Environment Protection Engineering

Vol. 41 2015 No. 2

DOI: 10.5277/epe150205

JOÃO MARTINHO[1], BRUNO CAMPOS[1], ISABEL BRÁS[1], ELISABETE SILVA[1]

THE ROLE OF COMPOST PROPERTIES IN SORPTION OF HEAVY METALS

The feasibility of various composts to operate as sorbents for heavy metals (Cu and Zn) removal from wastewater has been evaluated. Three commercial composts obtained from municipal solid wastes (MWS), sludge sewage (SS) and poultry manure (PM) were selected as potential sorbents. Kinetic and equilibrium tests were conducted in order to assess the equilibrium conditions to remove metals from aqueous samples. For all composts, the maximum time necessary to reach the equilibrium was 240 min. The Freundlich and Langmuir isotherm models were found to fit the sorption data. The SS compost proved to be the one with highest removal capability for both assessed metals, while MWS compost showed to be the less suitable for this purpose. These results can be explained in terms of the compost surface properties, namely, with the cation exchange capacity.

1. INTRODUCTION

European environmental regulations, regarding the landfill disposal of waste, establish guidelines in order to reduce the input of organic solid wastes in landfill, encouraging the development of methods to safeguard natural resources and obviate wasteful use of land [1]. Therefore, new alternatives for recycling these wastes should be found. Composting is one of the methods mostly used for recycling of organic solid wastes. The compost is mainly used as a soil conditioner due to the carbon and nitrogen content. However, compost production has increased quickly over the past decade resulting in a great increase in its availability. In fact, many producers have difficulties in finding markets for this product. Alternative uses must be found for compost to maintain this recycling advantage. Compost is a mixture of organic and inorganic matter. The organic content can be divided into two main groups: non-humic substances and humic ones [2]. This characteristics allows the compost to interact with various

---

[1] Departamento de Ambiente, Escola Superior de Tecnologia e Gestão de Viseu, Campus Politécnico de Repeses, 3500-510 Viseu, Portugal, corresponding author Isabel Brás, e-mail: [1]ipbras@estv.ipv.pt

pollutants in water and therefore be seen as a barrier against the dispersion of pollutants in the environment. Heavy metals are important environmental pollutants. The presence of metal ions in several anthropogenic activities has been proven to be hazardous and entail threats to the environment. Metal ions like copper, lead, mercury, cadmium and chromium are known to be toxic in nature, non-biodegradable and tend to accumulate in living organisms, causing an assortment of diseases and disorders [3].

Several treatment methods have been suggested for heavy metals mitigation in the environment, like chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and co-precipitation/adsorption. Nevertheless, the search for cost effective, alternative technologies or sorbents for metals treatment from contaminated wastewater streams is needed. Natural materials that are available in large quantities, or even certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents [4]. In fact, Ho et al. [5] reported natural products to be good sorbents for heavy metals. The authors quote materials like peat, wood, pine bark, banana pith, rice bran, soybean and cottonseed hulls, peanut shells, hazelnut shell, rice husk, sawdust, wool, orange peel, compost and leaves to have an important sorbent behavior.

Keeping this in mind, the main purpose of the present work was to evaluate the feasibility of different composts to operate as sorbents to capture heavy metals from wastewater in order to propose other roles for these materials than its use as soil amendment. The focus of the present paper is to present laboratory data highlighting Zn and Cu sorption on three different commercial composts available in Portugal.

2. EXPERIMENTAL

Three composts commercialized in Portugal were selected as potential sorbents to remove heavy metals from wastewater, the first produced from municipal solid wastes (MWS), and the other two made from sludge sewage (SS) and poultry manure (PM) wastes. Physical and chemical characterization of composts has been reported elsewhere [6]. Cation exchange capacity (CEC) was evaluated by the sodium acetate method [7]. The composts were oven dried at 55 °C for 24 h and then sieved to #10 mesh (2 mm) particle size to perform the sorption batch tests. All experiments were carried out at 18–22 °C. pH of the solutions was adjusted to 5–6 with HNO_3 (1%) or NaOH (1%). Examinations of the sorption kinetics of Zn and Cu ions were conducted in a beaker. 2 g of compost were mixed with 200 cm^3 of 200 mg/dm^3 metal solution, obtained by dissolving metal sulfate in water. Samples were collected over time to evaluate the concentration of the heavy metal. The equilibrium batch experiments were carried out, separately for each metal, in beakers with 100 cm^3 of solutions of concentrations ranging from 0 to 250 mg/dm^3. The amount of the compost for each assay was 1 g, and the beakers were shaken in a continuous rotary mixer for 5 h. After solid settling, the liquid phase was collected for metals quantification by the atomic absorption spectrophotometry (Perkin Elmer, AAnalyst 300).

3. RESULTS AND DISCUSSION

The physical and chemical characteristics of composts, extremely important to understand the mechanism of sorption of metals, is given in Table 1, as reported by Vaz-Moreira et al. [6].

Table 1

Physical and chemical characterization of composts

Property	Compost		
	MSW	SS	PM
pH	5.6	4.2	9.0
Electric conductivity, mS/cm	10.9	1.6	7.6
Moisture, %	45.5	59.6	24.7
Organic matter content, %	73.3	82.4	46.8
CEC, meq/g	3.3	3.9	3.5
Zn, mg/kg dry matter	820	637	646
Cu, mg/kg dry matter	285	299	86
Ni, mg/kg dry matter	61	38	19
Cd, mg/kg dry matter	1.3	1.9	1.2
Cr, mg/kg dry matter	213	62.3	30
Pb, mg/kg dry matter	219	79	149

Among the composts analyzed, the SS compost has lower pH and electric conductivity and higher organic matter content as well as CEC, 82.4% and 3.9 meq/g, respectively. From the acidic composts, it has the lowest total metal concentration. In other turn, PM compost has an alkaline character, less organic matter, moisture and heavy metals content.

The cation exchange capacity (CEC) is the amount of cations that a material can hold on its negative charged groups or Lewis base functional groups at the compost surface. These active sites are responsible for the electrostatic interactions between positively charged bivalent cations and the solid surface. In these kinds of organic materials, the organic matter humified, namely the humic and fulvic acids, should increase the CEC. In fact, these acids release hydrogen ions to the solution, leading to pH decrease, and therefore, making available their conjugate bases to interact with metals in solution. The highest electric conductivity of the MSW compost is probably related to its highest heavy metal content and therefore less capability to interact with exogenous cations. This characteristics may be responsible for the lowest CEC, 3.3 meq/g. PM compost has utmost pH, as a consequence of hydroxyl release to the water, and low organic matter content, showing an evidence of lower content in humic and fulvic acids.

3.1. KINETICS

The sorption kinetics is very important to evaluate the mechanisms of retention of the metal species by the composts and to acknowledge the time necessary for the system to reach equilibrium. The experimental data from assays performed with Cu and Zn were fitted with first and second order kinetic models [8]. The appropriate method to fit the experimental data was assessed by the error between the experimental and theoretical data in each model. In Figures 1 and 2, the kinetics experimental data and the second order kinetic model adjustment for Cu and Zn, respectively, showing a good agreement between the experimental data and the theoretical model.

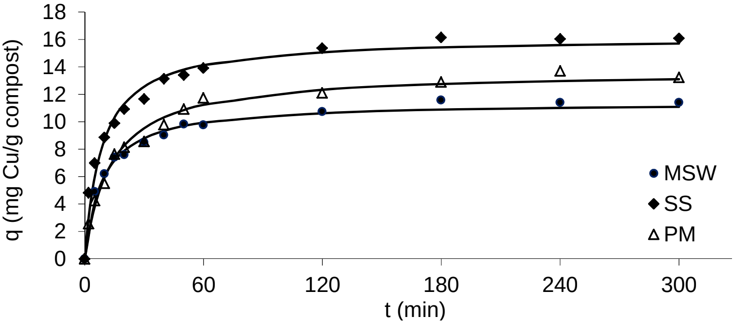

Fig. 1. Amount of Cu sorbed on 1 g (*q*) of compost over time; experimental data (symbols) and the second order model adjustment (continuous line)

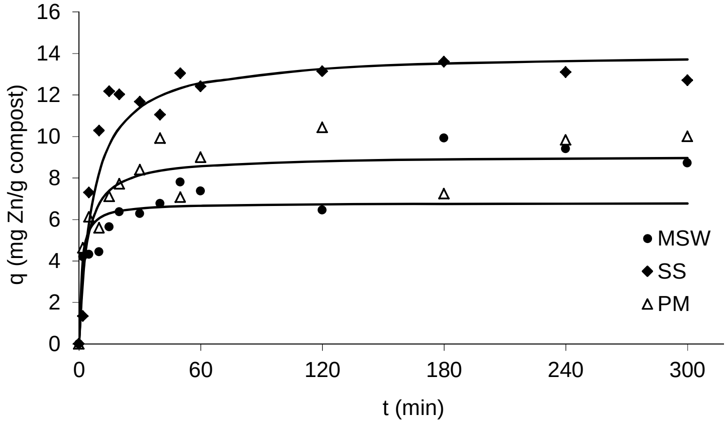

Fig. 2. Amount of Zn sorbed on 1 g (*q*) of compost over time; experimental data (symbols) and the second order model adjustment (continuous line)

The time necessary to reach the equilibrium is attained when the sorption capacity (q_t) does not change above 5% [9] upon time. The time necessary to achieve equilibrium for the systems Cu–composts was approximately 180 min, except for PM compost where the time required was 240 min. The equilibrium plateau was higher for SS compost suggesting greater affinity of Cu to this compost.

The experimental data for the systems Zn–composts exhibit higher variability, presenting poor correlation with the theoretical models. For the SS and PM composts, the time necessary to attain the equilibrium was 120 min. The system Zn–MSW revealed higher variability probably due to experimental errors. The sorption capacity for Zn is higher on the SS compost. It seems that MSW and PM composts have similar sorption properties.

Cu and Zn retention by MSW compost was around 60% and 46%, respectively. The SS compost revealed 80% Cu removal and 60% Zn removal. PM compost showed the removal around 60% and 50% for Cu and Zn, respectively. It seems that the compost presenting high sorption displayed high CEC as well.

3.2. SORPTION EQUILIBRIUM

To understand the possible mechanisms of sorption of metals, the Langmuir, Freundlich and linear mathematical models [8] were examined (Table 2). The model fitting best experimental data can be evaluated by the correlation coefficient (*r*) or by the error associated to the residuals – deviations between the experimental data and the mathematical model.

Table 2

Isotherm parameters for Cu and Zn in each compost

Parameter	Compost					
	MSW		SS		PM	
	Cu	Zn	Cu	Zn	Cu	Zn
Langmuir						
q_m, mg/g	4.5809	37.3134	10.3093	14.881	5.4855	-7.9051
K_a, dm^3/mg	0.035	0.0054	0.0614	0.1969	-0.7774	-0.0086
r^2	0.9979	0.9426	0.9963	0.9999	0.9645	0.5581
Error, mg/g	1.4112	1.7798	0.7630	2.1293	3.5636	3.3475
Freundlich						
K_f, dm^3/g	0.1311	0.3082	1.4187	4.1115	0.0538	0.025
$1/n$	0.8368	0.8263	0.4191	0.3179	1.0183	1.459
r^2	0.9213	0.8824	0.9709	0.9585	0.9881	0.9888
Error, mg/g	4.0792	1.9465	0.6301	2.0516	3.2093	0.6272
Linear						
K_d	0.0109	0.1653	0.0681	0.1345	0.0998	0.2192
r^2	0.4839	0.9480	0.8452	0.9306	0.8903	0.9929
Error, mg/g	2.4976	2.6162	2.6545	7.7765	4.8834	2.5321

In the present work, the criterion applied was the error as suggested by Tseng et al. [10]. The absorption constants and other sorption parameters are displayed in Table 2. q_m is the monolayer sorption capacity, K_a – the Langmuir constant, K_f, n – the Freundlich constants; K_d the distribution coefficient, r – the correlation factor.

Linear isotherm model revealed a poor correlation with the experimental data in contrast to the Freundlich and Langmuir models, suggesting that the latter ones should be responsible for the sorption process (Figs. 3, 4). However, Gilbert et al. [11] suggested that in the equilibrium, cations may be distributed linearly on the vegetal compost, and the sorption potential increases uniformly upon the solute concentration in the aqueous phase. This model is usually accepted to describe systems where the solute concentration is low and for solid surfaces with reduced sorption potential.

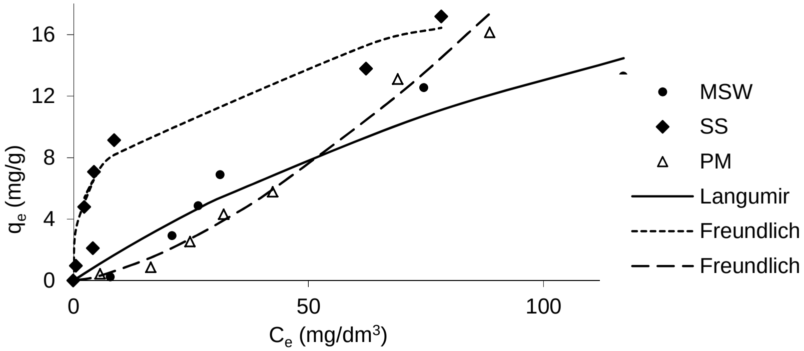

Fig. 3. Equilibrium data for sorption of Cu in various composts and the isotherm models that best fit the experimental data; q_e – amount of Cu sorbed in equilibrium, C_e – equilibrium concentration

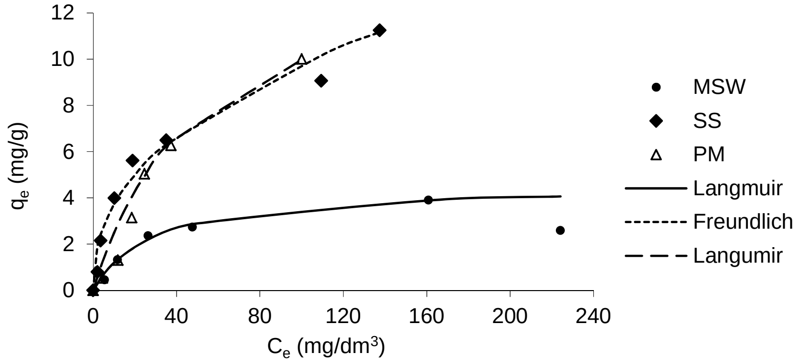

Fig. 4. Equilibrium data for sorption of Zn in various composts and the isotherm models that best fit the experimental data; q_e – amount of Zn sorbed in equilibrium, C_e – equilibrium concentration

The isotherms describing best sorption of Cu on each compost under examination are shown together with the experimental points in Fig. 3. Langmuir isotherm seems to be more suitable to describe the sorption of Cu on the MSW compost, while for the sorption on SS and PM composts, the Freundlich isotherm better fits the experimental data. Nevertheless, for the SS compost, the coefficient $1/n$ equals 0.32, pointing to its favorable sorption properties, in contrast to the value 1.46 for Cu–PM sorption system.

Figure 4 shows the equilibrium data for sorption of Zn on the composts. The best model to describe the sorption on MSW and PM composts is the Langmuir isotherm, while for SS compost – the Freundlich isotherm. In this case, the $1/n$ value of 0.42 represents the most favorable sorption.

A typical mechanism described by the Langmuir isotherm is sorption on external surfaces of microporous solids, limited to formation of a monomolecular layer. The results of the sorption experiments for Cu and Zn indicate that the MSW compost should belong to this kind of sorbents. The equation representing the Freundlich isotherm predicts that the amount of solute sorbed increases due to the formation of multi layers and is usually the case of nonporous solids or with macropores. The saturation of sorbent surface is achieved when capillary condensation occurs. A typical behavior represented by this model was characteristic of SS compost for sorption of both metals. The PM compost did not reveal a consistent performance. Cu sorption was inefficient with the Freundlich parameter $1/n$ being above 1.

It seems that the three composts are more efficient in retaining Cu rather than Zn. In Table 3, the maximum sorption capacities of the composts under evaluation are given. Ulmanu et al. [12], report data in the same order of magnitude for the compost obtained from mowed garden grass. These results were expected regarding data achieved under different experimental conditions reported by Ho et al. [5] and Grimes et al. [2], with sorption materials like tree fern and vegetal compost (green and domestic waste). The interaction of metals with the chemical structures of the compost surface can be considered as complexation, stabilized by electronic effects strongly dependent on the ionic potential; that is, the charge to radius ratio of bivalent metal ions from fourth period of the periodic table, known as the Irving Williams series.

Table 3

Maximum sorption capacity $q_{\max}$ [mg/g]
of each compost for Cu and Zn

Compost	$q_{\max}$ Cu	$q_{\max}$ Zn
MSW	11.1	6.8
SS	15.7	13.7
PM	13.1	9.0

SS compost has higher capability for the sorption of these heavy metals. The maximum sorption, $q_{\max}$, of Cu and Zn achieved by SS compost was: 15.7 and 13.7 mg/g, respectively. Regarding the values of CEC reported above, the sorption behavior is consistent with the cation exchange capacity, that is, the sorption increases with the CEC. The physical and chemical characteristics of sorbents and sorbates are closely related with the sorption extent. Grimes et al. [2] reported that the copper sorption on a compost from green and household wastes depends on both the organic and the inorganic fraction of the sorbent. Sewage sludge compost, SS, has higher organic matter content (82.3%), lower pH (4.9) and higher CEC (3.9 meq/g). Carboxylic and phenolic groups, characteristic of the compost organic matter, are closely related to the electrostatic interactions between the bivalent soluble cations (Cu^{2+} and Zn^{2+}) and the surface structures. Low pH of SS compost also suggests the release of H^+ to the solution and the formation of carboxylate bases with negative charge, establishing strong ionic links with metals positive charges. Regarding the PM and MSW composts, the former had higher sorption capacity but lower organic matter content, although its CEC was higher. This phenomenon can be explained by the fact that the PM compost has high lignin content. As mentioned by Bailey et al. [4], lignin has a high sorption capacity, due in part to the polyphenols and other functional groups at the surface. Consequently, it is possible to realize that the sorption interactions are closely related with these parameters.

Nowadays, several low-cost sorbents have been studied to replace activated carbon or ion exchange resins for the removal of heavy metals from aqueous solutions [4]. This study has shown that composts can be good sorbents for heavy metals such as Cu and Zn, hence, can be used instead of active carbon in wastewaters activated carbon filters. Adding to this use, in order to maintain the composts recycling advantages, this study highlighted that the composts may have a synergistic behaviour as pollution controllers. In fact, the application of these materials on soil, namely in landfill cover materials, road slopes, lands around industrial critical areas subject to spills, can act as “natural” barriers to heavy metals dissemination in the environment. The usual application to the soil as organic amendments contributes to the increase of organic matter and, as the experimental results showed, as heavy metal scavenger.

4. CONCLUSIONS

In the present work, sorption of cations of heavy metals such as Cu^{2+} and Zn^{2+} from aqueous solutions onto three composts commercialized in Portugal was studied. For the three composts, the maximum time necessary to reach the equilibrium was 240 min. The composts have shown ability to sorb the metals in different degrees, which was high for the compost with high organic matter content and CEC. The SS compost confirmed high capacity to capture both heavy metals, with maximum sorption capacities of 13.7 mg/g for Zn^{2+} and 15.7 mg/g for Cu^{2+}. The compost less suitable for the initial purpose was MWS one, which showed the sorption of 6.8 mg/g for Zn^{2+} and 11.1 mg/g for Cu^{2+}. On the three composts, Cu^{2+} was retained with higher extension than Zn^{2+}.

ACKNOWLEDGEMENTS

This work was supported by the Strategic Project PEst-OE/CED/UI4016/2011.

REFERENCES

[1] Council Directive 99/31/EC, *On the landfill of waste*, L 182, 1999.

[2] GRIMES S., TAYLOR G., COOPER J., *The availability and binding of heavy metals in compost derived from household waste*, J. Chem. Technol. Biot., 1999, 74, 1125.

[3] WHO, *Guidelines for Drinking Water Quality*, World Health Organization, Geneva 2006.

[4] BAILEY S., OLIN T., BRICKA M., ADRIAN D., *A review of potentially low-cost sorbents for heavy metals*, Water Res., 1998, 33, 2469.

[5] HO Y., HUANG C., HUANG H., *Equilibrium sorption isotherm for metal ions on tree fern*, Process Biochem., 2002, 37, 1421.

[6] VAZ-MOREIRA I., SILVA M.E., MANAIA C.M., NUNES O.C.P., *Diversity of bacterial isolates from commercial and homemade composts*, Microbial Ecol., 2008, 55, 714.

[7] THOMPSON W., LEEGE P., MILLNER P., WATSON M.E., *Test Methods for the Examination of Composts and Composting*, The US Composting Council, US Government Printing Office, 2001.

[8] COONEY D.O., *Adsorption design for wastewater treatment*, Lewis Publishers, Boca Raton 1998.

[9] BRÁS I.P.L., *Utilização de Casca de Pinheiro como adsorvente para remoção de pentaclorofenol de águas contaminadas*, Dissertação de Doutoramento, FEUP, Porto 2005.

[10] TSENG R., WU F., JUANG R., *Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons*, Carbon, 2003, 41, 487.

[11] GILBERT O., PABLO J., CORTINA J., AYORA C., *Sorption studies of Zn(II) and Cu(II) onto vegetal compost used on reactive mixtures for in situ treatment of acid mine drainage*, Water Res., 2005, 39, 2827.

[12] ULMANU M., MARAÑÓN E., FERNADEZ Y., CASTRILLÓN L., ANGER I., DUMITRIU A., *Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents*, Water Air Soil Poll., 2003, 142, 357.