Removal of lead from contaminated soil: Application of soil washing

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Abstract:

In the present study, experiments were conducted to optimize the use of two chelating agents such as EDTA and $CaCl_2$ in removing lead from an artificially contaminated soil. It was proved that at a soil/solution ratio of 2:1 and molar concentration of 0.03, Na_2EDTA could remove 96.8% lead from a soil with initial lead content of 19.3mg/g. This value varied depending upon the pH of the environment and the duration of mixing period. In the case of CaCl2, the soil/solution ratio was of 5:1. Optimum performance was noted at molar concentration of 0.4M and 59.3% removal of lead from contaminated soil was achieved for this chelant. Hence it is shown that for achieving better performance in soil washing great care has to be given in selecting a chelating agent which is suitable for a soil and importance has to be given to control the parameters influencing the removal efficiency.

Keywords:

Soil washing, chelating agent, batch study.

1. Introduction:

During the last decade, contamination of soils by heavy metals has been recognized as an important environmental issue, including in the area of public health. Great efforts have been made to develop technology for the remediation of contaminated soils. Several techniques, such as hydraulic or hydro geological isolation of contaminated sites and the physical immobilization of pollutants (Raghavan et al., 1989; Rulkens et al., 1995; Kedziorek and Bourg, 2000) are available for practical applications. While these methods confine the dispersion of contaminants, they do not remove them. Pollutant extraction is achieved by soil washing, a technique which can be applied in situ or after excavation of the contaminated soil (Figure.1). The extraction process consists in the transfer of contaminants from the solid to the aqueous phase by chemical leaching. Soil washing involves the separation of contaminants from soil solids by solubilizing them in a washing solution. The technology is generally applied as an ex situ method. Soil washing usually employs wash solutions that contain acids, bases, chelating agents, alcohols or other additives.
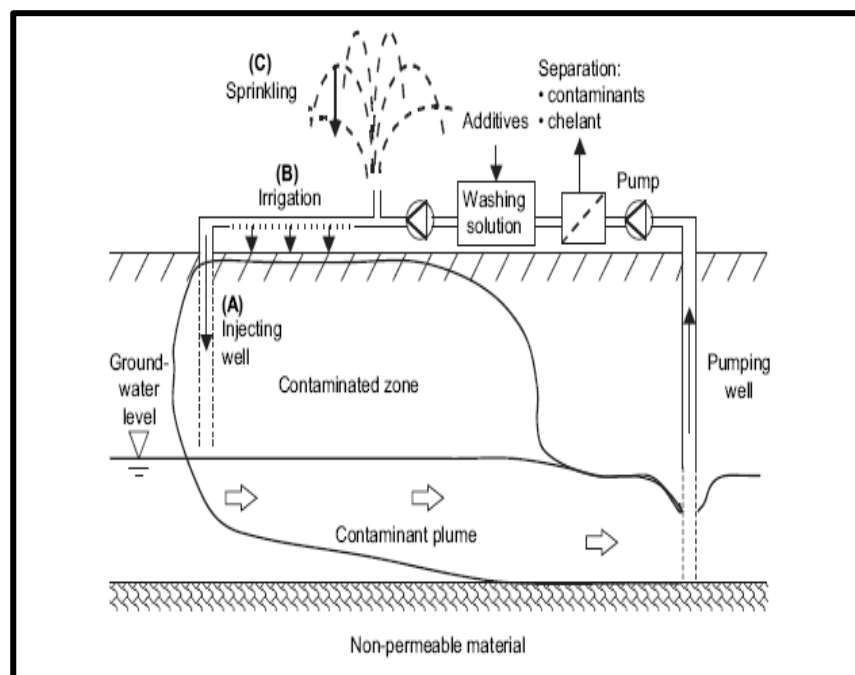

Figure. 1: Flow chart of in situ soil flushing via the injection (A), irrigation (B) and sprinkling (C) of the soil-washing solution

Heavy metals can be extracted from polluted solids by using acid or complexing solutions. Urlings, (1990) demonstrated the feasibility of decontaminating a sandy soil polluted by cadmium (Cd) by sprinkling the soil with a 0.001 M HCl solution with a resulting pH of 3.5 and collecting the Cd aqueous solution with drains placed in the polluted soil.

A good chelant should have certain qualities such as,

- Extraction strength - The chelant should be able to form strong, stable complexes with toxic metals over a wide pH range.

- Extraction selectivity towards target toxic metals.

- The potential for recovering the spent chelant. If the chelant is to be recycled and reused in the process several times, it should have low biodegradability in soil.

- The metal-chelant complexes should have low adsorption affinity towards solid soil surfaces.

- The chelant should have low toxicity and a low potential to harm the environment.

- The chelant should be cost-effective.

Ethylene diamine tetra acetic acid (EDTA) is considered as a powerful chelating agent which can remove heavy metals from soil (Yang and Lin, 1998; Peters, 1999). EDTA has two advantages with respect to other chelates that is its relatively low biodegradability in groundwater systems (Nowack, 1996) and its strong complexing capacity with heavy metals. Most studies dealing with the extraction performance of EDTA or other chelating reagents involve batch experiments (Hong and Pintauro, 1994; Li and Shuman, 1996; Bordas and Bourg, 1998).

Lead, Cadmium and Mercury are the 'big three' among all heavy metals due to the greatest potential hazard to humans and the environment (Ghani et al, 2007). Industries producing batteries, electroplating unit's oil refineries etc are contributing to lead contamination. As a natural consequence of the rapid growth in the use of electronic equipments and gadgets like computers and peripherals, television sets, cell phones, digital cameras etc in India, disposal of e-waste is recognised to become a major environmental problem in the near future. Broken lead-containing glass from televisions and monitors, and soldering on printed circuit boards, if disposed without proper care, can lead to leaching of lead and this in turn will pollute soil and water resources. Landfills, though widely used for waste disposal, are prone to leaking and e-waste disposed of in landfills can leach heavy metals into the soil and more dangerously contaminate the water table.

This paper discusses the application of batch studies for removing lead from artificially contaminated soil using EDTA and $CACl_2$ solution. The influence of parameters such as, pH,

period of mixing and molar concentration of washing solution on removal of lead from artificially contaminated soil is studied.

2. Materials and methods:

2.1. Soil used in the study:

The soil used in the study was collected from NITC campus, Calicut District, Kerala. Representative disturbed samples were taken from pits and brought to the laboratory without any moisture loss. The soil was mixed thoroughly, stored in poly-ethylene bags and kept in containers without any moisture loss. The soil samples so collected were tested for basic index properties as per IS 2720: 1991. The results are presented in table.1. As per IS 1498-1970, the soils are classified as CI (clay with intermediate plasticity).

Table. 1: Index properties of soil

Property	Values Soil A
Grain size distribution	
Gravel size (%)	3
Sand size (%)	19
Silt size (%)	48
Clay size (%)	30
Consistency limits	
Liquid limit (%)	44
Plastic limit (%)	23
Shrinkage limit (%)	9
Plasticity index (%)	21
IS classification of soil	CI

2.2. Artificial contamination:

In this investigation, lead nitrate $(Pb(NO_3)_2)$ salt of analytical reagent grade was used for preparing lead solutions used for artificially contaminating the soil. The soil was contaminated with lead nitrate solution of 2000ppm concentration. Soil samples soaked in the solutions were kept in containers and left undisturbed for adsorption to take place. The contaminated soil sample taken out of the solution after 90 days of soaking was then dried, powdered to pass through 2mm IS sieve and stored in poly-ethylene bags and used for further investigation. The adsorbed amount of lead was observed as 19.3mg/g by testing the concentration of the residual solution used for soaking with the help of an ion meter.

For the soil washing studies the leaching chemicals used were EDTA and $CaCl_2$. 1M concentration of EDTA solution was prepared by dissolving 374.22g of $Na_2EDTA.2H_2O$ in 1 liter distilled water. Dissodium salt of EDTA is used as it is said to have certain advantages in comparison to other salts of EDTA (Raghavan et al., 1989; Moutsatsou et al., 2006). As reported by Moutsatsou et al. (2006) use of Na_2EDTA as an extracting agent presents three important advantages: (a) pH of the final solution is usually alkaline and facilitates the development of further mechanisms for metal retention (e.g: precipitation), (b) Na_2EDTA is slowly biodegraded in groundwater and (c) Na_2EDTA possesses a high complexation capacity. One molar concentration of $CaCl_2$ was prepared by dissolving 110.98g anhydrous $CaCl_2$ in 1 liter distilled water.

2.3. Batch studies:

The dried soil sample was taken in 250ml polypropylene tubes for conducting further studies. The washing solution was added to all tubes maintaining the L:S (Liquid : Solid) weight ratio required for the investigations. For EDTA solution the ratio was kept as 2:1, similar to the value 1.5:1 reported by Makino et al., 2007. For $CaCl_2$ solution the ratio was 5:1. The molar concentration of EDTA solution used was varied from 0.01 to 0.05M. The molar concentration of $CaCl_2$ solution used was varied from 0.2 to 1M. The amount of solution used was reduced in the case of EDTA considering its economical use. But as the effectiveness was high compared to $CaCl_2$, less molar solution was enough for the studies conducted. A small L:S ratio was selected by Andrade et al., 2007 to reduce the amount of washing solution and chemicals as high amount of liquid may lead to problems regarding management of bulk amount of waste water. But in this study the molarity of EDTA is very less compared to that reported by Andrade et al., 2007 and hence economy is achieved. The tube was shaken for equilibrium period at

room temperature and centrifuged for 10min at 3000rpm. The supernatant was filtered through a 0.45µm filter paper. Concentration of lead in filtrate was measured using an ion meter.

3. Results and discussion:

3.1. Effect of molar concentration:

To study the effect of concentration of washing solution on percentage removal of lead from contaminated soil, 20ml EDTA solution was mixed with 10g soil and shaken for 24hrs at 150rpm. The percentage removal of lead from soil was monitored continuously and the maximum percentage removal obtained at each concentration was observed. Figure.2 shows the maximum percentage removal obtained at each molar concentration of Na_2EDTA solution used for the study. It was noted that with increase in molar concentration of washing solution used, there was an increase in the amount of lead desorbed from the contaminated soil and the maximum percentage removal occurred for 0.05M solution (93.2%). But the rate of decrement in removal percentage for 0.04M and 0.03M solution was very minimal. It became high for 0.02M and 0.01M solutions. Hence for further studies a solution concentration of 0.03 M was used.
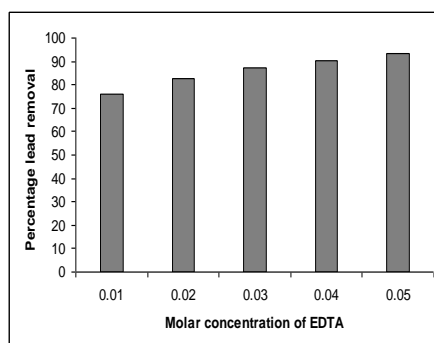

Figure. 2: Effect of molar concentration of EDTA on percentage lead removal

The effect of concentration of $CaCl_2$ solution on percentage removal of lead from contaminated soil was studied by taking 50ml $CaCl_2$ solution in polypropylene tubes with 10g soil. The tubes were shaken for 24hrs at 150rpm. The maximum percentage removal obtained at each concentration was observed. Figure.3 shows the maximum percentage removal obtained at each molar concentration of $CaCl_2$ solution. There was an increase in the percentage removal observed for lead when the molar concentrations were increased. But the removal percentages were low compared to that obtained with EDTA solution. The percentage removal varied from 41.3% to 56.3% corresponding to a concentration of 0.2M to 1.0M. Variation was somewhat

steady for 0.4M and 0.6M. For 0.2M the removal percentage was very less. Hence a molar concentration of 0.4M was used for further studies.
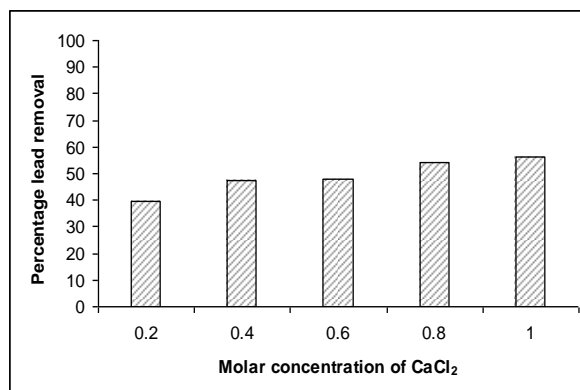

Figure. 3: Effect of molar concentration of CaCl₂ on percentage lead removal

3.2. Effect of period of mixing on lead desorption:

It is proved that the time of mixing plays a major role in the desorption of lead from contaminated soil (Moutsatsou et al., 2006). The desorption studies were carried out for 24hrs for both chemicals. Solution to soil ratio was 2:1 and molar concentration of 0.03M was used in the case of EDTA. For $CaCl_2$, these were 5:1 and 0.4M respectively. Initially, a highly fluctuating trend was observed for percentage removal in both cases. But after some period a nearly steady value was observed (Figure.4). This period was 3.5hrs for Na_2EDTA and 6hrs for $CaCl_2$ and it was considered as the equilibrium period for desorption. Moutsatsou et al., 2006 observed that 0.1M Na_2EDTA was most effective when the mixing period was less than 1hr. They got a removal efficiency of 42% for lead when the initial contamination level was as high as 64,195mg/kg (soil/liquid = 30g/l, 150rpm). Based on the results obtained for batch studies, in the present study the equilibrium period of shaking was fixed as 3.5hrs for Na_2EDTA and 6hrs for $CaCl_2$.
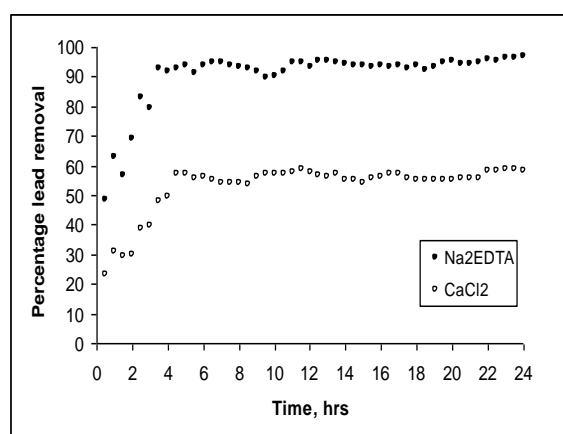

Figure. 4: Effect of period of shaking on percentage lead removal

3.3. Effect of pH on percentage removal of lead:

The influence of pH on removal percentage of lead using chelating agents was reported earlier by Finzgar and Lestan, 2007. In the present study conducted the effect of pH on lead removal from contaminated soil was investigated for both Na_2EDTA and $CaCl_2$ mixed soil. In the case of EDTA, an L: S weight ratio of 2:1 and a molar concentration of 0.03M was used. PH of the washing solution was varied from 1 to 14. In the case of $CaCl_2$ the L: S weight ratio was kept as 5:1 throughout the study and the molar concentration of 0.4M was used. Figure.5 shows the effect of pH on removal percentage of lead while all other parameters remained the same for washing with each solution.

The studies on pH have shown that when the pH was reduced from 14 to1 there was increase in lead removal percentage in case of Na_2EDTA. It was maximum (94.3% -96.8%) when the pH was in the range 3-1. The least value, 31.4%, was observed when pH was 14. Tuin and Tels (1990) found that acidification to pH 2.5 increased the amount of Pb extracted by EDTA substantially for one soil, but only slightly for another. The present study also highlights the effectiveness of Na_2EDTA at low levels of pH value. But in another study, Peters and Shem (1992) reported that removal of Pb by EDTA was insensitive to pH adjustment in the pH range of 4.0 to 12.0. Hence it can be said that a generalization is not possible and the study has to be undertaken for each kind of soil to predict the suitability of a particular chelant in removing any metal from it. The maximum removal of lead occurred at pH 9 when $CaCl_2$ was used for the study (59.3%). The removal rate was less than this when the pH was increased as well as decreased.
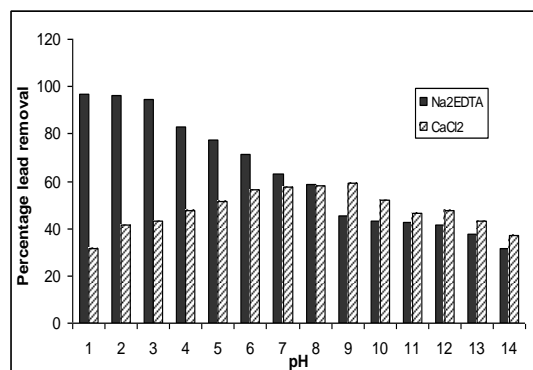

Figure. 5: Effect of pH on percentage lead removal

The experimental results from the present study have shown that when Na_2EDTA was used higher removal efficiency of lead from contaminated soil was achieved compared to $CaCl_2$. However the percentage lead removal obtained with both these chelating agents were higher

than the results obtained by some other researchers (Finzgar and Lestan, 2007, Moutsatsou et al., 2006). The reason for it may be due to the nature of artificially prepared sample used for the studies. Peters, 1999 reported that, when artificially contaminated soil is used for these kind of studies, (a) a selective adsorption of pollutants occur at ion-exchange positions on soil matrix which facilitates their extraction and transportation into the liquid phase. On the contrary, real waste is not expected to have metals in loosely bound forms and pollutants are probably situated in positions that do not favor their transportation into the liquid phase. (b) Metal formations in synthetic soil samples are usually simple i.e., single metal compounds. On the contrary, in real mining–metallurgical waste there is always a complicated metal speciation. Therefore, the interaction between the complicated metal forms and the solvent will probably differentiate metal mobilization rate and (c) the process become simple when restricted number of metals (maximum 3) are used in studies. These may be the reason for obtaining higher removal rates in the present study also when EDTA is used. But the study with $CaCl_2$ gave only reduced removal rate compared to EDTA enhanced soil washing and this may probably be due to the competition between divalent cations (Raghavan et al., 1989). But in highly acidic soils, the application of EDTA may increase the acidic nature of soil and in order to keep the soil nature unaltered the application of $CaCl_2$ may be suggested in such conditions.

4. Conclusions:

The present study has proved the effectiveness of two chelating agents, Na_2EDTA and $CaCl_2$ in removing lead from a local soil which was artificially contaminated in the laboratory. It was observed that, solution pH influence the removal very much. While low pH enhance the removal by EDTA a moderately high pH was good for $CaCl_2$. The influence of molar ratio and time on removal rate was studied and reported in each case. It is concluded that, soil washing using these kind of chelating agents can be recommended for remediating highly polluted soils, but it is essential to study the optimum conditions and influencing parameters for better removal by conducting batch studies.

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