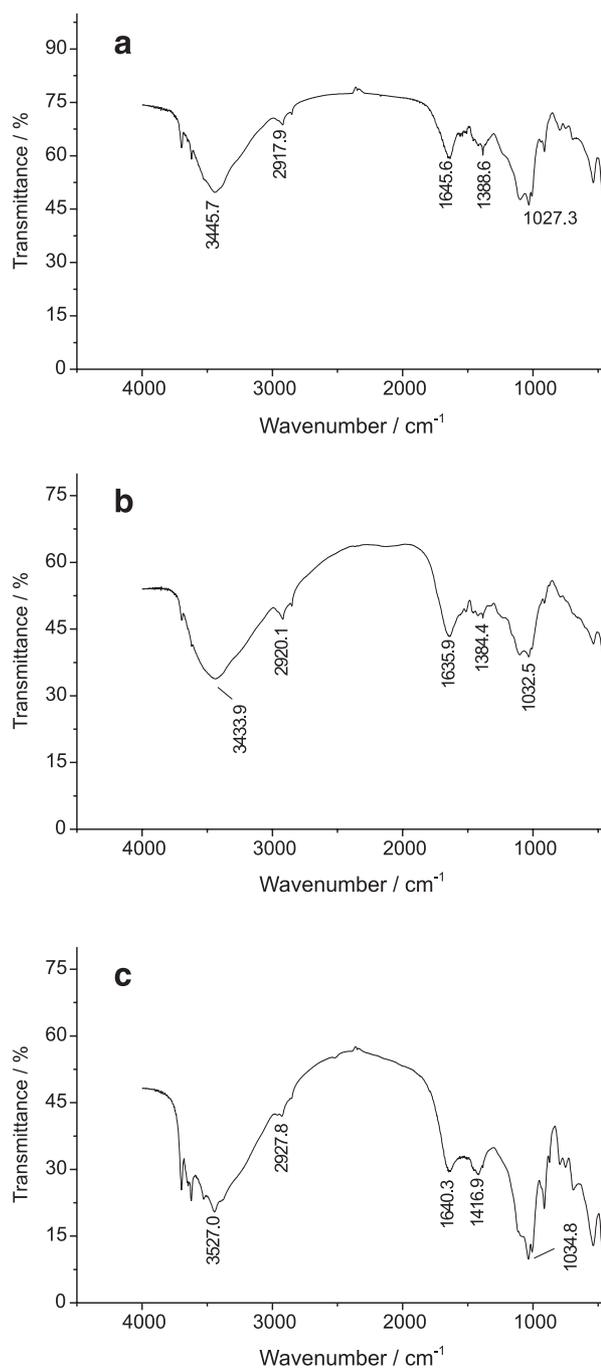


Figure 3. Infrared spectra of (a) MH, (b) SM and (c) XA vermicompost samples. For details, see text.

assigned to the C-H bond from aliphatic groups (Figure 3a: 2917.9 cm^{-1} ; Figure 3b: 2920.1 cm^{-1} ; Figure 3c: 2927.8 cm^{-1}). Between 2000 to 1000 cm^{-1} , the absorption can be attributed to the presence of C-O and C=O bands¹² (Figure 3a: 1027.3, 1388.6, 1645.6 cm^{-1} ; Figure 3b: 1032.5, 1384.4, 1635.9 cm^{-1} ; Figure 3c: 1034.8, 1416.9, 1640.3 cm^{-1}).

The importance of total cadmium determinations in vermicompost is related to the natural concentration of this element in the material. After microwave-assisted decomposition of three vermicompost samples, measurements revealed that total Cd concentrations were lower than the detection limit of FAAS (0.08 mg L^{-1}). These results indicated the low concentration of naturally occurring cadmium present in the vermicompost.

Results of the factorial design are indicated in Table 6 and, according to the mathematical treatment given by Matthias,⁷ a response surface (Figure 4a) was obtained from these data. The surface reveals optimized values near to 0.5 on the pH axis for the cadmium adsorption process. It is important to note that this value is normalized, therefore it is necessary to find the corresponding value on the true pH scale (it is near 5); this conversion is possible using literature procedures.⁷ The equation obtained from the data shown in Table 6 [% Cd adsorption = 36.97 + 12.25 pH – 15.00 pH²] was taken into consideration in order to achieve the response surface (Figure 4a). The parameter agitation time is not shown in this equation because the error associated to this variable was higher than the coefficient related to it. This Figure also indicates that Cd adsorption was independent of the shaking time. These results can be explained in terms of the predominance of cationic exchange that may indicate that equilibrium between the Cd(II) content in the liquid and in the solid phases is rapidly attained. Another response surface representation comprises contour graphics (Figure

Table 6. Data from factorial design

pH ^a	Shaking time ^a	Cd adsorption (%) ^b
-1	-1	7.30 ± 0.58
0	-1	38.68 ± 0.39
1	-1	34.01 ± 2.38
-1	0	11.61 ± 1.10
0	0	34.84 ± 1.05
1	0	34.64 ± 1.39
-1	1	9.06 ± 0.27
0	1	34.48 ± 2.07
1	1	32.22 ± 1.29

^a The values -1, 0 and 1 as in Table 1; ^bMean of 3 replicates ± standard deviation.

4b) that are obtained when constant values are attributed to dependent variables. In this specific situation, the parallel lines indicate that any variation of agitation time (within the studied interval) does not modify the cadmium adsorption, but the pH value strongly influences the analytical response. From this contour graphic, it is also possible to verify that the best pH for cadmium adsorption is attained near to 0.5 (normalized scale) or 5.0 (pH scale).

Electron micrographies of vermicompost are shown in Figures 5a-c. These figures show a surface area with an irregular morphology as well as a high number of pores. This morphology can corroborate to high CEC values, such as those obtained, due to the high number of sites for metal adsorption.

The isotherm in Figure 6 shows a tendency towards saturation. This kind of isotherm is classified as Langmuir because it follows the mathematical model indicated by equation 1:¹³

$$qM = a \cdot b \cdot C_{eq} M \cdot (1 + a \cdot C_{eq} M)^{-1} \quad (1)$$

where qM = quantity of adsorbed metal in vermicompost

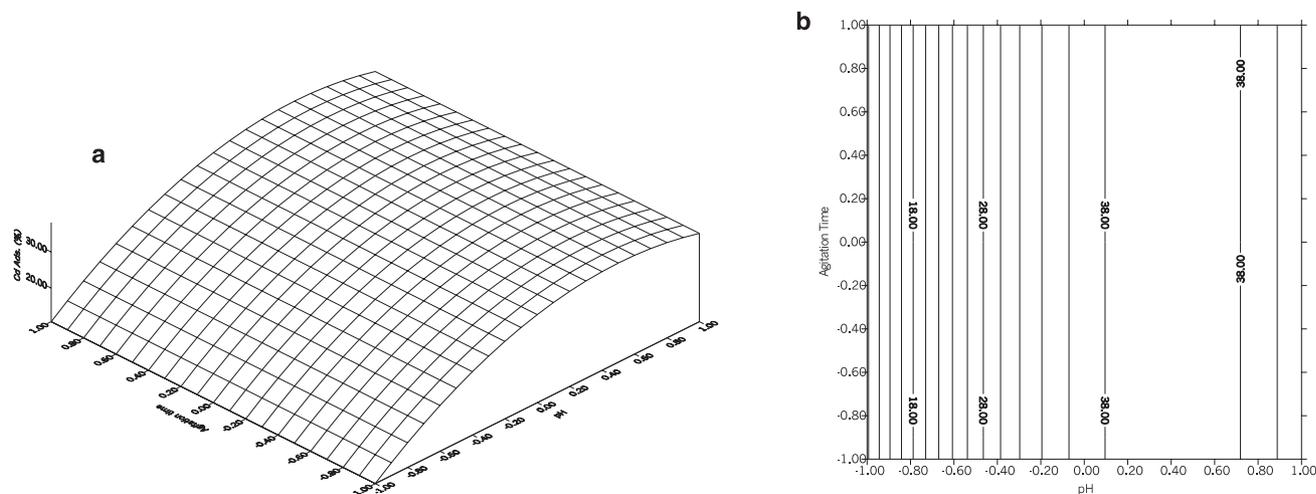


Figure 4. a) Cadmium adsorption (%) obtained by factorial design for XA vermicompost relating agitation time and pH. The values of time (from -1.00 to +1.00) are related to 5 – 60 min of agitation and the pH values (from -1.00 to +1.00) are related to 2 – 6; b) Contour graph related to Figure 4a. Numbers correspond to Cd adsorption (%).

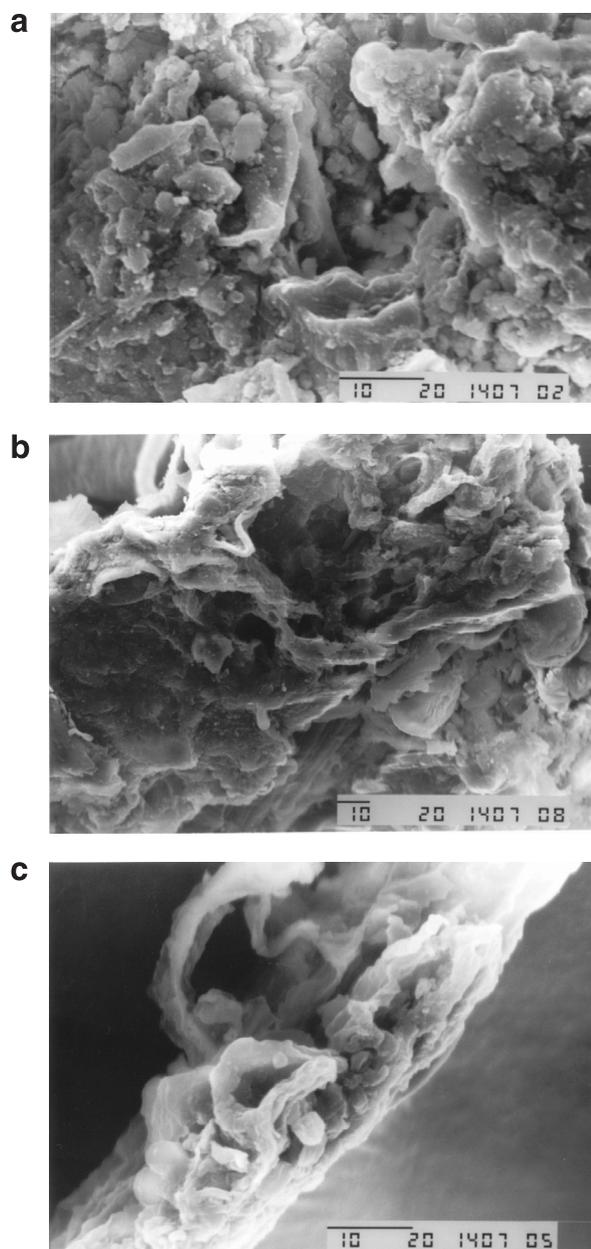


Figure 5. Electron micrograph of (a) MH, (b) SM and (c) XA, with magnifications of 2000, 750 and 2000 times, respectively.

(mg g^{-1}); a = constant, related to adsorption energy, and expressed by equation:

$$b_0 \exp(-\Delta H/RT) \quad (2)$$

Here, b_0 = constant, including the entropy term, R = universal gas constant, T = absolute temperature. This constant (a) can be expressed as L mg^{-1} ; b = highest metal adsorption capacity in the vermicompost (mg g^{-1}); $C_{\text{eq}}M$ = equilibrium metal concentration (mg L^{-1}).

According to the literature,¹⁴ equation 1 can be linearized, yielding equation 3:

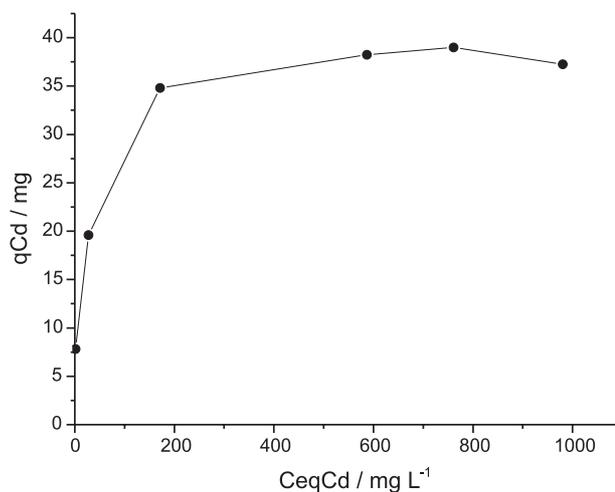


Figure 6. Langmuir isotherm for cadmium, where q_{Cd} is the quantity of cadmium adsorbed in vermicompost and C_{eqCd} is the equilibrium cadmium concentration.

$$C_{\text{eq}}M/qM = (a \cdot b)^{-1} + (b)^{-1} \cdot C_{\text{eq}}M \quad (3)$$

From the inverse of the angular coefficient indicated in Figure 7 (linearization of the results from Figure 6), it is possible to calculate the maximum adsorption capacity for cadmium in the vermicompost (38.6 mg g^{-1}). When compared to different adsorbent materials,¹⁵ vermicompost presents an expressive cadmium adsorption capacity.

In the pre-concentration experiments, it was possible to confirm the cadmium adsorption potential of vermicompost, because this material exhibited both high enrichment factor (EF) and pronounced recovery for synthetic and real samples. According to the literature,¹⁶ EF values can be calculated from the ratio of sample and the elution volume. In the present work, an EF of 100 was obtained. Based on this same reference,¹⁶ cadmium

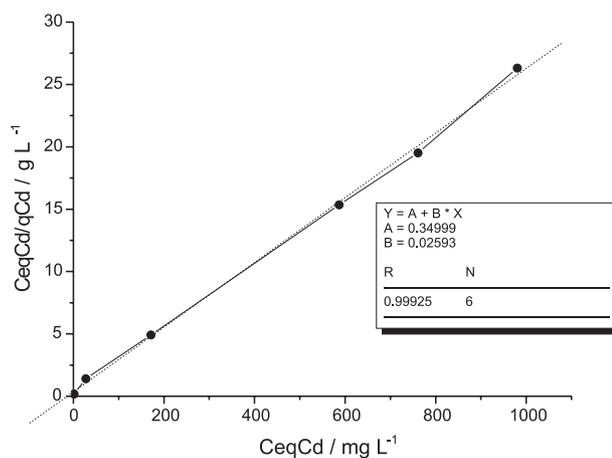


Figure 7. Linearization of Langmuir isotherm for cadmium, where $C_{\text{eqCd}}/q_{\text{Cd}}$ is the ratio between the equilibrium concentration and the quantity of cadmium adsorbed in vermicompost.

recoveries were calculated from the ratio between the cadmium concentration found by FAAS (pre-concentrated samples) and that concentrations seen in the synthetic or real samples after their preparation or enrichment with $5 \mu\text{g L}^{-1}$ Cd respectively. The cadmium concentration determined by GFAAS in the synthetic solution after its preparation was $4.76 \pm 0.06 \mu\text{g L}^{-1}$, whereas the concentration of this metal in the eluent solutions (10 mL of $1.0 \text{ mol L}^{-1} \text{ HNO}_3$) was $456 \pm 23 \mu\text{g L}^{-1}$ (determination by FAAS). Thus, a recovery of ca. 96% was observed. For real samples (mineral waters enriched with Cd), the eluent solutions presented Cd concentrations of $479 \pm 31 \mu\text{g L}^{-1}$, while in directly determined samples, the Cd concentration value was $4.84 \pm 0.04 \mu\text{g L}^{-1}$. Therefore, a recovery of 99% was calculated. As additional information, the natural concentration of Cd in mineral water was always below the detection limit of the GFAAS technique ($< 0.17 \mu\text{g L}^{-1}$).

It was necessary to use a vermicompost mass of at least 120 mg in order to compensate the competition effects between Cd^{2+} and the main constituents of mineral waters [Ca, Mg, K at 13.4, 5.0, 1.9 mg L^{-1} (determined by FAAS/FAES) and Na at 10.2 mg L^{-1} , as indicated in the label]. When 60 mg of vermicompost were used for real samples, recoveries between 50 and 60% were verified. In the synthetic sample (without concomitants ions) a vermicompost mass of 60 mg was sufficient for quantitative recovery of cadmium.

Conclusions

This work presents data to support the applicability of vermicompost in adsorptive processes. The results highlight vermicompost as a potential material for cadmium adsorption. For cadmium preconcentration procedures, this potential was confirmed, as high pre-concentration factors and recoveries were obtained. This characteristic is of high analytical interest, as vermicompost is easily available at low cost (ca. US\$ 100 per ton).

Related to adsorption behavior, it is possible to predict that vermicompost may adsorb other metallic species as efficiently as Cd^{2+} . This affirmative is based on the structural properties of vermicompost, as this material demonstrates desirable characteristics (e.g., high CEC values), which can be applicable to different metals. In this way, studies should be carried out to investigate the use of this material in relation to the adsorption of other metals.

According to all these characteristics, use of vermicompost for determination of environmental contaminants is feasible; mainly those related to determining the results of treatments of effluents heavy high initial metal concentrations.

For environmental purposes, when complex matrices are considered, an increase in the vermicompost mass could be made to compensate possible differences in the adsorption properties due to the presence of concomitants.

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