Preliminary Study of the Adsorption Capacity of Pb, Zn and Cd Through Zeolite and Organic Compost

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Abstract

Reactive materials have been used as a solution to prevent potentially toxic metal contamination stemming from mining waste disposal. These materials are characterized by a high cation exchange capacity (CEC) and a predominance of negative charges, favoring their potential utilization in metal cation immobilization. Therefore, the aim of this study is to compare the sorption capacity of common metals in mining areas (Pb, Zn and Cd) with zeolite, an inorganic material traditionally studied and used for this purpose, and compost, a low-cost organic material, that in comparison to zeolite, has been sparsely researched. Two Cuban commercial clinoptilolite zeolites were evaluated: natural zeolite (NZ) and NaCl treated zeolite (TZ). Two municipal solid waste-derived composts were also assessed with differences in the composting method: windrow (WC) and static pile (SPC). Batch equilibrium experiments showed that the selectivity of removal of TZ, WC and SPC followed the order Pb > Cd > Zn. The only exception was NZ (Pb > Zn > Cd). In general, all materials presented higher performances than Pb (with adsorption efficiency more than 95%). The SPC was revealed to be the best adsorbent of Pb, but with a similar removal percentage for the TZ. The TZ was significantly more efficient in retaining Zn. In the case of the Cd, the WC and TZ showed the highest removal percentage. These results suggest that compost, a low-cost byproduct, can adsorb a considerable concentrations of metals, and thus is able to compete with zeolites for use, isolated or combined with other materials, as an effective sorbent in metal contamination.

Keywords

Reactive materials • Batch equilibrium • Contaminated mine areas

1 Introduction

Potentially toxic metals naturally occur in the earth's crust at geogenic concentrations. However, mining accelerates the release of these elements into the environment, affecting the natural ecological balance (Salomons 1995), resulting in soil contamination by a wide range of elements, such as arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), chromium (Cr), mercury (Hg), selenium (Se) and zinc (Zn) (Förstner and Wittmann 1983).

It is estimated that Europe contains about 2.5 million potentially contaminated sites. The waste disposal and treatment are the main contributors to soil contamination (38%) and potentially toxic metals account for approximately 35% of the soil contamination and 31% of the groundwater contamination (Van Liedekerke et al. 2014). In Latin America, natural metal concentration in soil is high and diverse. On the one hand, this countries have a long mining history, but without adequate environmental laws. Regulations for natural resources protection have improved since the 1980s in Brazil and since the 1990s in some countries, such as Bolivia, Chile, Peru and Ecuador. Therefore, does not exist the complete inventory presenting polluted sites in the region, only several metal contamination problems examples (Utmazian and Wenzel 2006; MMSD América del Sur 2002). In Brazil, there are several abandoned mining areas, such as the Ribeira Valley region, where the Pb, Zn and Ag extraction, produced millions of tons of waste (tailing and slags) (Kasemodel et al. 2016).

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The remediation is generally not a priority in these countries, due to technical and financial implications. Furthermore, the metal mining industry has not only been important in the last decades, currently, new investments in ore exploration has still been made (MMSD América del Sur 2002). Thus, it is necessary to develop different technological approaches able to treat and stabilize contaminants in an efficient, eco-friendly, and cost effective way.

In addition, an alternative to the final disposal of mining wastes are landfills, which aim to reduce the migration of contaminants through a liner and barrier covering (Sharma and Lewis 1994). The use of constructive materials with high adsorption potential may be favorable, since it increases the safety of structures. In this category are the reactive materials of an inorganic character, such as zeolites, and of an organic character, such as the composts originated from composting.

Zeolite minerals are crystalline and hydrated aluminosilicates with microporous crystalline structures, which can also be produced synthetically (Pabalan et al. 2001). In contrast, organic compost, resulting from composting, is the product of organic waste management and is a considerable portion of the municipal solid waste (Epstein 1997).

Zeolites have been shown to have great potential to remove cationic metal species, associated with ion-exchange, in their characteristically large surface areas (Pabalan et al. 2001; Simantiraki and Gidarakos 2015). Some studies have also confirmed the high capacity of immobilization of metallic contaminants by the composts as a function of the humic substances, such as humic and fulvic acids (Simantiraki and Gidarakos 2015; Paradelo and Barral 2012).

The purpose of this study was to evaluate the equilibrium adsorption of clinoptilolite zeolites and municipal solid waste-derived composts to compare the adsorption efficiency of these reactive materials for Pb(II), Zn(II) and Cd(II). This metal cations were chosen because they are important and frequent contaminants in metal ore mining residues. This research was conducted with the hope that it might help develop alternatives for the recuperation of abandoned and contaminated mining areas using a single or multi type, low cost and environmentally friendly material.

2 Materials and Methods

The compost samples were made using food waste submitted to two different composting processes: windrow composting (WC) and static pile compost (SPC). The second type of adsorbent material was zeolite (clinoptilolite) extracted from a mine in Cuba by the Brazilian company (CELTA Brasil Ltda). Two types of zeolite were evaluated: natural zeolite (NZ) and chemically treated zeolite using sodium hydroxide (NaCl) (TZ).

2.1 Materials Characterization

The pH (H_2O and KCl), redox potential (Eh) and electrical conductivity (EC) were determined according to the methodology proposed by EMBRAPA (2011), using ratio of 1:2.5 (mass:volume), with stirring of the samples and standing for 60 min. Then, the ΔpH is calculated using the difference between the pH in KCl and the pH in H_2O. The determination of the composts cation exchange capacity (CEC) followed the titulometry method (MAPA 2013) and the zeolite CEC was provided for the supplier. The specific surface area (S_{BET}) and porosity (average pore radius and total pore volume) were found by determining the nitrogen adsorption/desorption isotherm using a Quantachrome NOVA 1000. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of $P/P0 = 0.98$. The X-Ray Fluorescence (XRF) was determined in an X-Ray Fluorescence Spectrometer (Axios Advantage, Panalytical).

2.2 Metal Sorption Experiment

Equilibrium adsorption studies were conducted through contact between the composts (particles smaller than 2.0 mm and oven dried for 48 h at 50 °C) and zeolites in single-solute systems, for a predetermined contact time. Single contaminant solutions containing Pb(II), Zn(II) or Cd (II) (frequent contaminants in metal ore mining residues) were prepared after dissolving the corresponding chloride salts with deionized water, achieving concentrations around 150 mg L^{-1}. In 50 mL Falcon tubes, 1 g of each reactive material, which had been continuously stirred with 50 mL of each contaminant solution (optimum adsorbent:solution ratio of 1:50) was added to a horizontal shaker at a rate of 10–20% at room temperature (approximately 25 °C). After agitation for 24 h, the extracts were centrifuged and filtered through Unifil filter paper (weight of 80 g m^{-2} and particle retention of 4–12 μm).

The physicochemical parameters (pH and CE) were monitored with measurements of the initial values (immediately after contact of the adsorbent with the contaminant solution) and final values (after 24 h of contact, immediately after filtration). The concentrations of Pb, Zn and Cd present in the filtered extracts were analyzed in the Atomic Absorption Spectrophotometer (PinAAcle 900F PerkinElmer). For the calibration curves, three points were used with different concentrations, obtained from the dilution of the respective PerkinElmer standards in deionized water. All calibration curves have a correlation coefficient greater than 0.995.

With the results obtained, it was possible to calculate the respective removal percentage and removal capacity of each metal, using the following formulas (Soares and Casagrande 2000):

$$q_e = \frac{[V_{solution}(C_0 - C_e)]}{M_{reactive\ material}} \qquad (1)$$

$$R = \left[\frac{C_0 - C_e}{C_0}\right] \times 100 \qquad (2)$$

Wherein q_e is the adsorbed concentration or the removal capacity after equilibrium (mg g^{-1}); $V_{solution}$ is the volume of solution (L); C_0 and C_e are the initial concentrations and equilibrium concentrations (mg L^{-1}); $M_{reactive\ material}$ is the exact mass of the reactive material sample (g) and R is the removal percentage (%).

3 Results and Discussion

3.1 Materials Characterization

The physicochemical properties of organic and inorganic materials, which affect the metal removal, are presented in Table 1. In the present study, all the materials showed low acidity, wherein composts have higher pH values (7.4 and 6.4) compared to zeolites (6.2 and 5.6); oxidizing conditions and predominance of negative charges, principally the NZ (ΔpH = −2.5). These characteristics facilitate high cation retention. Sorption is the most dominant mechanism in determining the effective removal of metals (Yong and Mulligan 2004). Thereby, the specific surface area (S_{BET}) and cation exchange capacity (CEC) are the most indicative parameters to predict this process. According to the results, the CEC of NZ demonstrated to be higher (180 $cmol_c$ kg^{-1}) than both compost samples (34 e 29 $cmol_c$ kg^{-1}). The CEC of zeolite is similar to the theoretical value of clinoptilolite (220 $cmol_c$ kg^{-1}), considering the isomorphic substitution and its typical unit cell (Pabalan et al. 2001). The alkali-treatment of the zeolite provided an increase in the S_{BET} (60.09 m^2 g^{-1} for the NZ and 76.82 m^2 g^{-1} for the TZ). The S_{BET} for composts presented a wide range of values (5.69 m^2 g^{-1} for the WC and 62.99 m^2 g^{-1} for the SPC). The X-Ray Fluorescence (XRF) analysis of zeolites indicated that its main components are clinoptilolite with more than 80% SiO_2 and Al_2O_3. The composts were also primarily composed of the oxides, SiO_2 and Al_2O_3 (55.5% for the WC and 70% for the SPC).

3.2 The pH of Solutions Before and After Agitation

The pH of a solution considerably affects the degree and extent of adsorption, in so far as it regulates the adsorption force of H^+ and OH^- ions and the degree of ionization (Weber 1972). This adsorption study did not adjust the solutions' pH. The pH values varied between 4.7 and 6.3 in the solutions containing Pb; between 5.0 and 6.3 in the solutions containing Zn; and between 4.5 and 6.1 in the solutions containing Cd (Fig. 1). According to Dick et al. (2016) in pH values ranging from 4.0 to 5.0 dissociation occurs in most of the COOH groups. Therefore, the pH conditions of this study favored cation exchange. In addition, the decrease in pH with agitation (as observed for Zn) may be indicative of the predominance of the ion exchange mechanism, releasing more H^+ ions and, consequently, leaving more sites free for adsorption (Bartczak et al. 2015). Nevertheless, the increase in pH values (as observed for Pb and Cd) may be related to the release of OH^- ions due to the adsorption of metal cations (Sharma and Forster 1993) or metal ions being withdrawn from the solution and H^+ ions are also removed. Furthermore, other adsorption mechanisms may also be acting, such as the electrostatic attraction of the negative charges present on the surface of the adsorbents (Table 1) by the metal cations or the physical adsorption related to porosity (Table 1).

3.3 The Electrical Conductivity (EC) of Solutions Before and After Agitation

For all the metals studied (Pb, Zn and Cd), the samples containing the reactive materials and the contaminant solutions had higher EC values compared to the respective blank solutions (Fig. 2). With agitation, there was also an increase in the EC values (Fig. 2). This increase may be due to an inherent mechanism of adsorption which is the cation exchange, anteriorly reported, with the release of various previously adsorbed cations and the subsequent binding of the metal cations present in the synthetic solution. Therefore, this increase of cations in the solution may have increased EC values.

3.4 Removal Percentage of Pb, Zn and Cd

With the exception of NZ, the trend of the removal on the reactive materials (TZ, WC and SPC) followed the order

Table 1 Physicochemical properties of zeolites (NZ = natural zeolite, TZ = treated zeolite) and organic composts (WC = windrow compost, SPC = static pile compost)

Parameters	Zeolites		Composts	
	NZ	TZ	WC	SPC
pH (1:2.5 in H_2O)	6.2	5.6	7.4	6.4
pH (1:2.5 in KCl)	3.7	4.8	6.4	5.5
ΔpH (pH_{KCl}–pH_{H2O})	−2.5	−0.8	−1.0	−0.9
Eh (mV)	+297	+275	+268	+330
EC ($\mu S\ cm^{-1}$)	67	6000	665	157
CEC ($cmol_c\ kg^{-1}$)	180	ND	34	29
S_{BET} ($m^2\ g^{-1}$)	60.09	76.82	5.69	62.99
V_{pores} ($cm^3\ g^{-1}$)	0.08301	0.13880	0.03341	0.01113
R_{pores} (Å)	27.63	36.13	117.50	35.33
XRF	SiO_2 (75.4%); Al_2O_3 (13.5%); CaO (4.0%); K_2O (2.1%)	SiO_2 (72.0%); Al_2O_3 (12.6%); K_2O (3.8%); CaO (1.9%)	SiO_2 (44.5%); Al_2O_3 (11.0%); Fe_2O_3 (5.8%); CaO (1.6%)	SiO_2 (55.2%); Al_2O_3 (14.8%); Fe_2O_3 (6.7%); CaO (0.8%)

Eh: redox potential; EC: electrical conductivity; CEC: cation exchange capacity; S_{BET}: specific surface area; V_{pores}: total pore volume; R_{pores}: average pore radius; XRF: X-Ray Fluorescence
ND = Not determined

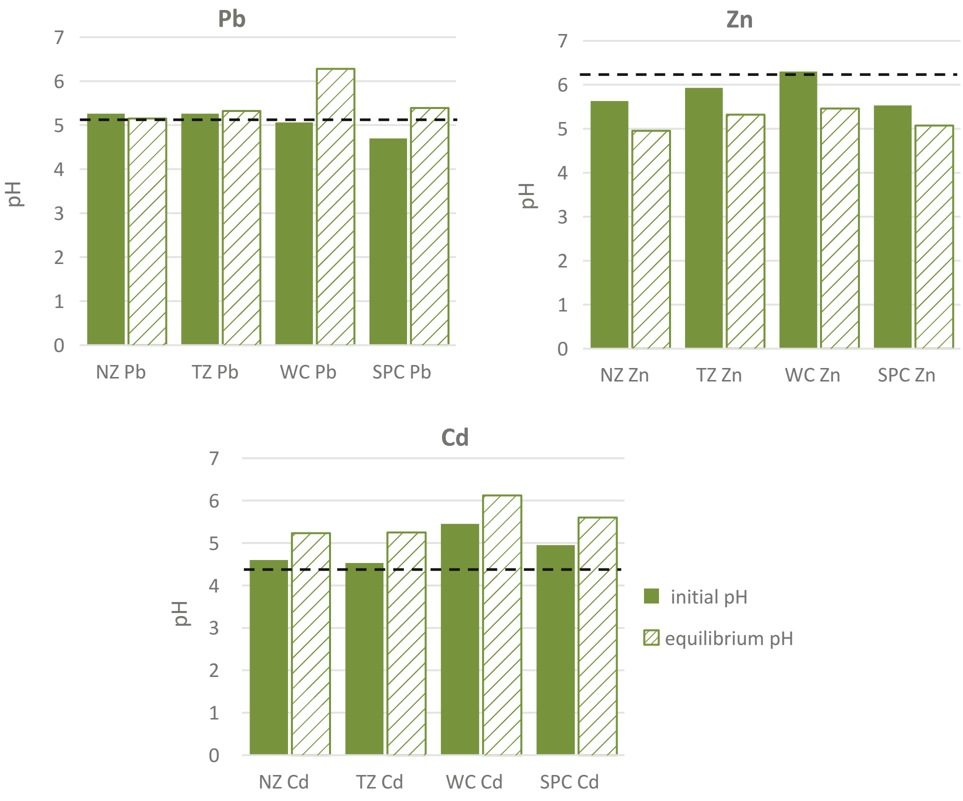

Fig. 1 The pH values of solutions containing Pb, Zn or Cd before agitation (initial pH) and after agitation (equilibrium pH). The dashed line represents the initial pH value of the blank metal solution. NZ = natural zeolite, TZ = treated zeolite, WC = windrow compost, SPC = static pile compost

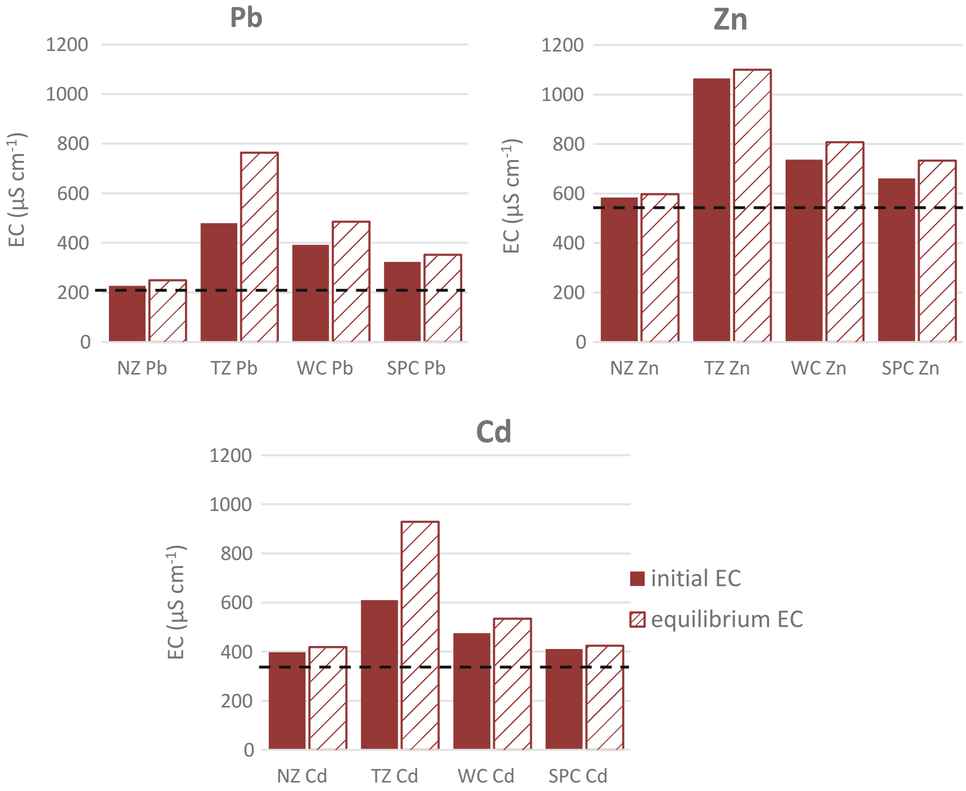

Fig. 2 The electrical conductivity (EC) values of solutions containing Pb, Zn or Cd before agitation (initial EC) and after agitation (equilibrium EC). The dashed line represents the initial EC value of the blank metal solution. NZ = natural zeolite, TZ = treated zeolite, WC = windrow compost, SPC = static pile compost

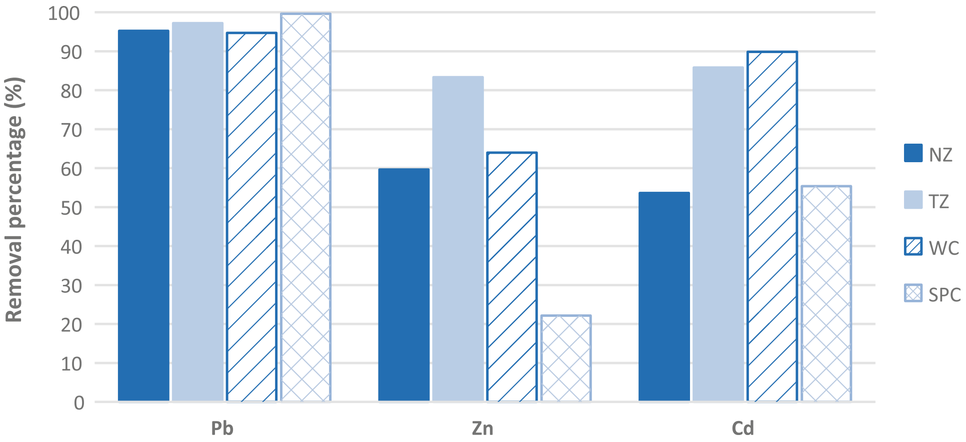

Fig. 3 Removal percentage of Pb, Zn or Cd in zeolites (NZ = natural zeolite, TZ = treated zeolite) and organic composts (WC = windrow compost, SPC = static pile compost)

Pb > Cd > Zn (Fig. 3). All of the materials performed well in Pb retention (with adsorption efficiency of more than 95%). The SPC revealed to be the most adsorbent of Pb (99.6% of removal). The TZ presented the highest rate of adsorption of Zn (83.4%). The WC demonstrated the highest percentage of Cd removal (89.8%), but with similar values to those of TZ (85.9%). Both zeolites have similar efficiency for Zn and Cd sorption.

3.5 Removal Capacity of Pb, Zn and Cd

Sorption studies are usually conducted with different types of reactive materials and under different conditions, like pH values, temperatures, concentration solutions and optimum adsorbate/solution ratio, which makes direct comparisons of the results difficult. A general trend of best removal of Pb by zeolite and compost has been observed by other researchers

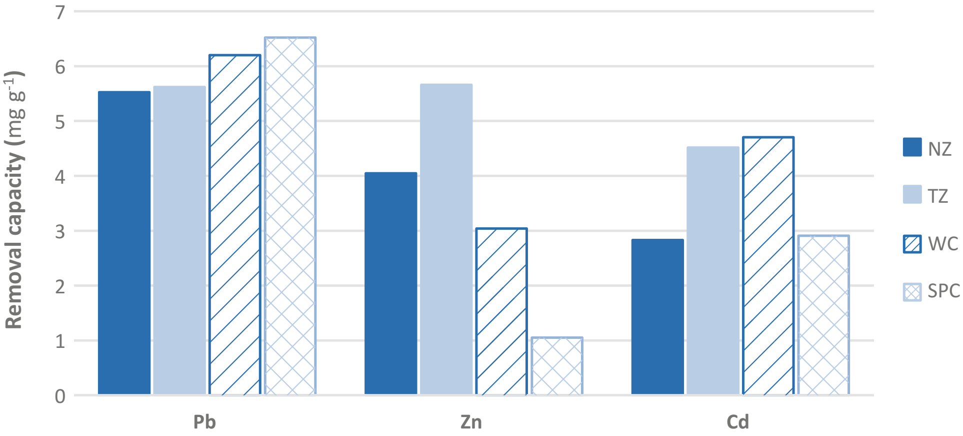

Fig. 4 Removal capacity of Pb, Zn or Cd in zeolites (NZ = natural zeolite, TZ = treated zeolite) and organic composts (WC = windrow compost, SPC = static pile compost)

(Paradelo and Barral 2012; Nguyen et al. 2015). In this study, the Pb removal capacity values ranged from 5.525 (NZ) to 6.521 mg g^{-1} (SPC) (Fig. 4). The maximum removal capacity of these materials is likely higher in saturation conditions. The Pb maximum removal capacity by zeolite from a single metal solution obtained by Nguyen et al. (2015) was 9.97 mg g^{-1} and by compost presented by Paradelo and Barral (2012) was 196 mg g^{-1}. In the case of Zn, contrary to the results of this study (Fig. 4), Simantiraki and Gidarakos (2015) showed a higher Zn maximum removal capacity by compost (1.11 mg g^{-1}) compared to zeolite (0.97 mg g^{-1}). The selectivity order of Cd maximum removal capacity in this study (Fig. 4) is in agreement with Simantiraki and Gidarakos (2015) (1.46 mg g^{-1} for zeolite < 2.96 mg g^{-1} for compost). Therefore, zeolites and composts are efficient adsorbents in the removal of metals. However, the best immobilization capacity is determined by the physicochemical, chemical and hydraulic properties, associated with the origin of these materials.

4 Conclusions

The comparative assessment of this study showed that the removal percentage and removal capacity of Pb, Zn and Cd by zeolites and composts yielded the following ranking: Pb > Cd > Zn (the only exception is NZ: Pb > Zn > Cd). All of the materials indicated a higher performance for Pb (with adsorption efficiency of more than 95%). The SPC, TZ and WC performed better in terms of removal of Pb, Zn and Cd, respectively. According to the results, composting may not only be a viable and efficient alternative to waste management, but also be used as adsorbents in contaminated mining areas, ensuring social and economic benefits. The composts, unlike extracted zeolites from specific sites, have the advantage that they can be made at the using site. However, further research is required to know the adsorption potential in other concentrations and the desorption of Pb, Zn, or Cd from compost materials. The over time composts' stability is an important consideration and a possible limitation of use that should be better evaluated.

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