©gopalax -International Journal of Technology And Engineering System(IJTES):
Jan –March 2011- Vol.2.No.3.

Removal of Heavy Metal by Screening Followed by Soil Washing from Contaminated Soil

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***Abstract* - Soil contamination by heavy metals is increasing day by day. Now a day's metal contamination is a persistent problem at many contaminated sites all over the world. Cadmium, chromium, copper, lead, mercury, nickel and zinc are considered the most hazardous heavy metals found in most of the contaminated sites. Many techniques have been studied for the decontamination of soils, which includes physico-chemical as well as biological methods. Soil washing a physico-chemical method is one such alternative that has shown very high efficiency for heavy metal removal from soils and sediments. In this paper an attempt has made to evaluate soil washing technology for heavy metal removal i.e., Pb and Cr from the contaminated soil by optimizing the various parameters like reaction time, solution pH, solid/ liquid ratio and EDTA concentration. The effect of soil washing on the different particle size is also determined.**

***Index Terms* - Contamination, Heavy metals, Soil washing, EDTA, Particle size**

1. INTRODUCTION

Metals contamination is a persistent problem at many contaminated sites. Major soil contaminants are volatile organics, hydrophilic and hydrophobic organics, heavy metals and radioactive materials [1]. The most common heavy metals found in the contaminated sites are Cadmium, chromium, copper, lead, mercury, nickel and zinc. These heavy metals are one of the main sources of environmental pollution and affect the human health, life of animals. The main sources of heavy metals are industrial discharge, energy production, chemicals used in agricultural production, construction, vehicular exhaust and particulate emission, coal and fossil fuel combustion. Metals are relatively immobile in subsurface systems due to precipitation or adsorption reactions. For this reason, remediation activities at metals-contaminated sites mainly focused on the solid-phase sources of metals, i.e., contaminated soils, sludges, wastes, or debris [2]. The remediation technologies available for the decontamination of soils from heavy metals are mainly divided into two groups: immobilization i.e. in situ chemical fixation and separation i.e. soil washing [3]. Soil washing is a relatively simple and useful ex situ remediation technology, in which washing water added and heavy metal can be transferred from the dredged sediment to the wash solution [4]. To increase the performance of soil washing various additives can be added, such as acid washing (e.g. H_2SO_4 and HNO_3), chelating agents (e.g. EDTA, EDDS and DTPA) or surfactants (e.g. rhamnolipid). Acid washing leads to decreased soil productivity and affect the chemical and physical structures of soils due to mineral dissolution. Chelating agents such as EDTA, NTA, DTPA form strong metal-ligand complexes and highly effective in remediating heavy metals from the contaminated soils [5]. Soil washing is useful for treatment of soils contaminated with heavy metals, hydrocarbons but it is less effective for voc and pesticides [6].

2. MATERIALS AND METHODS

A. Soil

The soil samples were collected from VIT University campus. The collected samples were air dried at room temperature. The soils sample were sieved by using 2.36mm sieve to remove stones and large particles, and then thoroughly mixed with hand to ensure uniformity. The sample stored in a plastic bag at room temperature for further experiments.

B. Soil Contamination Procedure

About 5 Kg of sieved air dried soil was thoroughly mixed with deionized (DI) water containing dissolved salts of lead nitrate $Pb(NO_3)_2$, potassium dichromate $K_2Cr_2O_7$. The conc. of heavy metals is around 5000ppm. The soil and heavy metals were thoroughly mixed with the help of hand for 7 days. After that the contaminated soil under goes particle size distribution by sieving of varying sieve size i.e. from 1700 microns – 53 microns. To determine the heavy metal content of different particle size soil samples were digested using EPA 3050B method.

The physical and chemical characteristics of the soil are shown in Table 1. Soil pH was determined by using 1:5 soils to water ratio using pH meter. Total organic matter was determined by Walkley and Black rapid titration method. The particle size distribution was performed by sieving method. Background conc. of heavy metals was determined by acid digestion ($HCl+HNO_3+H_2O_2$). All heavy metal analyses were performed by using Varian AA240 flame atomic adsorption spectrometer.

Table 1 Physicochemical characteristics of soil sample

Soil components	Content
Soil pH	8.48
Total organic carbon	1.50%
Medium sand (<2mm)	54.25%
Fine sand (<425µm)	41.1%
Slit and clay (<75µm)	4.3%
Metal ($mgKg^{-1}$)	Content
Pb	26
Cr	61

C. Soil Washing Procedure

Batch extractions of heavy metal contaminants using a common extractant concentration of 0.01M were conducted in 250 mL conical flask. The flask contained 2 g of soil and 10 mL of EDTA was agitated using an orbital shaker at a speed of 150 rpm at room temperature (28–33 ˚C) for 6 hrs. The suspensions were centrifuged at 3000 rpm for 10-15 min and the supernatants were then filtered through normal filter paper for heavy metal analysis. The concentrations of metals were measured by flame atomic absorption spectrometry (AAS). The washing solution was prepared from analytical grade reagents. All tests were performed in triplicates and the results were presented as average of the triplicate extracts.

In the experiment different operating variables for removal of heavy metals from soil using EDTA, including the different EDTA concentration, liquid to solid ratio, solution pH, RPM, was studied. EDTA disodium salt is chosen for the experiments. In the conc. experiment, four different concentrations (0.005, 0.01, 0.05, and 0.1) of Na_2EDTA were chosen. The liquid/solid ratio investigations were conducted by 4, 5, 7, 10 and 15 ml of 0.01M Na_2EDTA, giving liquid/solid ratios of 4, 5, 7, 10, and 15 respectively. The pH from 2-10 was adjusted with diluted HNO_3 and NaOH. In the RPM experiment, four different (50,100,150 and 200) were chosen. The kinetic study was performed in the tubes containing 2 gm of soil and 10 ml of DI water and with Na_2EDTA for 0, 0.5, 1, 2, 4, 6, 8, 12, 18, 24, 30, 36, 48 h.

3. RESULTS AND DISCUSSIONS

A. Particle Size vs. Contamination

As the particle size decreases the heavy metal concentration in the particle increases shown (in fig 1). The main reason for this is that the small particle size has larger surface area and it may be a clay soils. Soils contain mineral and humic constituents and in the smaller fraction these are found in more concentration. These humic and mineral substances carry hydroxyl and carboxylic surface functional groups. The acid-base characteristics of these functional groups contribute to the formation of a surface charge that plays an important role in metal retention. Hence metal conc. increased in smaller fraction [7].

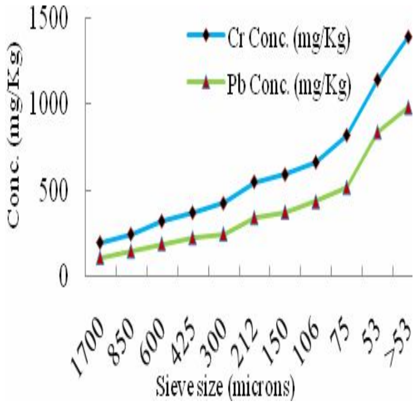

Figure 1. Particle size vs. Contamination Concentration

B. Kinetics of Metal Extraction

Extraction time plays a very important role in soil washing. In order to comprehend the washing process and determine the optimum contact time for contaminants removal, a kinetic study was performed by soil washing with DI water and 0.01M Na_2EDTA. The kinetic study indicates that the DI water cannot remove Pb from the soil. The main reason for the least extraction of lead is due to its strong association with residual soil fraction. Pb mainly forms the inner sphere surface complexation with the soil [8]. The removal of Cr with DI water vary from 16.18% - 33.49% with increase in time. The kinetic experiment indicated that the EDTA induced a two step desorption process, in which a rapid desorption within first hour was followed by a subsequent gradual release that occurred over the following hours. As the contact time increase with EDTA the metal removal also increased shown (in fig 2). For Pb removal varies from 30.3% - 47.8% and for Cr it varies from 21.3% - 38.4%. From the kinetic study 6 hr was chosen for further experiments. Because the removal of metals is all most constant around 6 hr. The pH of solution increased constantly with mixing time. Because during the mixing time a dynamic reaction occurred between solution and soil.

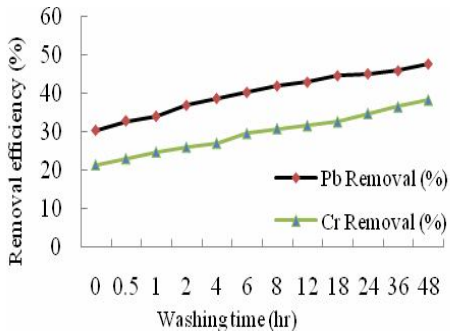

Figure 2. Removal of Pb and Cr with EDTA

C. Effect of EDTA Concentration

Different concentrations of EDTA were used and the extraction results are shown (fig 3). The removal of Pb and Cr increased with increasing EDTA concentration from 0.005 to 0.1M. The removal of Pb vary from 41.99 % - 53.87 %. The Cr removal efficiency vary from 39.21 % - 48.35 % with increase conc. of EDTA. Compare to Pb, Cr removal efficiency is less. Cr is less depended on EDTA concentration. A study by Zhang et al. shows that EDTA complexation is dominant for cationic metal removal. Cr is mainly found in the soil as Cr (VI). Cr (VI) is anionic and bound with other cationic metals like Zn and form $ZnCrO_4$. Due to this they slightly adsorbed to the clay minerals.

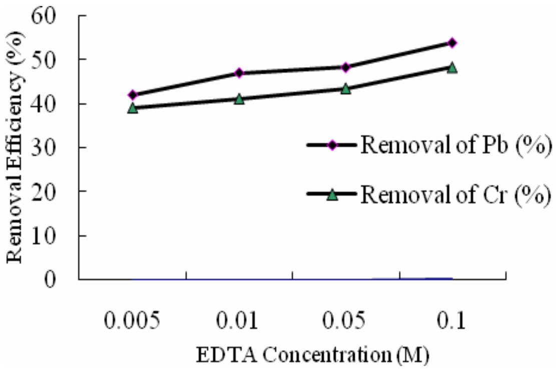

Figure 3. Effect of EDTA concentration on removal of Pb and Cr

D. Effect of pH

Solution pH is another important factor determining the efficiency of soil washing. Because it can influence the soils retention of metals by adsorption. When the pH of 0.01M Na_2EDTA solution is below 3, Na_2EDTA becomes less soluble and precipitates. During the extraction EDTA can form stable and soluble complexes with heavy metals thus greatly improving the solubility and mobility of Na_2EDTA, making the precipitate become soluble and react with heavy metals. The removal efficiency varies from 32.18 to 54.27 % for Pb and 35.35 to 48.09% for Cr shown in (fig 4). In case of Pb pH 4 shows the highest removal efficiency because at low pH dissolution of metal oxide takes place [9]. For Cr highest removal efficiency was at pH 8. In general, a lower solution pH gives higher extraction. In case of Cr, Cr mainly bound to the Zn and form $ZnCrO_4$. This complex formation affects the solubility of salts. Zn is removed by adding base to increase the pH to form the insoluble Zn $(OH)_2$. If excess of base is added Zn will form soluble complexes.

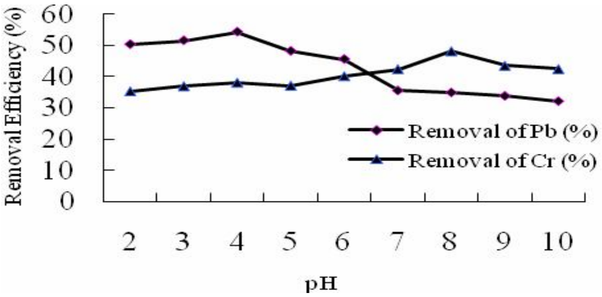

Figure 4. Effect of pH on removal of Pb and Cr

E. Effect of Liquid/Solid Ratio

In order to determine the effect of liquid/solid ratio, a series of extraction were conducted maintaining the concentration of Na2EDTA at 0.01M and increasing the liquid/solid ratio. The results shown in (fig 5). Increasing the liquid/solid ratio had a positive effect on the extraction of heavy metals. The maximum removal efficiency shown at liquid/solid ratio of 5. The removal efficiency vary from 44% - 52. 96% for Pb and 34.49% - 41.05% for Cr with varying S/L ratio. With the same concentration i.e. 0.01M increasing the liquid/solid ratio means Na_2EDTA dose is increased. It seems that when increasing the Na_2EDTA dose, only a small portion was effectively transformed into metal-chelant complexes, while the excess remained in free from or might form complexes with other cations like Ca, Mg, Fe, and Al etc.

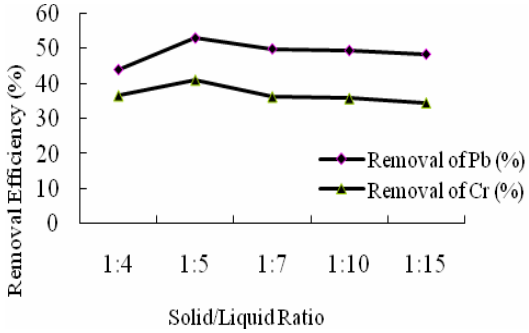

Figure 5. Effect of solid/liquid ratio on removal of Pb and Cr

F. Effect of RPM

RPM is one important factor determining the efficiency of the soil washing. Different RPM 50,100,150 and 200 were used and extraction results shown in (fig 6). As the RPM increases the extraction of heavy metal from soil also increases. For Pb the removal efficiency vary from 49.77% - 62.21%. For Cr efficiency varies from 34.47%- 39.21%. For this experiment EDTA conc. was 0.01M and liquid to solid ratio was 5. The removal efficiency increase with increase up to certain RPM then no further increase was observed when the RPM become higher.

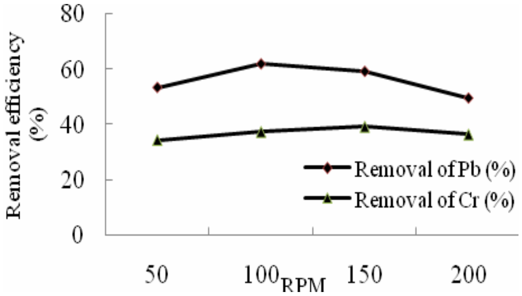

Figure 6. Effect of RPM on removal of Pb and Cr

G. Effect of Soil Washing on Particle Size

The particle size has effect on soil washing. The larger particle size weakly bound with the heavy metal compared to the smaller particle size. Due to weak bond it is easier to remove the metals from the larger particle size. For this experiment soil samples were differentiated into different particle size. Then the different particle size was mixed and effect of soil washing was determined. For Pb removal efficiency varies from 31.59% - 44.57%. For Cr the efficiency is 34.72% - 47.06% shown in (fig 7). For Cr the removal efficiency is more compare to Pb, because in case of Cr the heavy metals are loosely bound. Pb is less extractable in soil due to strong bond with the soil.

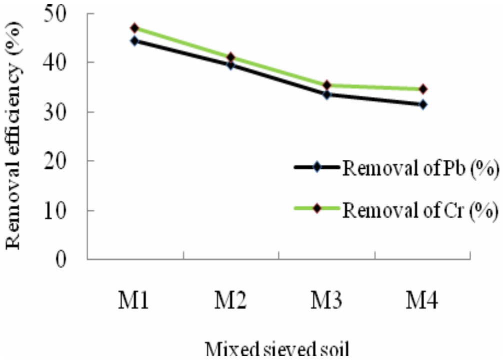

Figure 7. Effect of soil washing on particle size

Where M1= 1700+850 micron sieve size, M2= 600+425+300 micron sieve size, M3= 212+150+106 micron sieve size, M4= 75+53+>53 micron sieve size.

4. CONCLUSION

This work shows that as the concentration of EDTA increases the removal efficiency also increases. Pb shows highest removal at pH 4 and for Cr it is pH 8. For liquid/solid ratio 1:5 shows the maximum removal efficiency for both Pb and Cr. The consecutive extractions using low concentrations were more effective than a single soil extraction with concentrated EDTA. The use of highly concentrated EDTA can increase the extraction efficiency but it adversely affects the soil microorganisms and plants. At RPM 100 Pb shows the maximum extraction but for Cr maximum extraction is at 150 RPM. In case of soil washing the larger particle shows the highest removal efficiency due to weak bond between soil particle and heavy metals.

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