

HEAVY METAL DESORPTION STUDIES ON THE ARTIFICIALLY CONTAMINATED AL-QATIF SOIL

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ABSTRACT: In this study, the relevance of mineralogy on the desorption capacities of Cu^{+2} and Pb^{+2} from artificially contaminated Al-Qatif soil has been investigated. The desorption capacities of both Cu^{+2} and Pb^{+2} using ethylenediaminetetraacetate (EDTA) as decontaminating solution are determined. The effect of decontaminating solution dosage and liquid to solid ratio on desorption capacities are examined. Under identical conditions, the removal efficiency of Pb^{+2} ions are found to be higher than Cu^{+2} ions. This has been attributed mainly due to the differences in surface charges of specific retention sites which hold these metal ions. Further, the heavy metal ion solubility and surface properties of respective clay minerals decide the desorption rate in soil systems as the pore fluid pH reaches the heavy metal solubility range or point of zero charge of the clay minerals. These studies provide valuable insight with regards to their applicability as potential barrier materials for containing industrial leachates.

Keywords: Copper, Decontaminant, Desorption, EDTA, Lead, Mineralogy, Surface area.

1. INTRODUCTION

Soil is a basic building block for the most terrestrial ecosystems and a complex heterogeneous medium consisting of both solid and fluid phases. The ability of these soils in absorbing and desorbing metal ions from the aqueous phase assumes importance since it governs both the environmental and agricultural issues [1]. The clay fraction predominantly affects the metal ion concentrations in environmental systems owing to their ability in adsorbing these ions and further in releasing the same in part or whole when subjected to prevailing atmospheric conditions [2].

For ex situ systems, the contaminants are generally adsorbed on to the fine grained soil fraction and extraction of heavy metal ion complexes has been confirmed by the use of various chelating agents like citric acid, diethylenetriaminepentaacetic acid (DTPA), sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA) and strong acid such as hydrochloric acid (HCl), nitric acid (HNO_3) have been used to desorb metals from soils [3-6].

But, most of these research studies did not emphasize on the effect of clay mineralogy or the effect of H^+ ions on the desorption response. Based on the solubility of heavy metals and the surface properties of clay minerals, desorption of heavy metal ions in soil systems occurs as the pH of the pore fluid in the soil reaches the solubility range of the heavy metal or is lowered to the point of zero charge of the clay minerals [6]. The amount of H^+ ions available in the pore fluid and the nature of clay minerals are considered important factors in desorption processes and need to be evaluated.

Two common types of heavy metal contaminants, copper and lead are considered in the study. Pollution of soil and water by copper may arise from copper mining and smelting and other industrial uses. Also, acute concentration of copper in solutions leads to Cirrhosis of the liver in children. On the other hand, lead is a non-essential element and it is not as bioavailable as other metals. It is a poisonous metal and its intake can damage nervous connections (especially in young children) causing blood and brain disorders. Long-term exposure to lead or its salts can cause nephropathy, and colic-like abdominal pains. Hence, in the present study, soil washing methodology has been employed to reduce the toxicity of Cu^{+2} and Pb^{+2} , by using a chelant in the form of EDTA, since chelating extraction of heavy metals has been proposed as an effective remediation technique for contaminated soils. The effect of liquid-solid ratio in enhancing the extractability has also been studied. The studies will enable to estimate the fraction of metal ion available for achieving selective recovery of Cu^{+2} and Pb^{+2} individually from the contaminated soil systems.

2. MATERIALS

The tests were conducted on samples collected from Al-Qatif, a coastal oasis region located on the western shore of the Persian Gulf in the Eastern Province of Saudi Arabia ($26^\circ 56' 0''$ N, $50^\circ 1' 0''$ E). The sampling was carried out at a depth of 3.0 m. The physical properties and chemical composition are reported in Tables 1 and 2 respectively.

3. METHODOLOGY

Particle size analysis based on laser diffraction as per ASTM B822 - 02 [7] was carried out on the selected soil sample. Laser diffraction relies on the fact that particles passing through a laser beam will scatter light at an angle that is directly related to their size. As particle size decreases, the observed scattering angle increases logarithmically. Larger particles therefore scatter light at narrow angles with high intensity whereas smaller particles scatter light at wider angles but with low intensity. From Figure 1, it can be seen that major portion of the selected soil has a gradation ranging from 0.1 to 10 μm . This finer fraction is critical to the study as it affects desorption of Cu^{+2} and Pb^{+2} quite considerably.

The predominant minerals were determined by carrying out XRD using Bruker D8 Advance system. Samples were scanned from 2° to 60° (2θ) using 2.2kW Cu anode long fine focus ceramic X-ray tube at a scanning rate of 1 degree per minute. XRD patterns of samples were then compared with standard patterns [8]. Fig. 2 depicts comprehensive X Ray diffraction analysis. In addition to Quartz, Dolomite, Illite, Muscovite, and Palygorskite, the presence of Montmorillonite (a smectite group mineral known to induce significant swelling upon interaction with water) is noteworthy.

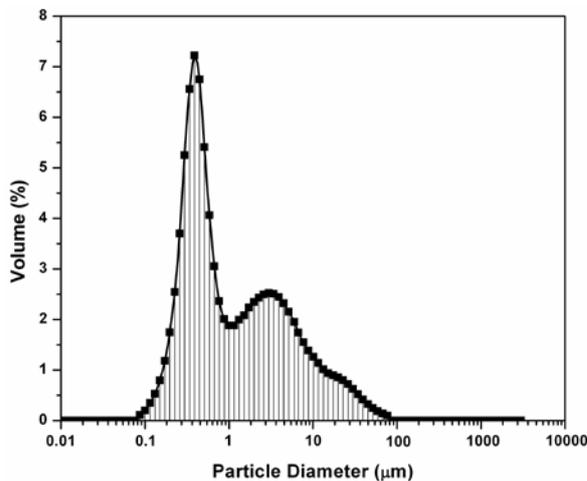


Fig.1 Particle Size Distribution Curve by Laser Diffraction Analysis

3.1 Contamination Procedure

About 0.5 kg of oven dried soil was thoroughly mixed with deionized double distilled water in a 1:1 ratio, containing dissolved nitrate salts of copper nitrate, $\text{Cu}(\text{NO}_3)_2$ and lead nitrate, $\text{Pb}(\text{NO}_3)_2$ separately. The entire slurry was allowed to age at controlled temperature ($23 \pm 0.5^\circ\text{C}$) for a period of 2 months. The slurry was mixed frequently during the

course of aging period. At the end of aging period, the mixture was oven dried and acid digestion technique using US EPA Method 3050B [9] was employed on the respective samples below the boiling point to determine the Cu^{+2} and Pb^{+2} concentrations. Table 3 gives the metal concentrations of the selected metal ions before and after contamination.

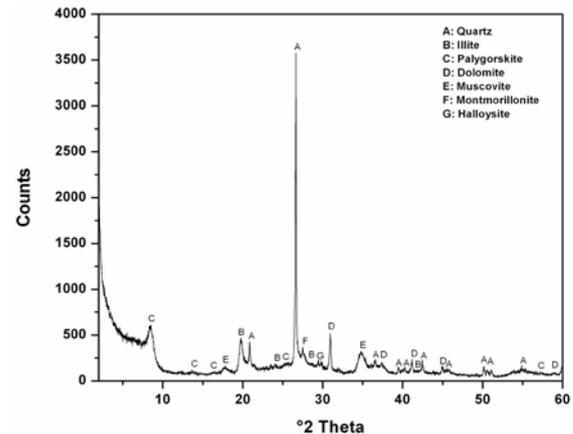


Fig. 2 X - Ray Diffraction Analysis

Table 1 Physical properties of the soil

Physical Property	Al - Qatif
Liquid Limit (%)	137
Plastic Limit (%)	60
Shrinkage Limit (%)	22
Plasticity Index (%)	77
Linear Shrinkage (%)	77
% Finer than 200 μm	99.1
USCS Classification	CH
Specific Gravity	2.71

Note: 'USCS' refers to unified soil classification System; 'CH' refers to clay with high plasticity

Table 2 Chemical composition of the soil

Chemical Composition	Al - Qatif (%)
K^+	1.8
K_2O	2.2
Al	3.3
Al_2O_3	6.3
Si	8.1
SiO_2	17.3
Ca^{+2}	0.7
CaO	0.9
CEC (cmol/kg)	137

3.2 Desorption Batch Tests

Batch desorption experiments were carried out by mechanically shaking series of bottles containing the artificially contaminated soil samples at different initial conditions. EDTA was used as a decontamination solution. The tests were

carried out by placing 1g of soil in 100 ml teflon bottles followed by addition of varying volumes (10 mL, 20 mL, 40 mL and 50 mL) of the washing solution (HNO₃). In order to determine the effect of concentration of decontaminating solution on the extractability of respective metal ion, the concentration of EDTA was varied as 0.1 M, 0.2M and 0.5M for each dilution ratio case. The samples were placed on a shaker table operated at 175 rpm at room temperature.

Table 3 Concentration of the metal ions

<i>Background concentration of the original uncontaminated soil</i>	
Cu ⁺²	13±0.5 mg/kg
Pb ⁺²	15±0.5 mg/kg
<i>Metal concentration of the contaminated soil</i>	
Cu ⁺²	833±2 mg/kg
Pb ⁺²	758±2 mg/kg

A 2-h reaction time was deemed sufficient based upon batch rate desorption tests conducted over a 48-h period. After mixing, the samples were allowed to settle for about 15 min and then filtered through a 0.45-µm membrane filter. The accuracy was established by preparing replicate of three aliquots for each test. In the present study, it has been assumed that the metal concentration of the filtrate represents that released from the contaminated soil. Removal efficiencies were determined by dividing the heavy metal release quantities by the initial quantity in the soil. The residual concentration of the heavy metal ions (Cu⁺² and Pb⁺²) in the filtered solution was determined using atomic absorption spectrophotometry (AAS). AAS calibrations were prepared from standard stock solutions.

4. RESULTS AND DISCUSSIONS

Generally, when metal-containing compounds are dissolved in water, the metallic component exists as mobile ions in solution phase. But when these metallic ions are complexed by inorganic or organic ligands, they will be present in aqueous solution only at very low concentrations in the pH range of natural surface and subsurface waters. When the concentrations of these metals exceed the solubility of their corresponding hydroxide or carbonate phase at a given pH value, metal precipitates will intermingle and become an integral part of the soil matrix which is of prime concern [10]. The removal efficiencies of Cu⁺² and Pb⁺² using deionized double distilled water and EDTA solution from artificially contaminated soil are summarized in Table 4.

Table 4 Effect of chelant (EDTA) concentration and liquid to solid (L/S) ratio on the removal efficiencies of Cu⁺² and Pb⁺²

Washing Solution	Removal efficiency (%)			
	DI Water	0.1M	0.2M	0.5M
<i>L/S Ratio 1:10</i>				
Cu ⁺²	19.1±0.5	55.3±0.5	68.7±0.5	81.2±0.5
Pb ⁺²	16.8±0.5	48.7±0.8	71.2±1.1	89±1.3
<i>L/S Ratio 1:20</i>				
Cu ⁺²	17.3±0.5	61.2±0.5	78.6±0.8	84.5±0.5
Pb ⁺²	15.7±0.5	58.6±0.7	81.3±0.5	90.6±1.2
<i>L/S Ratio 1:40</i>				
Cu ⁺²	15.6±1.7	76.5±1.6	85.3±1.3	91.1±0.9
Pb ⁺²	18.6±0.5	69.7±0.5	89.1±0.5	93.7±0.5
<i>L/S Ratio 1:50</i>				
Cu ⁺²	18.2±0.5	80.1±0.7	86.7±0.7	94.3±1.1
Pb ⁺²	14.8±0.5	77.6±0.7	91.1±0.5	96.2±0.7

The implication of using DI water is to arrive at the fraction of the metal that is weakly bound to the soil particles and is readily available for mobilization. It can be seen from Table 3 that, the fraction of Cu⁺² and Pb⁺² metal ions are strongly bound and is virtually independent of the soil to DI water ratio. Hence, the removal efficiencies are quite low and it is evident that, the remaining fractions of the metals are considered to be strongly bound and immobilized within the soil matrix under natural-water conditions. Also, with DI water, the resulting removal efficiency is due to rapid dissolution of weakly bound Cu⁺² and Pb⁺² ions retained at easily co-ordinated sites on the outer surfaces of clay matrix. Similar observations have been made by Abumaizar and Smith [11] when DI water was used to decontaminate Cd, Pb, Zn and Cr metal ions. Generally, in contaminated soils the total amount of metal ion concentration in the aqueous and solid phases is at levels much higher than those found in the solution phase. The solubility values of the metal ions are typically very small and it will not yield satisfactory removal efficiencies. Further, the respective metal ion solubility values are heavily dependent on predominant mineral phases that which are affected by pH and available ambient ligands.

The effect of 0.1M EDTA on the extractability of metal ions (Table 3) indicates that, there is a significant improvement in both Cu⁺² and Pb⁺² removal over flushing with DI water. The best removal efficiency for both the metal ions was obtained at a 1:50 soil to liquid ratio. Since, copper may be present in solution as either Cu²⁺ or Cu⁺, although the more oxidized Cu²⁺ predominates due to the redox reaction in aerated water. Both copper and lead ions are prone to complexation, especially with hydroxide and carbonate ligands. The ideal

mineral phases for metal complexation include those of oxide, hydroxide, carbonate and hydroxy carbonate, such as $MO(S)$, $M(OH)_2(S)$, $MCO_3(S)$ and $M_x(OH)_y(CO_3)_z$ [12].

The presence of montmorillonite in Al-Qatif clay has been confirmed by Fig. 2 and the uptake of Cu^{+2} and Pb^{+2} metal ions is considered to occur primarily by ion exchange process on to this mineral site. The calcium sites in Al-Qatif clay (Table 2) have the ability to successfully displace a high proportion of the metal ions retained on the clay sites at higher molar concentrations of EDTA, thereby resulting in higher removal efficiencies for both the metal ions. But, at lower molar concentrations of EDTA, the calcium ions have limited ability to dissolve precipitated hydrous oxides of Cu^{+2} and Pb^{+2} and hence relatively smaller amounts are desorbed in the extracting solution. Also, with increase in EDTA concentration, competition from hydronium ions for the available oxide surfaces starts diminishing which also results in the increased removal capacities. Hence, relatively higher amounts of Cu^{+2} and Pb^{+2} are flushed out into the washing liquid.

The difference in removal efficiencies between the metal ions may be due to the differences in surface charges of specific retention sites like dolomite, illite, muscovite, and palygorskite (as seen from Fig. 2) which hold these metal ions and also due to the particle size distribution (the selected soil has a gradation ranging from 0.1 to 10 μm as noted from Fig.1). The surface properties of carbonate and Fe-Mn oxide sites in Al-Qatif clay dictate the release of Cu^{+2} and Pb^{+2} as the pore fluid pH reaches the their solubility range or point of zero charge of the oxide sites, particularly at higher EDTA concentrations of 0.2M and 0.5M. From the batch chelant desorption tests, EDTA was extremely effective in decontaminating Cu^{+2} and Pb^{+2} from the artificially contaminated Al-Qatif soil. The removal efficiencies achieved were satisfactory and contaminated industrial repositories can be successfully treated with this technique.

4.1 Practical Importance of the Study

Heavy metal contaminated site is among the most common problem constraining cleanups and associated costs at industrial waste repositories in the Kingdom of Saudi Arabia. A typical soil washing technique involves, vigorous washing of the soil with water containing little amount of surfactants followed by solid/liquid separation for collecting the clay/silt fraction. This clay/silt fraction usually is treated by immobilization techniques and disposed off in a landfill while the bulk of the decontaminated soil is returned back to the site. But, in soils where heavy metals are present

in higher concentrations soil washing alone would not suffice and chelants are required to reduce the toxicity to target levels. The current study addresses these issues and gives valuable insight in selecting appropriate extractant (EDTA, in this case) for Al-Qatif soil in removing Cu^{+2} and Pb^{+2} metal ions. Depending on the target clean up level for respective metal ion, the feasibility of soil washing with EDTA may be readily determined using the data in Table 4 as a supporting guide. The employed technique is relatively cost competitive and extremely effective compared to existing methodologies.

5. CONCLUSIONS

The decontamination of metal contaminated soils is primarily controlled by the dissolution of the metal-mineral bond followed by the dispersion of the target metal ion in the selected extractant or into an easily extractable or residual form.

The results of batch washing tests indicate that Cu^{+2} and Pb^{+2} metal ions can be extracted from artificially contaminated soils independently using EDTA as a chelating agent. The use of DI water as a washing solution resulted in a lesser removal efficiency of $\approx 17 - 20\%$, for Cu^{+2} and Pb^{+2} metal ions, which confirms that these metal ions are strongly bound and are not readily mobilized in aqueous solutions.

The effect of 0.1M EDTA on the extractability of metal ions indicates that, there is a significant improvement in both Cu^{+2} and Pb^{+2} removal over flushing with DI water. There was a threefold increase in removal efficiency with 0.1M EDTA compared to DI water alone. With increase in concentration of EDTA solution, relatively higher removal efficiencies of $\approx 90 - 95\%$ were achieved. The mobility of Pb^{+2} ions was slightly higher than Cu^{+2} ions. The increase in liquid/solid ratio also aids in better removal efficiencies.

6. ACKNOWLEDGEMENTS

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