STECH,4(2), S/NO 10, MAY, 2015

International Journal of Science and Technology
(STECH)
Bahir Dar- Ethiopia
Vol. 4 (2), S/No 10, May, 2015: 86-106
ISSN: 2225-8590 (Print) ISSN 2227-5452 (Online)
DOI: http://dx.doi.org/10.4314/stech.v4i2.8

# Sorption-Desorption Tests on the Performance of Non-Hazardous Industrial Wastes in Decreasing Leachability of Trace Metals on Contaminated Lands

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## Abstract

Soil stabilization by addition of industrial solid wastes in order to increase trace metals retention and (a minor secondary effect) to dilute their concentrations is an environmentally friendly and attractive soil remediation process that attenuates trace metals impact. In this study, non-hazardous industrial by-products (sugar foam, gypsum, zeolitic materials and fly ashes) were tested using laboratory scale experiments to assess their performance on the remediation of acidic soil that has been affected by a pyritic source of contamination at Aljaraque, Spain. In this soil, the concentration of metals in the Aqua Regia and soil-water extracts confirmed the extent of the soil contamination since all seven trace metals (Cu, Cd, As, Pb, Zn, Co and Sb) analyzed from the Aqua Regia extracts and nine trace metals (Cu, As, Cd, Zn, Pb, Co, Sb, Ni and Cr) analyzed in soil-water extract were found above the intervention limits specified in the Junta de Andalucía (Spain) and Germany National Standard (DIN) respectively for both Agriculture and Industrial activities. Metal sorption and desorption capacity of the industrial wastes were estimated in a soil water extract medium. Fly ashes and zeolitic material were found to be the best candidate materials for soil remediation due to their ability to increase soil pH, exhibiting greater solid-liquid distribution coefficient ($K_d$), lower sorption reversibility ($K_{d,\ des}$) and lower desorption yields to almost all trace metals analyzed.

***Key words***: - amendment materials, contaminated soil, trace metals, soil remediation, leachability

## 1. Introduction

The presence of derelict lands due to pollution has become an issue of concern in the world as a whole (1-3). Industrial growth and mining activities have played a major role in this aspect (3); and recently there has been an increase in production of chemical substances whose release into the environment has reached a stage that societies are no longer able to control their impact, consequently affecting human health through food chain (2). These chemicals include heavy metals which are found in various forms within the environment (4) and they do accumulate in excess of the natural background, or leach to the level of potential pollution on surface and underground water (5). Therefore, the demand for cost effective soil treatment techniques which is efficient and environmentally friendly has generally became one of the key research activities in environmental sciences (1; 6).

Sorption entails all processes leading to the incorporation of metals in the solid phase, removal of chemical species from water through various processes such as adsorption, hydrophobic interactions, diffusion, ion-exchange, precipitation, complex formation, etc (4;7). Strategies for removing heavy metals from contaminated soils are directly related to their partitioning between soil and soil solution due to the shift in equilibrium for which changes such as soil pH, ionic strength, nature of the metal species, dominant cation, and ligands (inorganic and organic) present in the soil solution are the contributing factors (7). Since sorption is a process involving a two-phase system, it has a distribution coefficient ($K_d$) which evaluates the relationship between the sorbed metals and their relative distribution in both solid and liquid phases (4).

Various soil remediation techniques including excavation, biodegradation, solidification, volatilization, soil washing, electro-remediation, phytoremediation, etc have been so far applied to mitigate the impact of heavy metals contamination in soil. Nevertheless, most of these applied remediation techniques are in one way or the other found to be time consuming, slow in action, expensive and some of them environmental unfriendly as they involve the use of chemicals which greatly affect the soil structure, soil organic matter as well as soil microorganisms (8). The enhancement of metals immobilization by the addition of materials is increasingly seen as a valuable alternative strategy for a wide range of contaminated sites and at the same time an advantageous process of reuse of industrial by-products (9).

Soil stabilization refers to the reduction of chemicals or contaminants leachability and availability by converting them into least soluble following sorption process without changing their physical nature (10). The use of a number of materials including traditional agricultural products, organic matter and various industrial by- products has been suggested for that purpose (11). The latter choice is more advantageous as it reduces wastes, disposal charges and waste handling by converting them into industrial reusable co-products (9;11). Rigol *et al* (12) observed that given the dose in which the materials are applied to the contaminated soil, materials may significantly increase the retention of the contaminants if its distribution coefficient ($K_d$) exceeds that of the soil by at least two orders of magnitude. Consequently, candidate materials with a $K_d$ lower than or similar to that of the soil are not deemed capable for soil remediation (12).

In this study, a laboratory based assessment on the performance of industrial by-products on remediation of heavy metals contaminated acidic soil that has been affected by a pyritic source of contamination was carried out.

In order to accomplish the stated objective, the specific work plan was as follows:

- Characterization of the soil sample and assessment of the extent of metals contamination in the soil in terms of total extractable metals and water soluble metal.
- Quantifying the metals portion in the soil-water extract and decide whether the soil requires remediation.
- Testing of the candidate materials (industrial by-products) by applying sorption and desorption experiments under a simulated field condition.
- Mixing the soil with candidate materials and analyze the soil-material mixtures to verify materials suitability for soil remediation.
- Analysis of changes in the pH of the soil through the application of a pH titration test as a result of material addition.

## 2. Materials and Methods

### *2.1 Samples and reagents*

One mineral soil from Aljaraque (South-Western Spain) and four candidate materials for soil remediation were used in this study. The candidate materials tested include: sugar foam supplied by the sugar producer, Azucarera Ebro, gypsum was from Hidrocantábrico Energía, fly ashes and zeolitic material originating from a hydrothermal alkaline treatment of coal at a thermal power station in Narcea – Spain.

All samples were air-dried, homogenized and stored in plastic containers to avoid metal adsorption on storage as suggested by Ali and Aboul-Enein (13), and preserved at room temperature 25±0.5°C for the entire study period.

In all experiments conducted, double deionized water purified in a Milli-Q system was used. 37% HCl, 70% $HNO_3$ and NaOH used at various concentration came from Panreac Quimica Sau; $Ca(OH)_2$ and $H_2SO_4$ was from Merck. Glassware, filters, buffer solutions (pH 4, pH 7 and pH 10), standard solutions and other chemicals of analytical grade were used as received. To avoid metals cross contamination, all glassware and plastic containers used were soaked in 10% $HNO_3$ for at least 24 hours and thoroughly rinsed in double deionized water before use.

### *2.2 Main sample parameters for soil and material characterization*

Cation Exchange Capacity (CEC), exchangeable acidity, exchangeable cations, pH, carbonates, total organic matter, moisture and soil particle size distribution for Aljaraque soil sample; and also pH, organic carbon, $CaCO_3$ content, Cation Exchange Capacity (CEC), major elements (Fe, Mn, Ca, Mg, and Al) together with trace elements (Cd, Zn, Cu, Pb, As and Ni) for the candidates materials used in this study are secondary data adopted from the study done within the research group.

Trace metals (Zn, Cu, As, Ni, Cd, Cr, Pb, Co and Sb) for Aljaraque soil sample were determined by applying aqua regia extraction technique as described in ISO 11466 (14). A quality control soil (QC sample) and blank were tested in parallel applying the same ISO norm in order to verify artifacts in the analytical method and matrix effects from the samples. Moisture content in all samples was determined separately to all analytical experiment that requires moisture determination as described in Jones (15). In this experiment, a sample of 1g was dried at 105±2°C for 24h followed by weighing in an analytical balance to constant weight at nearest ±0.1mg. From this determination, a correction to dry mass was obtained which was applied to all respective analytical concentrations reported in this study.

### *2.3 Sorption and desorption test on candidate materials*

In this experiment a series of steps that simulated the remediation process for contaminated soils on a given field condition were involved. This included the quantification of the metal fraction leachable in water from the contaminated soil sample, calculating the heavy metal fraction sorbed in the soil remediating materials and the $K_d$ of heavy metals as well as their desorption distribution coefficients ($K_{d,\ des}$) and lastly the determination of desorption yields ($Y_{des,}$ %) as a percentage of the metals concentration in equilibrium to that sorbed in the candidate materials.

### *2.4 Quantification of water -leachable metals fraction from the contaminated soil*

The water extract from contaminated soil was prepared with L/S ratio of 10mL/g following the procedures recommended in literature (16). The resultant suspension was shaken at 30 rpm at room temperature for 16h for attainment of equilibrium, followed by centrifugation at 10000rpm for 15mins. The resultant supernatant of the contaminated soil water extract (wash-off solution) (Figure 1 (i)) was filtered through 0.45µm filters and the filtrate stored in polyethylene bottles at 4°C until further analysis.

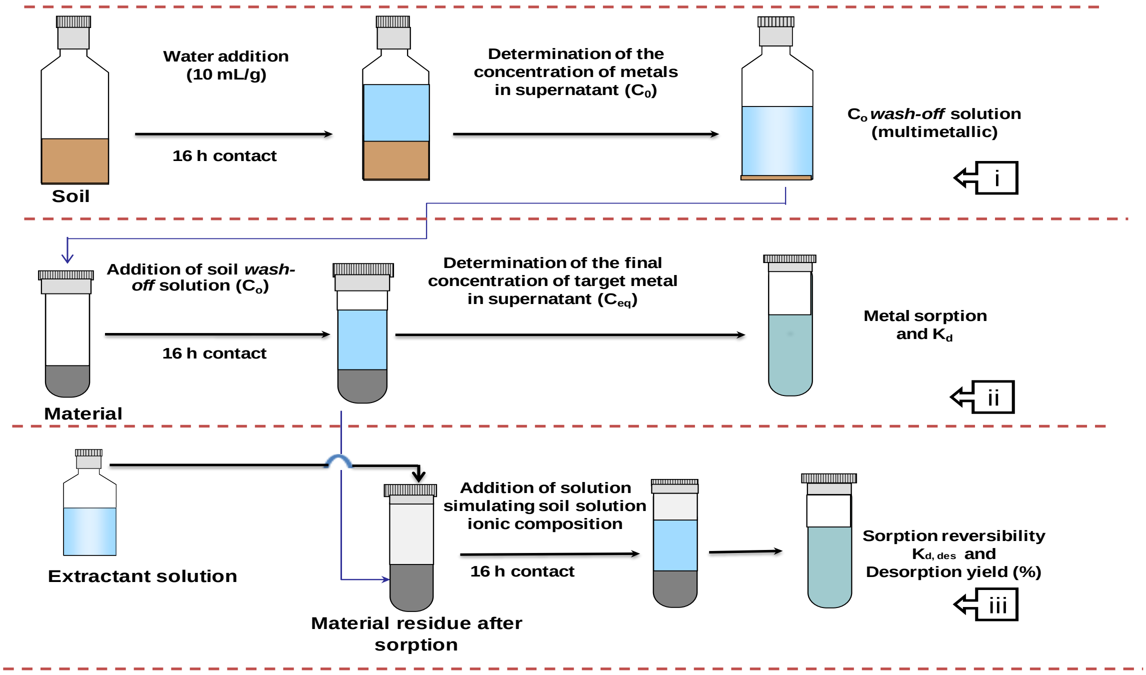

**Figure 1:** Scheme of sorption and sorption reversibility experiments

### *2.5 Determination of $K_d$ for heavy metals in the materials*

Sorption tests of the materials were carried out in 50mL bottles under a batch process to obtain the $K_d$ for heavy metals in the materials. Multimetallic water extract from the contaminated soil (wash-off solution) that ensures a satisfactory simulation of the field environment was used in this experiment as the contact solution. A volume of 20ml of the extract containing a given amount of the target metals was added into each bottle containing 2g of each candidate soil remediating materials and allowed to equilibrate. The suspensions were shaken at 30 rpm at room temperature for 16 hours (Figure 1(ii)). The resulting suspension was centrifuged and the supernatant filtered through 0.45µm filters. As pH has been reported a key factor in regulating the sorption-desorption of metals (17), a pH meter with a precision of ± 0.01 was used to determine the pH in the resulting solution after equilibration. Thereafter, the clear solution was stored at 4°C until further analysis. The equilibrium constant ($K_{d,}$ L/kg) of metals in the materials was quantified by the S/L concentration ratio after equilibration. The respective $K_d$ values were derived first by quantification of the metal's initial concentration in the contaminated soil-water extract ($C_{in}$) and the final contact solutions after equilibrium ($C_{eq}$). The concentration of heavy metals sorption in the material ($C_{sor}$) was calculated as in equation (1).

$$C_{sor} = \frac{\left[\left(C_{in} - C_{eq}\right)V_{Sol}\right]}{W_{Sample}} \quad \text{----------------------}(1)$$

Whereby:

$C_{sor}$ – is the concentration of metals sorbed in the solid phase of material (mg/kg); $C_{in}$ – is the initial concentration of metals in the equilibrium solution (mg/L); $C_{eq}$ – is the concentration of metals in the equilibrium at the end of the sorption experiment (mg/L); $V_{sol}$ – is the volume of solution (soil wash-off) (mL); $W_{sample}$ – is the mass of the material (g).

An equilibrium coefficient ($K_d$) was calculated as the ratio of metals concentration found in the S/L phases applying equation (2).

$$K_d = \frac{C_{sor}}{C_{eq}} \quad \text{-------------------------------}\ (2)$$

### *2.6 Determination of the reversibly sorbed heavy metals fraction from the materials*

From the sorption experiments 20ml of extractant solution (Figure 1(iii)) simulating the ionic composition of the soil water extract were added in the contaminated candidate materials. Two ions $Ca^{2+}$ and $SO_4^{-2}$ from $Ca(OH)_2$ and $H_2SO_4$ respectively were added as the only relevant ions existed in the wash-off solution of the contaminated soil. The suspension was shaken at 30 rpm at room temperature for 16h followed by centrifugation and the supernatant filtered though 0.45µm filters. The clear solution was stored at 4°C until further analysis. The desorption distribution coefficient ($K_{d,\,des}$ L/kg) of heavy metals were quantified using equation (3).

$$K_{d,des} = \frac{\left( C_{Sor} - \left[ C_{eq.des} \left( {V_{Sol}}/{W_{sample}} \right) \right] \right)}{C_{eq,des}} \quad \text{-------------------------- } \mathit{(3)}$$

Whereby:

$C_{sor}$ – is the concentration of metals sorbed in the solid phase of material (mg/kg); $Ceq_{,\,des}$ – is the concentration of metals in the equilibrium at the end of the desorption experiment (mg/L); $V_{sol}$ – is the volume of heavy metals free solution (simulating soil solution ionic composition) (mL); $W_{sample}$ – is the mass of the material (g).

The percentage of heavy metals desorption from the solid phase of materials into liquid phase was also calculated at the onset of equilibration by applying equation (4).

$$Y_{des,\%} = \frac{C_{eq,des} \left( {V_{sol}}/{W_{sample}} \right)}{C_{sor}} \times 100 \quad \text{------------------------------- (4)}$$

### *2.7 Preparation of amended soil samples and determination of metal contents*

Soil amendment was done by mixing 10% of each industrial by-product into 90% of the soil as described in Rigol *et al.*, (18). In order to simulate the field conditions in the short term in both cases a three drying-wetting cycles were conducted which consisted of rewetting the mixture at field capacity, maintaining them in closed vessels at 40°C for 24h, and then drying them in open vessels at 40°C for 48h and thereafter the samples disaggregated, sieved through a 2mm nylon mesh and homogenized. The mixtures were then shaken for 24h and stored in plastic containers at room temperature. Sub-samples of mixtures were taken from the containers while performing the respective analysis.

### *2.8 Determination of trace metals in the soil water extracts*

A Perkin-Elmer Model OPTIMA ICP-OES equipped with a Perkin-Elmer AS-90 was used for the determination of trace elements (Cd, Zn, Cu, Pb, Ni, Cr, Co and As). The measurements of metal concentration were performed after dilution in 1% $HNO_3$ to minimize matrix interferences. For the low concentration levels of heavy metals in the extract from the desorption experiment after the equilibration, a Perkin-Elmer Model ELAN ICP-MS equipped with a PerkinElmer AS-91 auto sampler was applied. Standard solutions for ICP-EOS calibration were prepared following serial dilutions. The emission line and LOD used for each specific metal in the extracts were as shown in table 1.

**Table 1** Limit of detection and emission line used for the analysis of metals

| Metal | Emission Line (nm) ICP-OES | LOD (mg/L) ICP-OES | LOD (µg/L) ICP-MS |
|---|---|---|---|
| Ca | 317.933 | 0.1 | - |
| Mg | 279.077 | 0.1 | - |
| Al | 308.215 | 0.5 | - |
| Mn | 259.372 | 0.01 | - |
| Fe | 259.939 | 0.02 | - |
| Sb | 206.836 | 0.1 | - |
| As | 193.696 | 0.5 | 0.2 |
| Cd | 228.802 | 0.01 | 0.02 |
| Co | 228.616 | 0.01 | 0.1 |
| Cr | 267.716 | 0.01 | 0.1 |
| Cu | 324.752 | 0.01 | 0.1 |
| Ni | 231.604 | 0.1 | 0.2 |
| Pb | 220.353 | 0.2 | 0.05 |
| Zn | 213.857 | 0.025 | 0.2 |

### *2.9 Determination of metal contents in soil after material addition*

The concentration of trace metals (Zn, Cu, As, Ni, Cd, Cr, Pb, Co and Sb) in the soil mixed with materials was determined by applying aqua regia extraction technique following the ISO Norm 11466 (14). The obtained suspension was filtered through an ash-free paper filter (Whatman 40). These solutions were stored in polyethylene bottles at 4°C until further analysis.

### *2.10 pH titration test*

In this experiment, 2g of a sub-sample was weighed in an Erlenmeyer flask together with 200mL of double deionized water. The flask was placed on a horizontal magnetic stirring device. A pH-electrode and an automatic titration dispenser were attached to each flask. The initial pH of each sample suspensions was measured after a continuous stirring for 20min without an addition of acid or base, thereafter a consecutive addition of 100µL of $HNO_3$ or NaOH done using an automatic acid and base adding equipment BANCpH pretest assembly - model pH-103 as described in prCEN/TC 14997 (19).

## 3. Results and discussion

### *3.1 Characterization of the soil and material samples*

The main characteristics for Aljaraque soil and the candidates' materials (Industrial by-products) are shown in Table 2 and 3 respectively. Results from soil analysis shows that the soil sample from Aljaraque has been contaminated by a pyritic source hence be best categorized as mineral acidic soil due to its low carbonate content, low total organic matter, low CEC, low pH value and low content of exchangeable cations ($Ca^{2+}$, $K^+$, $Mg^{2+}$, $Na^+$) with very high exchangeable acidity and Fe contents (Table 3). High value for exchangeable acidity is a good indicator for the quantity of exchangeable $H^+$ plus the acidity derived from $Al^{3+}$ in soil solution and thus a basis for estimating the neutralization demand of the soil (20) and has a direct relation to the acidic nature of the soil which was found to be pH 3.0

**Table 2** General characteristics of Aljaraque soil sample

| Parameter analysed | Results | Units |
|---|---|---|
| Exchangeable acidity | 275.5 | $cmol_c/kg$ |
| Exchangeable Calcium | 0.9 | $cmol_c/kg$ |
| Exchangeable Potassium | 0.67 | $cmol_c/kg$ |
| Exchangeable Magnesium | 0.31 | $cmol_c/kg$ |
| Exchangeable Sodium | 1.12 | $cmol_c/kg$ |
| CEC | 3.0 | $cmol_c/kg$ |
| pH | 2.1 | - |
| Carbonates | < 3 | % |
| Total Organic matter | 13.51 | % |
| Sand (0.05 < Ø < 2mm) | 34.2 | % |
| Course Loam (0.02 < Ø < 0.05mm) | 42.8 | % |
| Fine Loam (0.002 < Ø < 0.02mm) | 4.8 | % |
| Clay (Ø < 0.002mm) | 18.2 | % |
| Moisture content | 6.2 | % |

**Table 3** Main composition of Aljaraque soil

| | | **Extractable Metals (mg/kg)** | | | |
|---|---|---|---|---|---|
| **Metal** | **Soil** | **[a]Limits** | | **Soil wash-off** | **[b]Limits** |
| | | Agriculture | Industry | | |
| Ca | 10113 | ∞ | ∞ | 4616 | ∞ |
| Fe | 308127 | ∞ | ∞ | 5378 | ∞ |
| Mg | 518 | ∞ | ∞ | 235 | ∞ |
| Al | 2346 | ∞ | ∞ | 415 | ∞ |
| Mn | 69 | ∞ | ∞ | 17 | ∞ |
| Cu | 1496 | 300 | 1000 | 157 | 1 |
| As | 1112 | 50 | 300 | 3.8 | 0.1 |
| Cd | 42 | 7 | 30 | 0.4 | 0.08 |
| Zn | 3145 | 600 | 3000 | 175 | 5 |
| Pb | 11373 | 350 | 2000 | 23 | 3 |
| Co | 146 | 100 | 300 | 4.6 | 2 |
| Sb | 425 | 15[b] | ∞ | 0.9 | ∞ |
| Ni | na | ∞ | ∞ | 5 | ∞ |
| Cr | na | ∞ | ∞ | 1 | ∞ |

na = not analysed

[a] = intervention limits of the Junta de Andalucía (15)

[b] = limits of Germany legislation (16) based on $NH_4NO_3$ and EU Directive (2003/33/CE) (17)

∞ = not specified

Table 4 shows the main characteristics of the candidate materials. All four tested candidate showed a basic pH in which gypsum had the lowest value pH 6.2 while fly ashes had the highest pH value of 11.7. Among the materials characterized, gypsum and sugar foam were found to contain traces of organic carbon while substantial amount of $CaCO_3$ was observed in sugar foam. Major metals ions were found in all materials at a large concentration. Although certain contents of trace metals in the materials were observed, their concentration was very low in comparison with that in the soil hence their effect in environmental become of no significant making them non-hazardous materials.

The major and trace metals extracted from the Aljaraque soil (Table 4) shows that Six out of seven tested trace metals including Cd, As, Cu, Pb, Sb and Zn were above the intervention limits of the Junta de Andalucía (21) for both Agricultural (for a soil with pH <7) and Industrial activities. The concentration of Co was found lower than the intervention limit for industrial activities but higher than that for Agriculture. Even though the limit for Sb was not specified in the Junta de Andalucía, yet its concentration was found higher than the value specified in Dutch intervention limit for Sb in soil i.e. 15mg/kg as reported by Conesa *et al*., (22). On the other hand, the concentration of Cu, As, Cd, Zn, Pb, Co, Sb, Ni and Cr determined in the soil wash-off were all above the intervention limits according to both Germany legislation (23) based on $NH_4NO_3$ trace element extraction in soil and EU Directive (2003/33/CE) (24). This confirmed that Aljaraque soil was highly polluted with heavy metals making remediation option inevitable.

### *3.2 Metals sorption and desorption on candidate materials*

### *3.2.1 Metals sorption on the candidate materials*

Table 5 shows the results of the $K_d$ of eight trace metals (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) between solid phase and liquid phase and the pH of the solution at the onset of equilibrium. These two parameters estimate the potential for mobilizing dissolved trace metals pollutants as well as their retention when in contact with the remediating materials in the soil (25). The approach of quantifying sorption capacity of the material using the solution obtained from the soil-water extract allows estimation of the sorption process that could take place at field level after the addition of the amendment material into the soil in which a multimetallic soil solution would interact with the material (26). Pb and As were found to have higher $K_d$ values >10000 L/kg in all candidates, a phenomenon that suggests greater sorption in all industrial by-products. Except for Cd in zeolitic materials, the concentration of other metals in both zeolitic materials and fly ashes could not be calculated in the solution after the equilibrium due to the fact that the concentration of metals after the equilibration was observed below limit of quantification. The other candidates were relatively less efficient by having a quantifiable concentration of trace metals in their solution after equilibration while gypsum observed the least by having a lower $K_{d\ des}$ values and least pH. In comparison, fly ashes and zeolitic materials showed higher pH that made their solution to remain alkaline after equilibration i.e. pH 10.4 and 9.5 respectively with the soil-water extract which had an acidic pH 3.0±0.5.

### *3.2.2 Metals desorption from materials*

Table 6 shows the results for the sorption reversibility behaviour for candidates on equilibration with the wash-off soil solution. Except for Cd in zeolitic materials and As in fly ashes, the concentration of other metals in both zeolitic materials and fly ashes were found below the limit of quantification. The other candidates were relatively less efficient by having a quantifiable concentration of trace metals in their solution after equilibration and sugar foam found the least. All candidates were the best in retaining Pb. Zinc had higher retention all except for gypsum. After the onset of equilibration, gypsum had a quantifiable amount of Zn which resulted into lowering of the $K_{d,\ des}$ values which meant a high sorption reversibility.

Table 7 shows the desorption yields for all materials. Generally all four candidates had a desorption yield below 10% making them promising for immobilizing metals after addition to Aljaraque soil. In some cases, the percentage desorption yields could not even be calculated since the metals concentration in the solution following desorption process after the onset of equilibrium was found lower than limit of quantification.

### *3.3 Effect of the addition of candidate materials in the soil on trace metal concentration*

The addition of materials into the soil at 10% dosage brought up a reduction in extractable metals concentration as a result of dilution (a minor effect of metals reduction in the contaminated soil (Table 8). All metals were found to be lower in concentration when compared to the concentration obtained in Aljaraque soil sample before the addition of the candidate materials. The limit of Sb was not specified in the Junta de Andalucía in either agriculture or industrial purposes, yet its concentration was analysed and found above the limit declared in the M.H.S.P.E. (Ministry of Housing, Spatial Planning and Environment) of Germany for agriculture.

Furthermore, it was observed that the addition of materials in the Aljaraque soil sample brought about a reduction in extractable Zn at the level below the intervention limits declared in Junta de Andalucía (21) for Industrial activities, although other trace metals (Pb, Cu, Co, As and Cd) concentrations were still above the intervention limits for both Agricultural (for a soil with pH <7) and Industrial activities.

## 4. Conclusions and Recommendations

- The characterization of soil in terms of pH, total content of trace metals and water-extractable metals is a crucial step prior to taking decisions regarding soil remediation. Moreover, Aljaraque soil presented a very low pH and a concentration for most trace elements above the intervention limits of the Junta de Andalucía. In addition, the concentration of most trace elements in the soil-water extract was above the intervention limits set by both the EU Directive and the Germany Standards (DIN) based on $NH_4NO_3$ extractable trace element that classifies the soil as non-hazardous material. This confirmed that Aljaraque soil was highly contaminated with trace metals and therefore remediation measures are required.
- The study of the sorption-desorption properties of the four candidates in the soil solution of Aljaraque soil together with the variation of pH in the contact

solution, showed that fly ashes and zeolitic material, with basic pH, presented the highest sorption capacity and the lowest sorption reversibility. Materials with neutral pH, presented an intermediate behavior. Therefore, the addition of fly ashes and zeolitic materials in Aljaraque soil is the best option for the *in situ* remediation.

- This study recommends that candidate materials should be assessed at laboratory scale in terms of sorption capacity and changes of pH before their use at field. Only those materials that can presumably decrease metal mobility, by an increase of either the pH or the specific sorption should be used. Other aspects, such as availability and cost, should be also considered to make the remediation process worthwhile and effective.

**Acknowledgements**

The financial assistance from EU to carry out this research is highly acknowledged.

**Table 4:** Main characteristics of the candidate materials

| **Sample** | **pH** | **$C_{org}$** | **$CaCO_3$** | **$^a$CEC** | **FE** | **Mn** | **Ca** | **Mg** | **Al** | **Cd** | **Zn** | **Cu** | **Pb** | **As** | **Ni** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (%) | (%) | ($cmol_c$/kg) | (mg/kg) | | | | | | | | | | |
| Gypsum | 7.6 | 0.02 | <3 | 0.50 | 53506 | 2240 | 144880 | 3288 | 4259 | <LOQ | 395 | 11 | <LOQ | <LOQ | 4 |
| Sugar Foam | 8.6 | 3 | 89 | 6.6 | 1108 | 107 | 289287 | 7369 | 821 | <LOQ | 30 | 23 | 7 | <LOQ | 1 |
| Zeolitic material | 11.3 | na | na | 270 | 36779 | 463 | 19219 | 4728 | 103370 | <LOQ | 108 | 72 | 46 | 37 | 53 |
| Fly ashes | 11.7 | na | na | na | 42606 | 632 | 38397 | 5614 | 130830 | <LOQ | 64 | 64 | 38 | 9 | 72 |

na =not analysed

[a]CEC, theoretical cation exchange capacity value, mathematically deduced from clay molecular formula.

LOQ = limit of quantification

**Table 5:** Solid-liquid distribution coefficients of trace metals in materials ($K_d$). Mean $K_d$ (L/kg) ±MU

| | | **Trace metals sorption: Equilibrium coefficient $K_d$ (L/kg)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **As** | **Cd** | **Co** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** |
| **Materials** | **Extract pH** | | | | | | | | |
| Sugar Foam | 6.9 | -$^a$ | -$^a$ | 76±5 | 2371±17 | 587±48 | 85±3 | -$^a$ | 85±7 |
| Gypsum | 6.2 | -$^a$ | 5.4±0.1 | 1.0±0.1 | 1044±292 | 251±34 | 1.0±0.1 | -$^a$ | 5±2 |
| Zeolitic material | 9.5 | -$^a$ | 103±16 | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ |
| Fly ashes | 10.4 | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ | -$^a$ |

-$^a$ = extremely high values of $K_d$, Values could not be calculated since metal concentration in the solution after equilibrium was below limit of quantification (LOQ) for $\alpha = 0.05$

**Table 6:** Sorption reversibility coefficients of trace metals in the materials ($K_{d,\ des}$). Mean $K_{d,\ des}$ (L/kg) ±MU

| | **Trace metals desorption distribution coefficient $K_{d,\ des}$ (L/kg)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **As** | **Cd** | **Co** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** |
| **Materials** | | | | | | | | |
| Sugar Foam | -[a] | -[a] | 703±69 | 216±46 | 1509±11 | 241±29 | -[a] | -[a] |
| Gypsum | -[a] | 176±8 | -[a] | 297±7 | -[a] | -[a] | -[a] | 345±14 |
| Zeolitic material | -[a] | 18.9±0.4 | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] |
| Fly ashes | 376±8 | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] |

-[a] = $K_{d,\ des}$ values were extremely high and could not be calculated since metal concentration in the solution after equilibrium was below limit of quantification (LOQ) for $\alpha = 0.05$

**Table 7:** Desorption Yield ($Y_{des,}$ %) ±MU

| | **Heavy metals desorption yield (%)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **As** | **Cd** | **Co** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** |
| **Materials** | | | | | | | | |
| Sugar Foam | 0.33±0.04 | $-^{b}$ | 1.4±0.1 | 4.5±0.9 | 0.7±0.1 | 4.0±0.5 | $-^{b}$ | 0.11±0.03 |
| Gypsum | 0.04± 0.01 | 5.4± 0.3 | $-^{b}$ | 4.04±0.05 | 0.11±0.03 | $-^{b}$ | 0.1± 0.1 | 3±1 |
| Zeolitic material | $-^{b}$ | 9.6± 0.6 | 0.03±0.01 | $-^{b}$ | 0.1 | 0.11±0.04 | 0.08± 0.01 | 0.1±0.2 |
| Fly ashes | 0.26± 0.01 | 1.1± 1.2 | 0.03± 0.04 | $-^{b}$ | $-^{b}$ | $-^{b}$ | $-^{b}$ | 0.1±0.1 |

$-^{b}$ = $Y_{des}$, % values were extremely low and could not be calculated as metal concentration in the solution after equilibrium was below limit of quantification (LOQ) for α =0.05

**Table 8:** Concentration of heavy metals extractable in Aqua Regia with respect to intervention limits; Mean value ± MU (mg/kg) for α =0.05

| | **Soil** | **Soil+Zeolitic Materials** | **Soil+ Fly ashes** | **Soil+ Sugar foam** | **Soil+ Gypsum** | **Heavy metals intervention limits** | |
|---|---|---|---|---|---|---|---|
| | Addition of materials 10% dose | | | | | **Agriculture (pH <7)** | **Industrial** |
| Cd | 42±3 | 32.4±0.4 | 33.1±1.4 | 31.8±0.6 | 31.9±0.6 | 7 | 30 |
| As | 1112±30 | 940±18 | 974±39 | 919±5 | 791±15 | 50 | 300 |
| Sb | 425±17 | 367±14 | 378±9 | 390±9 | 436±9 | 15* | - |
| Co | 146±7 | 116±4 | 115±4 | 113±2 | 127±5 | 100 | 300 |
| Cu | 1496±37 | 1176±48 | 1289±73 | 1222±82 | 1196±227 | 300 | 1000 |
| Pb | 11373±446 | 8953±322 | 8514 77 | 8734± 935 | 11257±769 | 350 | 2000 |
| Zn | 3145±4 | 2543±135 | 2673±160 | 2556±101 | 2288±128 | 600 | 3000 |

* Limits specified in the M.H.S.P.E. (Ministry of Housing, Spatial Planning and Environment), Germany.

## References

1. Ferber, U and Grimski, D. (2002). Brown fields and redevelopment of urban areas. Report from the contaminated Land Rehabilitation. Network for Environmental Technologies.
2. Wong, S.C; Li, X D; Zhang, G; Qi, S.H; Min, Y.S . (2002). Heavy metals in agricultural soils of the Pearl River Delta south China. Environmntal Pollution, 119: 33-44.
3. Vega, F A; Covelo, E.F; Andrade, M.I; Marcer, P. (2004). Relationships between heavy metals content and soil properties in mine soils, 524: 141-150.
4. Luo, X-S; Zhuo, D-M; Liu, X-H; Wang, Y-J (2006). Solid-solution partitioning and specification of heavy metals in the contaminated agricultural soils arround a copper mine in eastern Nanjing City, China. Journal of Hazadous Materials,131: 19-27.
5. Alloway, B. J. (1995). Heavy Metals in Soils. Chapman & Hall. Blackie, London.
6. Iskandar, K.I and Selim, H.M. (1999). Fate and transport of Heavy metals in the vadose zone. Lewis Publishers. Washington D.C .
7. Cappuyns, V and Swennen, R. (2008). The application of pHstat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and wastema terials. Journal of Hazardous Materials, 158:185-195.
8. Shi, W; Shao, H; Li, H; Shao, M; Du, S. (2009). Progress in the remediation of hazardous heavy metal - polluted soils by natural zeolite - A review. Journal of Hazadous Materials, 170: 1-6.
9. Janoš, P; Vávrová, J; Herzogová, L; Pilařová, V. (2010). Effect of inorganic and organic amendiments of the mobility (leachability of heavy metals in contaminated soil: A sequential extraction study. Geoderma, 159: 335-341.
10. Hamby, D.M. (1996). Site remediation techniques supporting environmental restoration activities-a review. The Sience of the Total Environment, 191: 203-224.
11. Garrido, F; Illera, V; Vizcayno, C; Garcia-Gonzalez, M.T. (2003). Evaluation of industrial by-products as soil acidity amendments:chemical and mineralogical implications. Journal of Soil Science, 20:397-408.

12. Rigol, A .P; González-Núñez, R; Santos, M. J; Vidal, M. (2010). Comparison of pHstat leaching tests to estimate metal availability in contaminated samples. Poster presentation. University of Barcelona, Spain.
13. Ali, I and Aboul-Enein, H. (2006). Instrumental Methods in Metal Ion Speciation. CRC Taylor and Francis, New York.
14. ISO 11466. (1995). Soil quality-Extraction of Trace Elements Soluble in Aqua Regia. Internation Organization for Standardization. Geneva, Switzerland.
15. Jones, J.B jr. (2001). Laboratory guide for conducting soil tests and plant analysis. CRC Press, Washington, D.C .
16. Rigol, A; Mateu, J; González-Núñez, R; Rauret, G; Vidal, M (2009) . pHstat vs.single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples, 632: 69-79.
17. Garrido, F, Illera, V and Garcia-Gonzalez, M. T. (2005). Effect of the addition of gypsum-and lime-rich industrial by-products on Cd, Cu and Pb availlability and leachability in metal-spiked acid soils. Applied Geochemistry, 20: 397-408.
18. Rigol, A; Mateu, J; González-Núñez, R; Rauret, G; Vidal, M. (2009). pHstat vs.single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. Analytical Chimica Acta, 632:69-79.
19. prCEN/TS 14997. (2007). Characterization of waste. Leaching behaviour tests. Influence of pH on leaching with continuous pH control. AENOR, Spain.
20. Sims, J.T. (1996). Lime requirement, in D.L. Sparks, Ed., Methods of Soil Analysis, Part 3. Madison, W.I : Chemical Methods, SSSA Book Series Number 5, Soil Science Society of America, pp. 491-515.
21. Junta de Andalucía (Consejeríamde medio ambiente). (1999). Los criterios y estándares para declarar un suelo contaminado en Andalucía y la metodología y técnicas de toma de muestray y análisis para su investigación. pp. 110-160.
22. Conesa, H.M; Wieser, M; Gasser, M; Hockmann, K; Evangelou, M.W.H; Studer, B; Schulin, R (2010). Effect of three amendments on extractability and fractionation of Pb, Cu, Ni and Sb in two shooting range soils. Journal of Hazardous Materials, 181: 845-850.
23. Prüeß, A. (1995). Action values for mobile ($NH_4NO_3$ - extractable) trace elements in soils based on the Germany National standard DIN 19730. 5b, D-76185.
24. European Directive. (2003). 2003/33/CE Criteria and procedures for acceptance of waste at landfills. European Union.

25. Egila, J and Okorie, E. (2002). Influence of pH on the Adsorption of Trace Metals on Ecological and agricultural adsorbents. Journal of Environmental Science, 27(II): 95 -98.

26. Erdem, E; Karapinar, N; Donat, R. (2004). Removal of Heavy Metal cations by Natural Zeolites, Journal of Colloids and interface science, 280:309-314