Determination of the Effect of Red Earth as an Ameliorant for Lead Contaminated Soils

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Abstract: The aim of this study was to assess the potential of Red earth/mud as an ameliorant for Pb contamination. The results showed a significant reduction of toxicity with soils contaminated with PbS, PbSO₄, PbNO₃, and PbCO₃. Critical issues raised during the study showed that red mud drastically reduced lead contamination most probably due to shifting of lead from the exchangeable to the Fe-oxide fraction through specific chemisorption and diffusion mechanisms including a reduction of solubility and mobility of Pb. However, speciation pattern of different lead compounds need to be tied to bioavailability to reliably characterize the adsorption behaviour of lead.

Key words: Red earth/mud, toxicity, ameliorant, lead contamination

INTRODUCTION

Red earth, also known as red mud, is a waste material formed through the Bayer process of alumina production in the aluminum industries (Lopez et al., 1998). Red earth contains mainly iron oxide (30-50%), with significant amounts of silica, aluminum calcium oxide and titanium, dispersed in a highly alkaline and caustic liquor (Nguyen and Boger, 1998). The treatment and disposal of this bauxite residue is a major operation and may account for 30-50% of the operational cost in an alumina refinery (Nguyen and Boger, 1998). According to Wong and Ho (1995), the red earth has been accumulated at a rate of over 60 million tonnes annually throughout the world. The toxicity and colloidal nature of the red mud particles as well as the relatively large quantities generated create a serious pollution hazard and necessitate improved disposal techniques (Akay et al., 1998). There have been many proposals of red mud utilization and currently, its use is in the manufacture of building materials and ceramics, as a filler in asphalt road, as an iron ore and a source of various minerals, but still a large volume is dumped in holding ponds for which a large area of land is required (Li, 1998).

Friesel et al. (2003) assessed the effects of various soil amendments on the lability of metals in relation to uptake by plants, dry-matter yield, pH and overall bioavailability. The results of a sequential extraction procedure revealed a relative enrichment of Cd in the Fe-oxide-associated fraction from red mud amended soil, suggesting an additional immobilization mechanism along with pH increase (Lombi et al., 2002). The same workers also found that of all the amendments tested, red mud was the most effective for increasing soil pH. This increase was most pronounced for acidic soil. In general, red mud-amended soils maintained pH values between 7.1 and 7.9 throughout their experiment, while the other amendments had little or no effect on soil pH.

Red earth was also used for the removal of nickel toxicity by Zouboulis and Kydros (1993), where red earth was found to act simultaneously as an alkalinity regulator. Lombi et al. (2002) assessed the ability of red mud to reduce mobility and availability of a range of heavy metals in soils.
contaminated by different sources and the results suggested that specific chemisorption and possibly metal diffusion into oxide particles, could also contribute to the mechanisms responsible for the fixation of metals by red mud.

Friess et al. (2004) assessed the effects of red mud on metal lability and bioavailability in soil and concluded that application rates have to be adjusted according to soil conditions (e.g., pH). In some cases, removal of pollutants (e.g., As, Cr, V) associated with red mud using leaching procedures may be required. Qiao and Ho (1999) investigated the effect of clay amendment on speciation of heavy metals in sewage sludge and found that red mud addition to sewage sludge compost significantly affected metal speciation. Red mud reduced metal mobility and the potential hazard of releasing metal from sludge due to further breakdown of organic compounds.

The adsorption of toxic heavy metal cations, such as Cu(II), Cd(II) and Pb(II), by red mud has been modelled (Apak et al., 1998) with the aid of a modified, Langmuir equation and a double-site binding model incorporating the effect of pH. It was concluded that the adsorption of the heavy metal cations, Cu(II), Cd(II) and Pb(II), by red earth can be interpreted with respect to pH and metal concentration by means of this approach. Heavy metal removal from aqueous and soil solutions utilising red mud has been studied and saturation capacities of red mud for Cu(II), Cd (II) and Pb (II) were found to be 63, 105 and 123 mg g−1, respectively (Apak et al., 1993; 1998; Apak, 1991). Red mud, as a composite adsorbent consisting of various hydrated oxides, showed a high capacity for these metals, necessitating further investigation of their binding potential onto the adsorbent surface.

With a review to simultaneously conserve the environment and utilising an important waste resource, Lopez et al. (1998) assessed the feasibility of using residues from bauxite refining, for the purpose of wastewater treatment. This experiment suggested that, after pre-treatment to neutralize alkaline components and induce formation of stable aggregates, red mud was suitable for use as a filtration medium for treatment of wastewaters, particularly those whose principal contaminants were phosphorus or heavy metals.

Increasingly stringent legislation regarding the quality of water has created a growing interest in the improvement of conventional treatment processes. Various methods of wastewater treatment have been examined and amendments based on adsorption have emerged as some of the most promising techniques (Cheremisinoff and Ellerbush, 1979; Pollard et al., 1992). Such techniques have included the use of activated carbon which is still very popular with different grades available, although it is quite expensive and the complete regeneration of carbon is not always possible (Lalvani et al., 1998). Considerable research work has been carried out to explore inexpensive adsorbents, especially industrial waste materials such as fly ash (Ferraiolo et al., 1990; Diama-dolcioulos et al., 1993), metal hydroxides (Namasi-avayam and Ranganathan, 1998), blast furnace slag (Dimitrova and Mahasngvip, 1998), biomass (Chang et al., 1997) peanut hull (Persiansamy and Namasiavayam, 1994), bagasse pith (Aly and Daifullah, 1998), carbonaceous material (Srivasta et al., 1989, 1997; Srivasta and Tyagi, 1995) and bagasse fly ash (Park et al., 1999).

Gupta et al. (1997, 1998 and 1999a) investigated the possible utilization of solid waste materials, being generated in some prime industries, for immobilisation of metals. Particular focus was applied to the potential of red mud as an adsorbent for the removal of toxic metal ions (e.g., lead and chromium) from aqueous solution (Gupta et al., 1998). It was concluded that red mud obtained from the aluminum industry was an efficient source for the removal of lead and chromium and could be used as a suitable adsorbent for the treatment of wastewater of various industries. Red earth/mud is also known to be suitable for removal of chlorophenols from water. Altundogan et al. (2000) used red earth to remove arsenic from aqueous solution by adsorption and the test showed that the resulting alkaline aqueous medium (pH 9.5) favoured the removal of As(III), whereas lower pH's required for the removal of As(V). However, the characteristic of Red earth in aspects such as its binding mechanisms, influence at pH of spiked soils and adsorption potential of red mud needs further investigation during this study.
The aim of this study was to assess the potential of Red earth/mud as an ameliorant for Pb contamination.

MATERIALS AND METHODS

The topsoil used in these experiments was collected from the top 25 cm of an agricultural field on the Craibstone estate, which is approximately 9 km North West of Aberdeen, at an elevation of 100 m. The pots had a diameter of 150 mm and a surface area of 17,600 mm². A Whatman 42 filter paper was placed on the base of each pot to prevent coarse material from passing through. Leaching pots were arranged on a leaching bench with holes wide enough to hold them. Funnels with aligned filter paper (Whatman 42) inside were placed under each pot placed on the leaching bench to collect leachate in a conical flask placed on the bottom of the shelf.

Preparation of Experimental Pots

Thirty pots were packed with either a mixture of soil, lead compounds and Red earth, or soil with lead compound only.

Control: 3 pots of soil only Soil
3 pots of soil + Red earth

Samples: 3 pots of soil + Pb compound
3 pots of soil + Pb compound + Red earth

Since 4 Pb compounds were considered (PBS, PbSO₄, PbNO₃, PbCO₃), the total number of samples was 24. This translates to thirty pots together with 6 pots of control.

The mixture of soil, Pb compound and Red earth under study was thoroughly shaken together in plastic bags of 1 kg capacity to allow homogeneity prior to packing the pots. The amount of red earth added to 1 kg soil in a pot, was 6.92 g.

The area where the bottles were placed was protected with black, plastic material to minimize the effect of light on leachate chemical properties. All the experimental treatments were carried out in triplicate.

Bioassay

Lux-marked bacterial biosensors were used during the study and the preparation of the biosensor and luminometer measurements were carried out as described. One hundred microliter of the resuscitated biosensor suspension was added to the samples at 15 sec intervals, accurately timed for measurement in the Bio Orbit 1253 luminometer (Labtech International, Uckfield, U.K). Each sample was exposed to the sensor for exactly the same time. Samples were incubated for 15 min before light output measurements were carried out at 15 sec intervals. This ensured the same exposure time to the potentially toxic elements for cells in each of the cuvettes.

Chemical Analysis

Stock Solution Preparation

1.599 g of lead nitrate, Pb(NO₃)₂ (analytical grade) was carefully weighed and dissolved in deionized distilled water. When dissolution was complete, it was acidified with 1 mL of 1M HNO₃ and diluted to 1 L with deionized water.

Preparation of Standard Solutions and Calibration

Standard Lead Solution was prepared by diluting the stock (lead) solution. Concentration ranges starting from 0.1, 0.5, 100, 200, 400, to a maximum of 800 g L⁻¹ which were used as calibration standards. Standard solutions of lead were prepared fresh for use from a stock solution of lead nitrate.
(0.1 mol L\(^{-1}\) in HNO\(_3\)). All standard and sample soil solutions were prepared to approximately 0.1 mol L\(^{-1}\) in HNO\(_3\). Care was taken to use specially purified water (deionized water) when diluting samples to final volume for quality control purposes.

Deionized water was also used during the final rinsing of all the plastic and glassware. This was after rinsing them first, in solution (with diluted nitric acid) in order to remove any possible traces of lead on them. During the determination of concentration two replicate determinations of absorbance were made for each sample. A blank of deionized water was used to zero the instrument.

A 10 µL sample was injected very carefully with the help of an auto sampler into the cold graphite furnace and, by means of an automatic temperature programmer, dried at 120°C for 35 sec and at 140°C for another 35 sec, then heated to 200°C and allowed to cool for 15 sec. These steps were performed, automatically, to remove solvent and any removable volatile matrix. Actual atomization of the sample followed and was performed at 1800°C, very rapidly, for 5 sec. During this time the signal from the chamber (absorbance) was recorded and displayed on the screen as a function of time. Finally, the furnace was heated for 5 sec at 2600°C. The purpose was to remove any residues and prepare the instrument for next sampling phase. During the atomization step, the absorbance was monitored at 283.3 nm, using a slit width of 0.7 nm, set at low level. Purging with argon was interrupted automatically during the absorbance scan. Background correction was provided by means of the deuterium background corrector, which automatically compensated for broadband absorption interferences.

Data Analysis

Two-way analyses of (ANOVA-Analysis of Variance) (except for biosensor experimental data which is One-way ANOVA) were carried out using the statistical package Minitab for windows, release 12.1 (State College, PA, USA). Mean differences were determined using t-test (paired two samples for means) and Pearson Correlations using Excel program (Microsoft™ Office 2000). Significant differences between treatments were elucidated using least significance difference (LSD) values. Graphs were generated using SigmaPlot for Windows version 9.0 (Jandel Corporation, CA and USA).

RESULTS

Chemical Analysis

Effect of Red Earth on Lead Concentration of Leachate

Red earth showed a significant effect as an ameliorant (i.e., reducing leaching of Pb) for soils contaminated with PbS and PbCO\(_3\) (p<0.001), PbSO\(_4\) and PbNO\(_3\) (p<0.01) over a period of 230 days as shown in Fig. 1 a-e. Similarly, the effect of red earth as an ameliorant was significant over time (days) and this was only observed for PbS (p<0.01) and PbNO\(_3\) (p<0.05). This observation was considered important in determining the suitability of red earth as an ameliorant of lead contaminated soils. Table 1 showed the significance of time factor when lead compounds were treated with Red earth/mud. All the treatments were affected by time as a factor except for PbSO\(_4\) and PbCO\(_3\). The time factor for contaminated soils treated with Red earth/mud is critical for design of mitigation strategies.

<table>
<thead>
<tr>
<th>Source of Pb</th>
<th>Treatment (Bone meal)</th>
<th>Time factor</th>
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<tbody>
<tr>
<td>PbS</td>
<td>***</td>
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<tr>
<td>PbSO(_4)</td>
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<tr>
<td>PbNO(_3)</td>
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<tr>
<td>PbCO(_3)</td>
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*** p<0.001; ** p<0.01; * p<0.05; ns: Non Significant
Fig. 1a: Lead concentration (µg L⁻¹) in leachate from soil contaminated with (a) PbS and treated/untreated with Red earth over a period of 230 days.

Fig. 1b: PbSO₄ and treated/untreated with Red earth over a period of 230 days.

Fig. 1c: PbNO₃ and treated/untreated with Red earth over a period of 230 days.
Fig. 1d: PbCO₃ and treated/untreated with Red earth over a period of 230 days

Fig. 1e: Lead concentration (μg L⁻¹) in leachate from soil contaminated with (i) PbS, (ii) PbSO₄, (iii) PbNO₃, (iv) PbCO₃ and treated/untreated with Red earth over a period of 230 days

so as to address emerging constraints from the contaminants. Comparison between the PbS and PbSO₄ (r = 0.5), PbS and PbCO₃ (r = 0.60), PbS and PbCO₃ (r = 0.6) treatment means showed a significant difference (p<0.05) while demonstrating a very close pattern of amelioration with red earth. Lead levels increased in various control samples over time after the equilibration phase with low values demonstrated in samples treated with red earth. The greatest difference of 9.14 μg L⁻¹ was observed when PbS was compared to PbCO₃ with the least difference of 2.1 μg L⁻¹ demonstrated when PbSO₄ was compared to PbCO₃. The difference between the blanks (control with/without) was not significant.

Effect of Bone Meal Treatment on pH Values of Leachate from Samples Spiked with Lead Compounds

During the experiment a significant (p<0.05) effect of Red earth on pH values was observed with various lead sources (Fig. 2) indicating that Red earth was acting as an alkaline regulator. The highest pH was observed with PbCO₃+RE (6.60±0.2) while the lowest pH was observed with PbNO₃-RE (3.40±0.15). However the biggest difference indicating the effect of RE was observed with PbNO₃, PbCO₃>PbSO₄ PbS and the control showed similar results demonstrating no significant of RE on the samples.
Fig. 2: Effect of Red earth treatment on pH values of various sources of lead

Fig. 3: Effect of red earth on Pb bioavailability in soils spiced with various lead compounds

**Biosensor Based Toxicity Test of the Leachate**

When soil samples spiked with various lead compounds (PbNO₃, PbCO₃, PbSO₄, and PbS) were treated to Red earth a significant effect was observed ($p<0.05$) (with the exception of PbCO₃) (Fig. 3). The highest difference was observed with PbS where on application of red earth significantly increased percentage bioluminescence from 63% $\pm$7 to 100.3$\pm$2.9. When the differences in percentage bioluminescence between samples treated with/without Red earth were further analysed the following trend was observed: PbS$>$PbNO₃$>$PbSO₄.

**DISCUSSION**

The alumina industry worldwide is facing a growing disposal problem of Red earth/mud creating increasingly technical, economic and environmental problems. During this study, the benefit of Red mud/earth was evaluated and its use as an ameliorant for lead contaminated soils was assessed. This
was to address contamination of soils, which is currently posing major problems all over the world. Red earth/mud (Bayer process) of bauxite minerals have the following composition (which strengthens its choice as an ameliorant during this study) according to Ciciù et al. (2003): SiO₂ = 9.58%, Al₂O₃ = 17.91%, Fe₂O₃ = 30.45%, CaO = 7.77%, MgO = 0.86%, Na₂O = 12.06%, K₂O = 0.38%, TiO₂ = 8.61%, P₂O₅ < 0.2%, Cu = 35 ppm, Pb = 163 ppm, As = 62 ppm, Zn = 56 ppm, Zr = 1150 ppm, V = 1476 ppm, Ba = 206 ppm, Cd = 23 ppm, Cr = 1237 ppm, Hg = 0.7 ppm, LOI = 12.38%. pH and specific gravity were 10.67 and 2.77 g cm⁻³, respectively.

A preliminary assessment was made regarding the scope for Red mud usage and its possible remediation potential as an ameliorant which also explored certain associated advantages such as: non-invasive, easily available and cost effective technology. The main principles of remediation technologies in terms of contaminant treatment include isolation, immobilisation, toxicity reduction, physical separation and extraction.

Environmental pollution by some of these metals (Cu, Cd, Pb, Cr, Ni etc.) is well recognised and can be detrimental to living systems (Vinod et al., 2002). Many other techniques for the removal of heavy metals (e.g., chemical in situ removal, ion exchange chromatography, reverse-osmosis, precipitation, adsorption etc.) in aquatic and terrestrial systems are available but are considered less efficient, costly and to some extent destructive (Bower et al., 1997; Dean et al., 1972). Knowledge of trace element mobility and speciation in contaminated soils is an important aspect of environmental evaluation. The addition of red earth/mud to metal contaminated soils generally causes the shifting of metals from the exchangeable to the Fe-oxide fraction and decreases acid extractability of metals (Brown et al., 2005). The mechanisms proposed by Lombi et al. (2002) suggest that specific chemisorption and possibly metal diffusion into oxide particles could be the mechanisms responsible for the fixation of metal by red mud. When Red Earth is added to contaminated soils, they can neutralize low pH and reduce metal mobility by different physical chemical mechanisms (increase of available adsorption sites) (Lombi et al., 2002).

In the current study, the reduction of Pb leached from all of the lead spiked experimental pots suggested that Red earth acted as an adsorbent when lead concentration (μg L⁻¹) was compared between leachate samples spiked with lead and the controls (Fig. 1 a-c), (Fig. 2). The heterogeneous adsorbency principle in red mud is associated with its ability to bind metal ions (M²⁺) onto one or two types of surface sites at pH< 6.0 and less than 50% surface coverage in the form of SOM⁺ monodentate surface complex, which results in the release of protons from the surface, effectively explaining the adsorption of metals (Apak et al., 1998). This observation was supported by a report by Sauvé et al. (2000) who indicated that the presence of Iron oxides (Red earth/mud) and also organic matter had a high capacity to adsorb Pb and concomitantly maintain a low free Pb²⁺ activity in solution.

The increase in pH values (>pH 5.0 in all cases, with the highest unit increase noted with PbNO₃) of the leachate was demonstrated during the current study (Fig. 2) for all the treatment involving red earth. This observation related to Red earth/mud of increasing pH values was supported by Zouboulis and Kydros et al. (1993) who earlier reported that Red earth/mud acted simultaneously as an alkaliinity regulator causing precipitation by forming insoluble hydroxides, thus acting as an adsorbent and a flocculent. The increase in pH was further reported to reduce the solubility of most Pb-bearing minerals, while increasing the adsorption affinity of iron oxides, organic matter and other adsorptive surfaces (Lombi et al., 2002; Sauvé et al., 2000). However increasing pH also increased Pb hydrolysis, inorganic matter ion-pair formation and organic matter solubility, potentially promoting higher dissolved concentrations of Pb (Brümmer et al., 1986; Sauvé et al., 1998a, b). Brun et al. (2005) reported that Red earth/mud is characterised very high alkalinities and its major constituents are crystalline hematite (Fe₂O₃), boehmite (γ-AlO(OH)), quartz (SiO₂), sodalite (Na₆Al₂Si₆O₁₈·4H₂O) and gypsum (CaSO₄·2H₂O), with a minor presence of calcite (CaCO₃), whewellite (CaC₂O₄·H₂O) and gibbsite Al(OH)₃.
Biosensor analysis of leachate toxicity showed that the application of red mud had rendered the leached fraction of the spiked lead less toxic, with an increase in percentage bioluminescence. The only lead compound which showed a degree of toxicity before the application of Red mud after 193 days was PbS. This could be attributed to the low solubility of lead sulphide when spikc into soil samples. Bataillard et al. (2003) showed that when lead was added as sulphate, between 10 and 20% of lead particles dissolved, regardless of the soil type with lead sulphide progressively oxidising over time.

Therefore red earth/mud application as an in situ inactivation technique (where an ameliorant was incorporated and mixed with lead contaminated soil) bound the toxic metals which essentially reduced their mobility in the soil thus reducing the contaminant leachability and bioavailability (Hartley et al., 2004). Moreover, the advantages of Red mud/earth which relate to factors such as retention of nutrients on infertile sandy soils, reduction of eutrophication of rivers and water ways (Summers et al., 1996a), groundwater recharge areas, improvement of pasture growth (Summers et al., 1996b), plant P uptake (Snars et al., 2004) and water retention in excessively drained soils (Vlahos et al., 1989) outstripped the disadvantages. The disadvantages that were attributed to red earth/mud include high pH values, salinity and absence of nutrients and organic constituents that could possibly suppress revegetation (Xenidis et al., 2005). However, precautionary principle is highly required as a public health concern for wide application of red earth/mud where off-site assessment is conducted before use to avoid recontamination of terrestrial or aquatic systems.

CONCLUSIONS

The potential for red earth as a heterogeneous adsorptive, cost effective and environmental friendly remediative technique for reducing the leaching of lead from contaminated soils was established. Critical issues raised in the study showed that red mud drastically reduced lead contamination most probably due to shifting of lead from the exchangeable to the Fe-oxide fraction through specific chemisorption and diffusion mechanisms including a reduction of solubility and mobility of Pb thus reducing its toxicity as demonstrated through the bioluminescence results. Through the use of a biosensor, leachate toxicity was found to be drastically reduced, except for PbS. However, speciation pattern of different lead compounds need to be tied to bioavailability based on an appropriate time scale to reliably characterize the adsorption behaviour of lead in the presence of red earth. Areas that need to be studied and assessed (for public health concerns) in depth for wide spread application of red earth/mud (in terrestrial and aquatic ecosystems) include off-site effects of red earth, appropriate stripping methods of chemically bound contaminants (e.g., trace metals, cyanide etc).

REFERENCES


