

## Evaluation of the interaction mechanisms between red muds and heavy metals

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Received 26 October 2005; received in revised form 7 December 2005; accepted 12 December 2005

Available online 19 January 2006

### Abstract

This paper investigated the heavy metal adsorption of non-treated ( $RM_{nt}$ ) and acid-treated red muds ( $RM_a$ ), bauxite ore processing waste, in order to evaluate how efficient they are in reducing metal solubility and bioavailability in polluted soils. Red mud samples were artificially polluted with solutions containing increasing concentrations of Pb, Cd and Zn. Cancrinite and hematite were the main phases of the red muds, and were also the components which adsorbed most heavy metals. The results showed that the  $RM_{nt}$  adsorption capacity for the three heavy metals was  $Zn \geq Pb > Cd$ . Acid treatment with HCl decreased the red mud's capacity to adsorb the heavy metals by 30%.

In order to study the different heavy metal–RM interaction mechanisms, all samples after artificial contamination were treated with solutions with gradually increasing extraction capacity.  $H_2O$  and  $Ca(NO_3)_2$  treatments only extracted very low concentrations of Pb, Cd and Zn, while EDTA treatment extracted the most adsorbed heavy metals from the sorbent particles. In particular the water-soluble and exchangeable metal fractions were higher in the  $RM_a$  than they were in the  $RM_{nt}$ , while the concentrations of Pb, Cd and Zn extracted with EDTA were lower.

The results showed that red muds can be used successfully to reduce the solubility and bioavailability of heavy metals in polluted soils.

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**Keywords:** Red muds; Heavy metals; Adsorption capacity; Remediation technologies

### 1. Introduction

Pollution of soils by heavy metals is a worldwide environmental problem. The replacement of traditional industrial activities by more innovative and economic ones has in many cases resulted in previous centers of production being transformed into areas of widespread pollution [1]. In addition heavy metals are generally persistent in nature, unlike organic contaminants such as pesticides, or petroleum by-products. They can, however, become mobile in soils so that a fraction of their total mass can leach to groundwater or can become bioavailable to plants, animals and humans [2].

The current technologies used to remediate polluted heavy metal soils mainly involve removing and replacing the soil, and are generally very expensive. This means that innovative in situ low-input and cheap technologies are urgently required

[3]. Thus it is necessary to develop low cost remediation methods which do not alter the physical and chemical properties of soils. Research has shown that adding soil amendments in situ favours chemical immobilization and reduces the mobility and bioavailability of metals through adsorption or precipitation [1,4]. Many different approaches have been proposed for the chemical immobilization of heavy metals in degraded soils some of which regarding the application of lime or of inorganic and organic amendments [1,5–7]. Among these, using various industrial residues as amendments to remedy contaminated soils seems to be promising. This would also reduce waste disposal and giving new value to industrial wastes through converting them into industrial by-products.

Particularly the red muds, a fine-textured residues which derive from the digestion of bauxite during the Bayer process, could be cost-effective composite sorbents capable of treating a variety of contaminants [8]. Significant amounts are produced as a by-product of refining (for 1 tonne of alumina produced, between 1 and 2 tonnes of red mud residues are produced), although the exact composition and quantity depends on the

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particular chemical and mineralogical composition of the bauxite [9]. Disposal of this residue contributes significantly to the overall production cost of alumina [10]. It is also an important environmental problem, because the waste dumps occupy large areas and the red mud itself is strongly alkaline (pH 10–12.5) [11].

Red mud is principally composed of fine particles of silica, aluminum, iron, calcium and titanium oxides and hydroxides, which are responsible for its high surface reactivity [12]. Because of these characteristics red muds have been the subject of many investigations [13,14], including some on the removal of toxic heavy metals from wastewater [8,15–17] and acid mine drainage [9], or on reducing the leaching of soil nutrients [18,19].

In this work we show the results on the adsorption behaviour of three heavy metals (Pb, Cd, Zn) in non-treated and acid-treated red muds. This was done to evaluate the principal Me–sorbents interaction mechanisms and to establish whether red muds can be used as amendments in the remediation of heavy metal polluted soils.

## 2. Materials and methods

### 2.1. Sample description

Red muds were obtained from the Eurallumina plant (Portovesme, Sardinia, Italy). The red muds were dried overnight at 105 °C, finely ground and sieved to <0.02 mm (RM<sub>nt</sub>). The red muds were also acid-treated (RM<sub>a</sub>) by twice washing with HCl 0.05N for 2 h at the ratio 1:25 (wt/wt) of red mud/HCl solution. After treatment the RM<sub>a</sub> was washed with distilled water and dried overnight at 105 °C. The acid treatment technique is a proven way of synthesizing a better adsorbent from red muds, capable of removing inorganic phosphorus and heavy metals [8]. The pH and electric conductivity (EC) values were determined in 1:25 ratio of red mud/distilled water (Table 1) [20]. The cation exchange capacity (CEC), determined with BaCl<sub>2</sub>–triethanolamine following the usual international methods, was 106.5 and 98.2 mmol<sub>(+)</sub> kg<sup>-1</sup> for RM<sub>nt</sub> and RM<sub>a</sub>, respectively (Table 1) [20].

Table 1  
Properties of red muds

Chemical parameters	RM <sub>nt</sub>	RM <sub>a</sub>
pH	11.5	7.0
EC (mS cm <sup>-1</sup> )	2.1	0.3
S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	18.87	25.16
CEC (mmol <sub>(+)</sub> kg <sup>-1</sup> )	106.5	98.2
Chemical phases (wt.%)		
Cancrinite [Na <sub>6</sub> Ca <sub>1.5</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (CO <sub>3</sub> ) <sub>1.6</sub> ]	51.0	42.0
Hematite [Fe <sub>2</sub> O <sub>3</sub> ]	27.0	31.0
Gibbsite [Al(OH) <sub>3</sub> ]	3.0	3.0
Boehmite [AlO(OH)]	9.0	9.6
Anatase [TiO <sub>2</sub> ]	3.0	3.0
Quartz [SiO <sub>2</sub> ]	2.0	3.0
Ca–Fe–V-oxide	3.5	4.0
MgO	1.5	3.0

The specific surface areas of the RM<sub>nt</sub> and RM<sub>a</sub> were measured by the BET/N<sub>2</sub>-adsorption method (Sorptomatic Carlo Erba). Wheeler's methodology was used to evaluate the distribution and the volume of the pores and also to elaborate the results of adsorption and desorption [21].

X-ray diffraction (XRD) analysis was carried out with a Rigaku D/MAX diffractometer (Cu K $\alpha$ ) equipped with a graphite monochromator in the diffracted beam. The pattern was collected in the 2 $\theta$  range from 10° to 70°. Crystalline phases were identified using the database of the International Centre for Diffraction Data for Inorganic Substances (Table 1) [22]. Aside from crystalline phases, about the 20% of the RM was made of amorphous oxides.

### 2.2. Adsorption and desorption of heavy metals

RM<sub>nt</sub> and RM<sub>a</sub> were artificially polluted with solutions containing increasing concentrations (from 0.6 to 3.0 mmol 25 mL<sup>-1</sup>) of Pb, Cd and Zn, derived from their nitrate salts, and shaken for 24 h (1:25 ratio of red mud/metal solution). The adsorption tests took place at controlled temperature and pH. A buffer solution of acetic acid–sodium acetate was used to maintain a constant pH (5.5–5.9 range) for the Pb, Cd and Zn-RM samples at each point of the isotherms (10 points on the whole were obtained).

The solid and liquid phases were separated by centrifuging and filtering.

The chemical forms of the heavy metals bound to the red muds were determined by a sequential extraction procedure, in order to study the contribution of the different interaction mechanisms. To extract the soluble phase, each sample polluted with heavy metals from the adsorption test was treated with 25 mL of distilled water (pH 6.5) and shaken for 2 h at room temperature. It was then treated with 25 mL of Ca(NO<sub>3</sub>)<sub>2</sub> 0.1N to extract the exchangeable phase, and with 25 mL of EDTA 0.02 M to extract the complexed phase [23]. After each step of the extraction process the samples were centrifuged and filtered to separate the liquid and solid phases. After the third washing, the residual fraction of metals was determined by drying the solid phase overnight at 105 °C and digesting it with HNO<sub>3</sub> and HCl (ratio 1:3) in a Microwave Milestone MLS 1200. The heavy metal concentrations were analysed using a Beckam D.C. plasma atomic emission spectrometer.

The data shown are the mean of three replicates.

## 3. Results and discussion

### 3.1. Characteristics of the adsorbents

Table 1 shows the semi-quantitative mineral composition of RM<sub>nt</sub> and RM<sub>a</sub>. Cancrinite, a sodium calcium aluminum silicate carbonate, was the main phase of RM<sub>nt</sub> (51 wt.%) and RM<sub>a</sub> (42 wt.%). This tectosilicate has an open porous structure and can be considered as a material with zeolitic-like properties [24]. The partial dissolution of cancrinite in the RM<sub>a</sub> after the acid treatment caused a relative increase in other phases, particularly of hematite (Table 1).

Table 2  
The Langmuir parameters  $b$  and  $K$ , relating to the capacity and intensity of adsorption

	$b$ (mmol g <sup>-1</sup> )	$K$ (L mmol <sup>-1</sup> )	$R^2$
Pb-RM <sub>nt</sub>	1.88	0.75	0.94
Pb-RM <sub>a</sub>	0.77	1.42	0.87
Cd-RM <sub>nt</sub>	1.35	0.79	0.96
Cd-RM <sub>a</sub>	0.91	2.07	0.77
Zn-RM <sub>nt</sub>	2.47	1.53	0.96
Zn-RM <sub>a</sub>	1.59	2.10	0.97

The N<sub>2</sub>-adsorption isotherms of RM<sub>nt</sub> and RM<sub>a</sub> were type III curves (figures not shown). These curves are typical of heterogeneous sorbents containing hydrous oxides, silicates and sulphates [25,26]. The specific areas of RM<sub>nt</sub> and RM<sub>a</sub> were 18.9 and 25.2 m<sup>2</sup> g<sup>-1</sup>, respectively. The higher specific surface area of the RM<sub>a</sub> was due to the “cleaning effect” of HCl treatment, which dissolved 9% of the cancrinite. A partial reorganization of the RM<sub>a</sub> particles, which caused an increase in the number of pores with lower radii (30–50 Å) and a simultaneous decrease in the number of those ranging from 60 to 90 Å, was also observed (figures not shown).

### 3.2. RM<sub>nt</sub> adsorption isotherms

The total quantity of heavy metals in the polluting solutions (3.0 mmol 25 mL<sup>-1</sup>) was high enough to satisfy the CEC of the RM<sub>nt</sub> (106.5 mmol(+) kg<sup>-1</sup>). For all the metals the adsorption in the RM<sub>nt</sub> was higher with respect to CEC.

Analysis of the adsorption isotherms showed that the heavy metals reacted differently to the adsorbing material. Metal adsorption in RM<sub>nt</sub> increased in the following order: Zn ≥ Pb > Cd (mmol g<sup>-1</sup>) (Fig. 1). Pb adsorption was higher when the concentration of the metal in the contact solution was lower (the Me<sub>ads</sub>/Me<sub>added</sub> ratio was higher than 0.85 at the first four points of the isotherm). The adsorption then decreased as the concentration of Pb in the solution increased and the gradient of the curves became less steep, until a plateau was reached (1.85 mmol g<sup>-1</sup>). The Cd-RM<sub>nt</sub> isotherm was similar to that of Pb, but the fraction of Cd adsorbed was lower (Fig. 1). The Zn adsorption efficiency were higher than those of Pb and Cd. Its isotherm shape was typical for adsorbent surfaces where adsorption is directly proportional to the concentration of the metal in solution and it did not reach a defined plateau (Me<sub>ads</sub>/Me<sub>added</sub> ratio increasing) (Fig. 1) [27]. This led us to conclude that RM<sub>nt</sub> could sorpt more Zn.

Experimental data of heavy metals adsorption were fitted into the Langmuir equation:

$$x/m = Kbc/(1 + Kc),$$

where the Langmuir parameter  $b$  refers to maximum adsorption capacity and  $K$  is a proportional constant of the adsorption energy [28] (Table 2). The application of the Langmuir model to complex and heterogeneous surfaces such as the red muds is not completely satisfactory, but it did allow us to compare the different metal-adsorption capabilities of these sorbents.

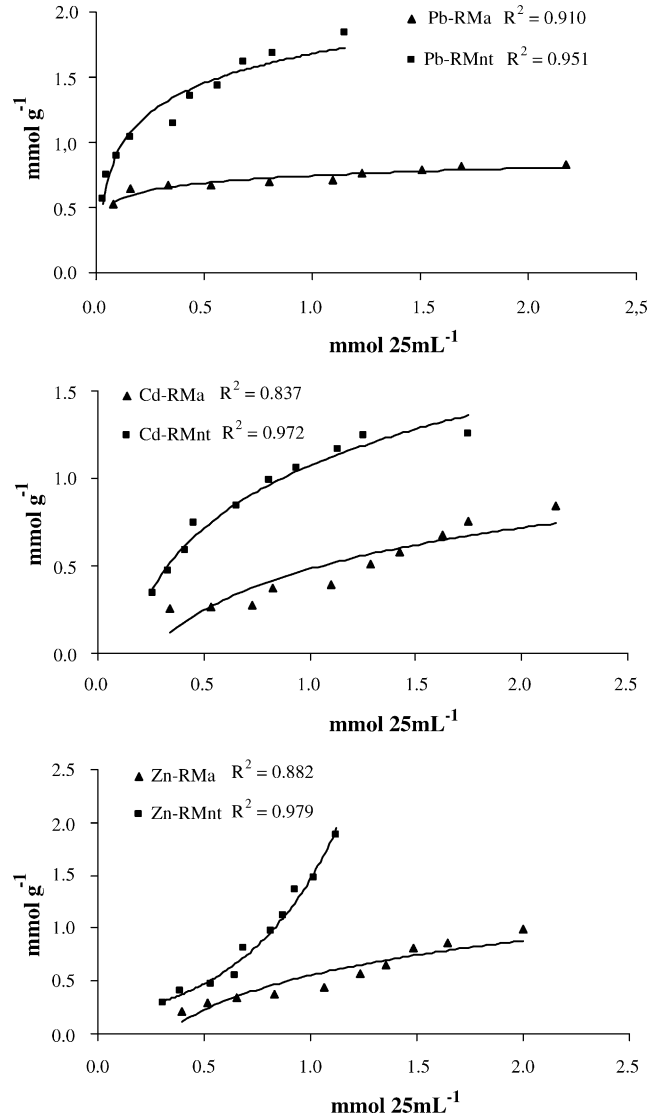


Fig. 1. Pb, Cd and Zn adsorption isotherms on red muds.

The  $K$  values of Zn and Cd were higher than the Pb value (+2.04 and +1.05, respectively). The maximum Zn adsorption ( $b$ ) in the RM<sub>nt</sub> was higher than Pb and Cd (+1.32 and +1.83, respectively) (Table 2).

All samples, after artificial contamination, were treated with solutions of gradually increasing sorption capacity, in order to study the different heavy metal–RM interaction mechanisms (Figs. 2 and 3). Different quantities of metal were extracted by RM<sub>nt</sub>, depending on the metal and on the extracting agent used. The fractions extracted with H<sub>2</sub>O are readily leachable and bioavailable in the environment, and these were always less than 0.01% of Pb and Zn adsorbed, and less than 5% of the Cd adsorbed. The fractions of Cd and Zn extracted with Ca(NO<sub>3</sub>)<sub>2</sub>, which quantify the relatively labile and potentially bio-available exchangeable fractions, were always lower than 1.5% of metals adsorbed, while no fraction of Pb was extracted with Ca(NO<sub>3</sub>)<sub>2</sub>.

The heavy metal concentrations extracted with EDTA, which quantify the relatively immobile and not readily bio-available or leachable metal [29], increased as the quantity of metal adsorbed

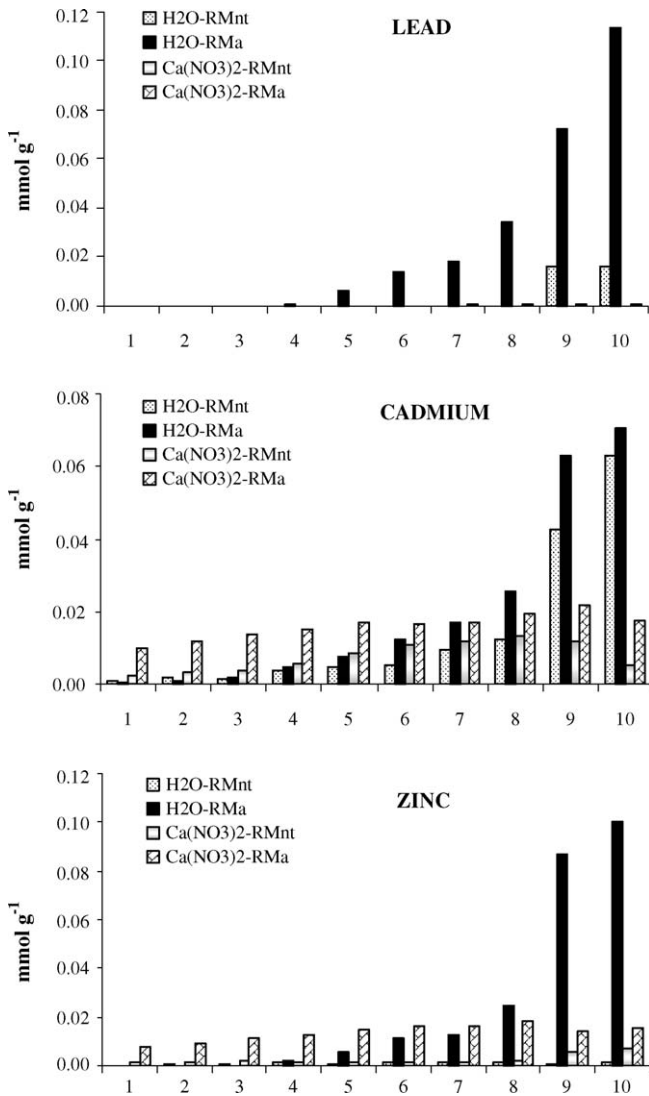


Fig. 2. Pb, Cd and Zn fractions extracted with H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub> from RM<sub>nt</sub> and RM<sub>a</sub>\*. \*The numbers in the X-axis correspond to the isotherm points.

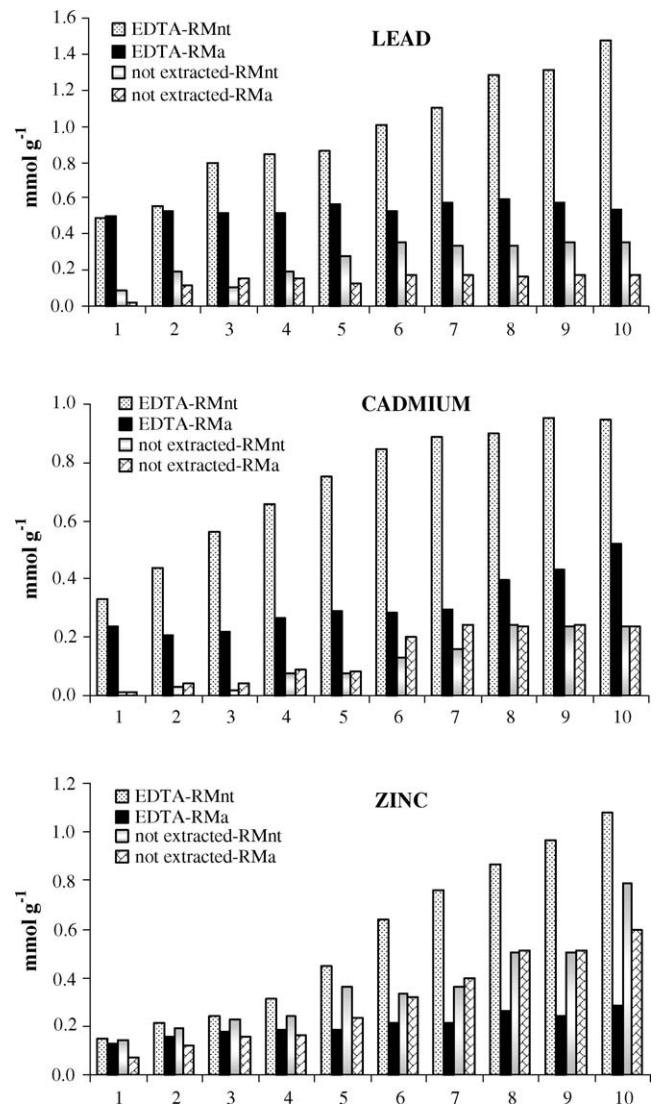


Fig. 3. Pb, Cd and Zn fractions extracted with EDTA and not extracted from RM<sub>nt</sub> and RM<sub>a</sub>\*. \*The numbers in the X-axis correspond to the isotherm points.

increased, and at the last point of the isotherm 80% of Pb, 75% of Cd and 57% of Zn adsorbed was extracted (Fig. 3).

The fraction of non-extracted heavy metals would not be expected to be readily released under natural conditions. The residual concentrations of Pb and Cd were always lower than 20% of the adsorbed heavy metals. The non-extracted fraction of Zn increased as the adsorbed metal concentration increased until the value of 0.79 mmol g<sup>-1</sup> was reached (42% of Zn adsorbed) (Fig. 3).

### 3.3. RM<sub>a</sub> adsorption isotherm

The quantities of heavy metals adsorbed on RM<sub>a</sub> were higher than the CEC, and followed the order: Zn > Cd ≥ Pb. However the adsorption was always lower (<30%) than that of RM<sub>nt</sub>, which agrees with the results of Apak et al. [8]. RM<sub>a</sub> adsorbed more Pb ( $Me_{ads}/Me_{added}$  ratio = 0.87) than Cd ( $Me_{ads}/Me_{added}$  ratio = 0.43) and Zn ( $Me_{ads}/Me_{added}$  ratio = 0.34), particularly

when the concentrations of metal solutions were low (0.6 mmol 25 mL<sup>-1</sup>) (Fig. 1).

The Langmuir model showed that the maximum RM<sub>a</sub> capacity to adsorb Zn was 2.05 higher than its capacity to adsorb Pb and 1.75 higher than its capacity to adsorb Cd. The *K* values increased in the following order: Zn > Cd ≥ Pb, and they were higher than the *K* values obtained for RM<sub>nt</sub> (Table 2).

More heavy metals were extracted by H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub> than by RM<sub>nt</sub> (Fig. 2). The fractions of soluble and exchangeable Pb and Zn were less than 15% of the metals adsorbed. The concentration of Cd extracted increased as the quantity of metal adsorbed increased, until a value of 0.09 mmol g<sup>-1</sup> was reached (10% of Cd adsorbed, Fig. 2).

The metal fractions extracted with EDTA at the last point of the isotherms were, respectively, 65, 62 and 28% of Pb, Cd, and Zn adsorbed (Fig. 3).



The non-extracted fractions of Pb (0.17 mmol g<sup>-1</sup>), Cd (0.24 mmol g<sup>-1</sup>) and Zn (0.60 mmol g<sup>-1</sup>) were, respectively, 20, 29 and 60% of the metals adsorbed (Fig. 3).

### 3.4. General discussion

Cancrinite and hematite were the principal phases which gave adsorbing capacity to the red muds. Cancrinite, at the pH of equilibrium in the adsorption experiments, had a negative charge density in its lattice [30]. This should be neutralized by metal adsorbed with outer-sphere bonds on the external surfaces and by the incorporation of metals in the cages and channels of cancrinite framework, if the hydrated ionic radius of the metals is compatible with the sizes of cancrinite cavities [31]. Thus the RM<sub>nt</sub>, which contains higher quantities of this tectosilicate, adsorbed more cations.

The acid treatments dissolved a portion of the cancrinite framework and also varied the structure of the red muds, causing an increase in the number of pores with lower radii (<50 Å), and a consequent increase in the specific surface area.

Since the pH of solutions at equilibrium in the adsorption experiments was in the 5.5–5.9 range, hydroxide precipitation of Cd and Zn can be excluded, while it is possible that a low precipitation of Pb-hydroxide occurred [32].

The Al, Fe oxides and hydroxides of the red muds, principally the hematite, were the other active components in heavy metal adsorption. Since the pH of solutions at equilibrium in the experiments was lower of the point of zero charge of the red muds, as reported by several authors ( $pzc = 8-8.5$ ) [15,16,33]; the adsorption of heavy metals on Al, Fe oxides and hydroxides occurred on positively charged surfaces through the formation of specific inner-sphere bonds.

The maximum adsorption capacity values of the three metals, obtained from the Langmuir's equation, agreed with the experimental results. The Zn had the highest values in both sorbents.

The quantities of metal extracted with H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub> in the RM<sub>a</sub> were similar to the values of CEC, while in the RM<sub>nt</sub> these fractions were lower (<50% of CEC value). Probably in the RM<sub>nt</sub> the higher fraction of cancrinite favoured the incorporation of Pb, Cd and Zn in the cages and channels of its lattice, and the metal once present within the structure remained trapped and was not water-soluble or exchangeable.

A gradual decrease of the Me<sub>ads</sub>/Me<sub>added</sub> ratio in both the sorbents was noted for the Pb and Cd. This was due to the increased occupation of active surface sites of the sorbents when the concentrations of metals increased in the aqueous solutions [34]. By contrast the Zn-isotherms did not reach a defined plateau, which shows that the red muds could adsorb more Zn. This particular behaviour may be because Zn has a smaller ionic radius and higher charge density than Pb or Cd, which means that its energy and sphere of hydration is greater [7]. When the Zn concentration in the solutions was low, its adsorption decreased because of its large hydrated ionic radius, but when the Zn concentrations increased a partial loss of hydration molecules may occur, so favouring Zn adsorption.

No difference was observed in the percentages of residual Pb in the two sorbents. By contrast the percentages of non-extracted Cd and Zn after sequential extraction in RM<sub>a</sub> were higher than in RM<sub>nt</sub>. These results were confirmed by Langmuir's parameter *K*, which showed higher adsorption intensity values for all three metals in the RM<sub>a</sub>. This was probably due to the relative increase of fractions such as hematite in the RM<sub>a</sub>, which complexed the metals with strong bonds.

## 4. Conclusions

The sequential extraction procedure showed that only low concentrations of the Pb, Cd and Zn adsorbed by the red muds were in the form of water-soluble and exchangeable fractions, while the greatest concentrations of the metals adsorbed were tightly bound and would not be expected to be released readily under natural conditions.

Red muds may be considered as effective sorbents capable of removing the heavy metals examined here from solution. Thus they could favour chemical immobilization and reduce the solubility and bioavailability of metals in polluted soils.

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