Heavy Metal Removal from Contaminated Soil Using Soil Washing Techniques

G. Resmi*†, Santosh G. Thampi** and S. Chandrakaran**

*Department of Civil Engineering, N.S.S. College of Engineering, Palakkad, Kerala, India
**Department of Civil Engineering, National Institute of Technology, Calicut, Kerala, India
†Corresponding author: G. Resmi; resmivinod@gmail.com

ABSTRACT

Heavy metals are discharged into the soil around us from various anthropogenic sources and also by the use of fertilizers, pesticides, pharmaceuticals, etc. In most cases, industrialization can be pointed to as the reason behind soil pollution. Contamination of soil leads to large-scale environmental degradation and health impacts. Many investigators have studied techniques for removing heavy metals from soil. Soil washing is an emerging area that can be implemented for this purpose. Studies were carried out in the controlled conditions of a laboratory environment to determine the suitability of soil-washing techniques for removing lead from polluted land. The results showing the influence of various parameters in soil washing, such as duration of washing, molar strength of the solution used, the weight ratio of soil to wash solution, etc., are presented in this paper. Batch studies were conducted to investigate the performance of chelating agents such as Na_2EDTA, HCl, HNO_3 and $CaCl_2$ with regard to the removal of lead from artificially contaminated locally available soil. Based on the batch studies, it is observed that the strength of the washing solution, the proportion of soil and solution, the period of agitation, etc. influence the removal of contaminants. Based on the studies, it is concluded that, while recommending soil washing using chelating agents for remediating lead-contaminated soils, it is essential to identify the influencing parameters and determine the optimum conditions so that higher removal can be achieved without any adverse effect.

INTRODUCTION

Contamination of land by the discharge of heavy metals is a matter of concern all around the world. Even in trace amounts, they give rise to land degradation and health impacts. Heavy metals are naturally occurring elements. But they are also generated by various anthropogenic activities like the production and use of fertilizers, pesticides, pharmaceuticals, etc. Activities such as the release of pharmaceutical waste, industrial waste, e-waste, batteries, pesticides, etc., are considered the main source of such pollution in urban and agricultural land (Chibuike & Obiora 2014). There are chances that these metals remain in the soil for a longer period and later lead to problems such as bioaccumulation. Extraction of these metals from polluted soils is usually carried out by using acids or selected solutions that develop complexes with them. Soil washing techniques were widely experimented with to remove heavy metals from soil. Techniques for removing a few metals namely, lead and zinc from contaminated soil by washing methods were reported by Wang et al. (2015). Some efforts have been made to investigate the capability of ethylene diamine tetra acetic acid (EDTA) for sorbed metal extraction (Yang & Lin 1998 and Peters 1999). Some researchers have already investigated the use of acids like hydrochloric acid (HCl),

nitric acid (HNO_3), and sulphuric acid (H_2SO_4) for removing heavy metals from soil (Peters 1999, Moutsatsou et al. 2006, Semer & Reddy 1995, Sun et al. 2001). For the extraction of these from the soil, extensive research has been conducted using organic acids as chelating agents (Wei et al. 2018). Few researchers have studied the application of potassium salts of EDTA (K_2H_2EDTA), calcium chloride ($CaCl_2$), and potassium hydroxide (KOH) for soil washing to remove lead (Samani et al. 1998).

The results of the studies carried out to investigate the effectiveness of soil washing technique and the influence of some parameters like molar strength of the washing solution, duration of washing, the weight ratio of soil to wash solution, etc. are presented in this article. Batch studies were conducted to investigate the performance of chelating agents such as Na_2EDTA, HCl, HNO_3 and $CaCl_2$ with regard to removing lead from polluted soil.

MATERIALS AND METHODS

Soil Used in the Study

The study was conducted at the NITC campus, Calicut District, Kerala, and soil samples were collected from the campus itself. Representative disturbed samples were
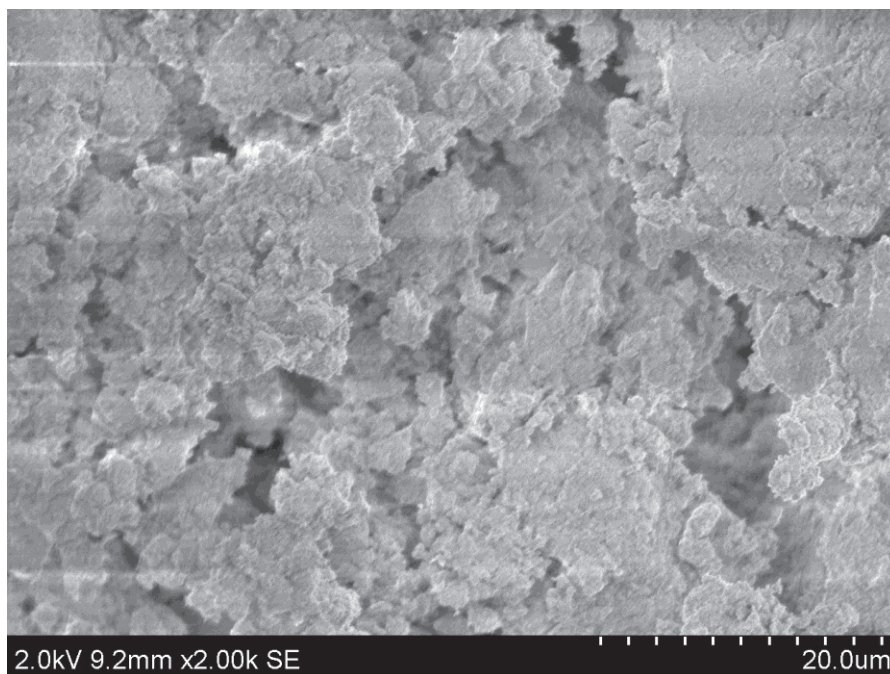
Fig. 1: SEM image of the soil used in the study.

obtained from shallow pits and carefully transported to the laboratory in such a way as to avoid any moisture loss. The soil was mixed thoroughly, kept in polyethylene bags, and stored in containers for the duration of the study. The SEM image of the dry soil sample is shown in Fig. 1.

Artificial Contamination

Sample preparation was carried out in a laboratory environment. For this purpose soil was soaked with a synthetic solution containing lead. In the study, lead nitrate (Pb $(NO_3)_2$) salt of analytical grade was selected. The soil was mixed with lead nitrate solution with a lead concentration of 2000 ppm. The synthetic lead solution was taken in containers, and soil samples were soaked in these. It was left without disturbance for 90 days for enhancement of sorption. The soil samples after sorption were then collected from the solution. Then it is properly dried, powdered, and passed through a 2 mm IS sieve. Later they are kept in polyethylene bags for the entire study period. The adsorbed amount of lead was observed to be 19.8 mg.g^{-1}.

Four washing reagents were selected for the investigation such as EDTA, CaCl$_2$, HNO$_3$, and HCl. 1M concentration of EDTA solution was prepared by dissolving 374.22 g of Na$_2$EDTA.2H$_2$O in 1L of distilled water. Disodium salt of EDTA was used as it is said to have certain advantages when compared to other salts of EDTA (Raghavan et al. 1989, Moutsatsou et al. 2006, Demont et al. 2018). It is reported

that the use of Na$_2$EDTA as a solvent for removing metals has shown some merits: (a) pH of the solution turns basic and leads to metal retention (b) Na$_2$EDTA does not degrade faster in groundwater and (c) Na$_2$EDTA has got a greater affinity to form complexes (Abumaizar & Smith 1999, Moutsatsou et al. 2006). 1M CaCl$_2$ was prepared by dissolving 110.98g anhydrous CaCl$_2$ in 1litre of distilled water. Similarly, 1M HNO$_3$ was prepared by mixing 64ml conc. HNO$_3$ and 943ml distilled water. 1M HCl was prepared by mixing 83ml conc. HCl and 920ml distilled water.

Batch Studies

Studies were conducted in batch mode to find out the effectiveness of soil-washing agents under selected conditions. The optimum duration of shaking and the desirable pH were also determined by conducting batch studies. The dried soil sample was taken in 250 mL polypropylene bottles and the washing solution was added to these bottles maintaining the desired ratio of soil weight to liquid volume (S: L). For conducting preliminary studies, this ratio was fixed as 1:1, similar to the value 1:1.5 as reported by Makino et al. (2007), and later this was varied upto 1:5. The same range of solid to liquid ratio was adopted with all other solutions used in this study.

The molar concentration of the EDTA solution used was varied from 0.01 to 0.05 M, the molar concentration of CaCl$_2$ solution was varied from 0.2 to 1 M and the molar

concentration of HCl and HNO$_3$ solutions were varied from 0.01 to 1 M. Less concentrated EDTA solution was used to achieve economy in usage. However, as the effectiveness was high compared to other solutions, a solution with low molarity was sufficient for the studies conducted. In an earlier study, a small liquid-to-solid ratio was selected by Andrade et al. (2007) to reduce the amount of washing solution and chemicals, as usage of a large amount of liquid may lead to problems regarding the management of the wastewater generated. 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 soil–solution mixture was shaken at 150 rpm for a period of 24 h at room temperature and centrifuged for 10 min at 3000 rpm. Approximately 10 mL of the supernatant liquid was passed using filter paper of 0.45 microns in size. The strength of the lead in the residue after filtration was checked with the help of an ion meter having an ion-selective electrode for determining lead. There was an assumption behind the process that the mass of lead observed in the filtrates was the actual representation of lead released from the soil mixed with contaminants. The quantity of lead obtained in the filtrate was divided by the initial mass of lead present in each sample before the washing process. This value indicated the overall efficiency of the soil washing technique.

RESULTS AND DISCUSSION

Results obtained from the batch studies are discussed below.

Effect of Soil-to-Liquid Ratio

For studying the effect of solid-to-liquid ratio on the percentage removal of lead from the soil, experiments were conducted at five different ratios - 1:1, 1:2, 1:3, 1:4, and 1:5 (Makino et al. 2007) and for five different molar concentrations of EDTA - 0.01, 0.02, 0.03, 0.04 and 0.05 M. The percentage removal of lead was observed to be as high as 98.9% when the solid-to-liquid ratio was 1:5, and the molar concentration was 0.05 M. The least value (75.1%) was obtained when the solid-to-liquid ratio was 1:1 and the concentration was 0.01 M. The results are presented in Fig. 2.

It was observed that when the solid-to-liquid ratio was 1:5, the removal rate was higher than that with a ratio of 1:1. The same trend was observed for all concentrations tested. The results show that the effectiveness of soil washing using EDTA improves as the volume of washing solution is increased. However, this is not advisable from the viewpoint of the economy of the process. Hence a washing agent that can achieve comparable results with low volume is desirable. The removal achieved corresponding to the 1:2 ratio was
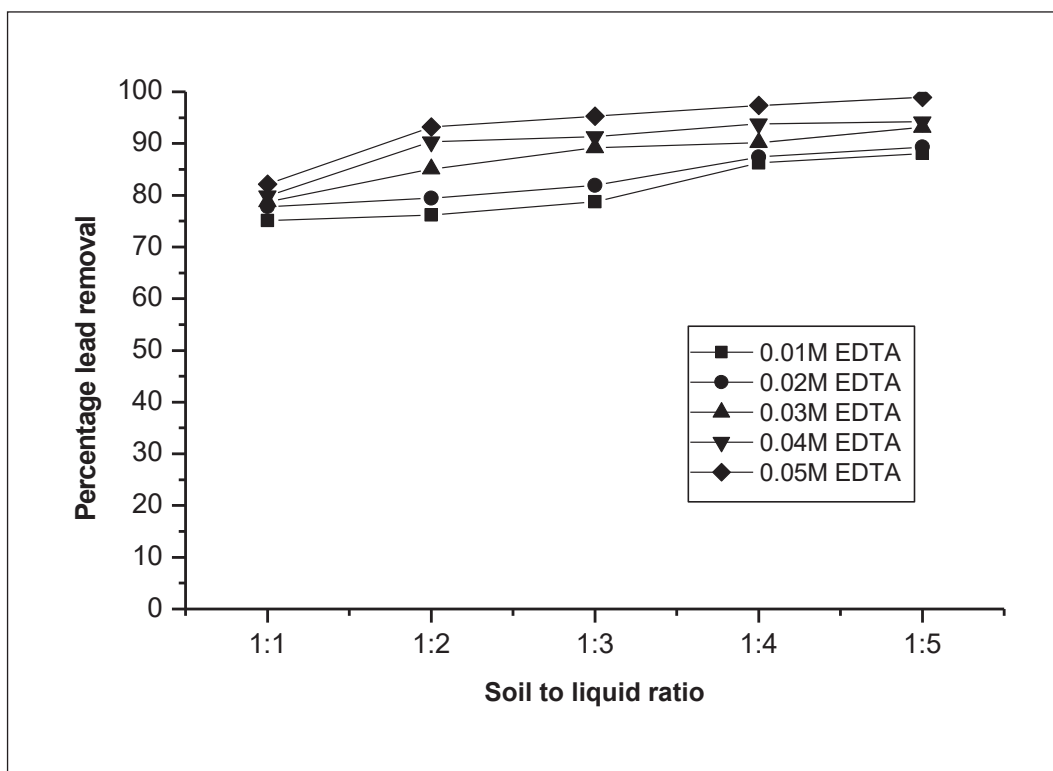

Fig. 2: Effect of soil to EDTA ratio on percentage lead removal.
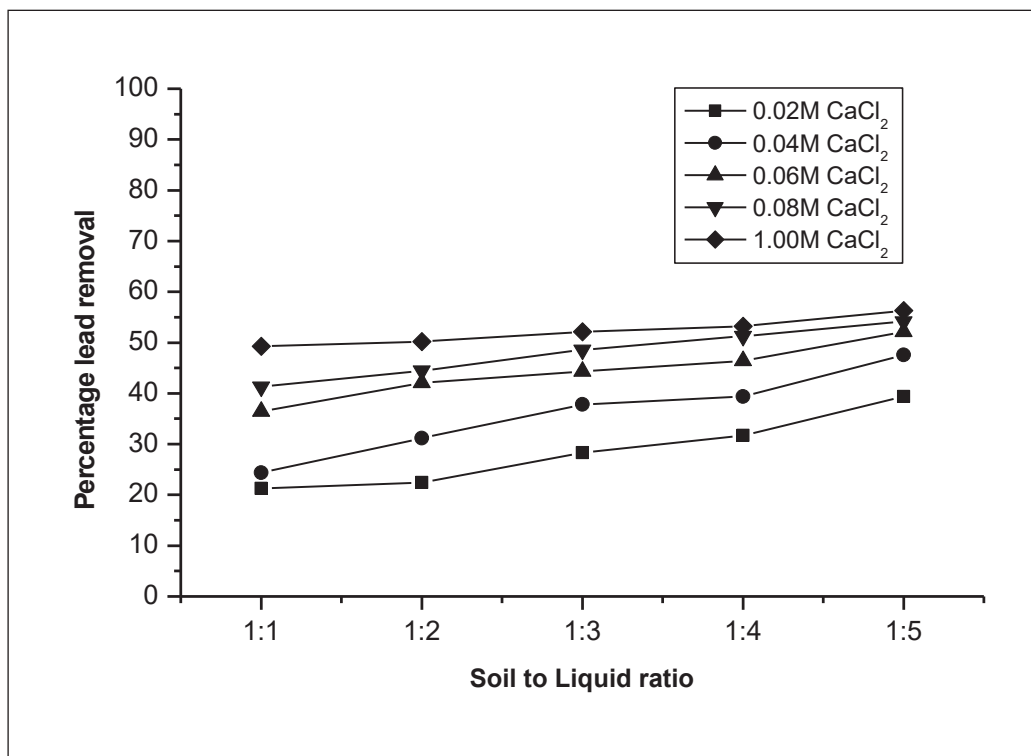
Fig. 3: Effect of soil to CaCl$_2$ ratio on percentage lead removal.

reasonably good (more than 90% removal is achieved). Hence for further studies with EDTA, this was fixed at a ratio of 1:2.

The effect of solid-to-liquid ratio on lead removal using CaCl$_2$ was also investigated at five different ratios - 1:1, 1:2, 1:3, 1:4, and 1:5. The soil-liquid mixture was kept for shaking at 150 rpm and the percentage of lead removal was computed and expressed in the graph (Fig. 3). The percentage lead removal was not as high as that achieved with EDTA (varying from 21.3% to 56.3%). In the majority of the cases investigated, the efficiency of metal removal was lower than 60%. The highest percentage of removal was observed at a proportion of 1:5, and this was selected for further studies.

The influence of solid-to-liquid ratio on lead removal with HNO$_3$ was studied by conducting tests at five different ratios as in the previous two cases, and the results are presented in Fig. 4. Similar to the previous case when the ratio of solid to liquid was 1:1, lead removal increased as the concentration of HNO$_3$ increased. Some fluctuation was observed in the range of ratios 1:2 and 1:4. At solid-to-liquid ratios 1:4 and 1:5, it was seen that there was a decrease in the percentage removal of lead at higher concentrations of HNO$_3$. The maximum percentage removal of lead

(82.1%) was achieved when the solid-to-liquid ratio was 1:3. Hence this ratio was used for further studies with HNO$_3$.

Results of experiments performed with HCl for removing lead are presented in Fig. 5. It was observed that as the proportion of liquid was increased, there was a good improvement in lead removal. At higher molar concentrations the removal was high. The maximum percentage removal (79.8%) was observed at a ratio of 1:5 and a molar concentration of 1.0 M. The rest of the batch studies using HCl were done at this solid-to-liquid ratio and molar concentration.

Effect of Contact Period on Lead Removal Efficiency

The influence of contact period on percentage lead removal was evaluated using EDTA, CaCl$_2$, HNO$_3$ and HCl as the washing agents. Each of the washing agents was mixed with contaminated soil and shaken for 12 h at 150 rpm. The solution concentrations were changed and the experiments were repeated. The results are presented in Fig. 6 to Fig. 9. In all the cases, rapid removal was observed in the initial stages. Thereafter, it increased gradually, and a steady state was attained after a while. This corresponds to the point of equilibrium and the contact period required for reaching
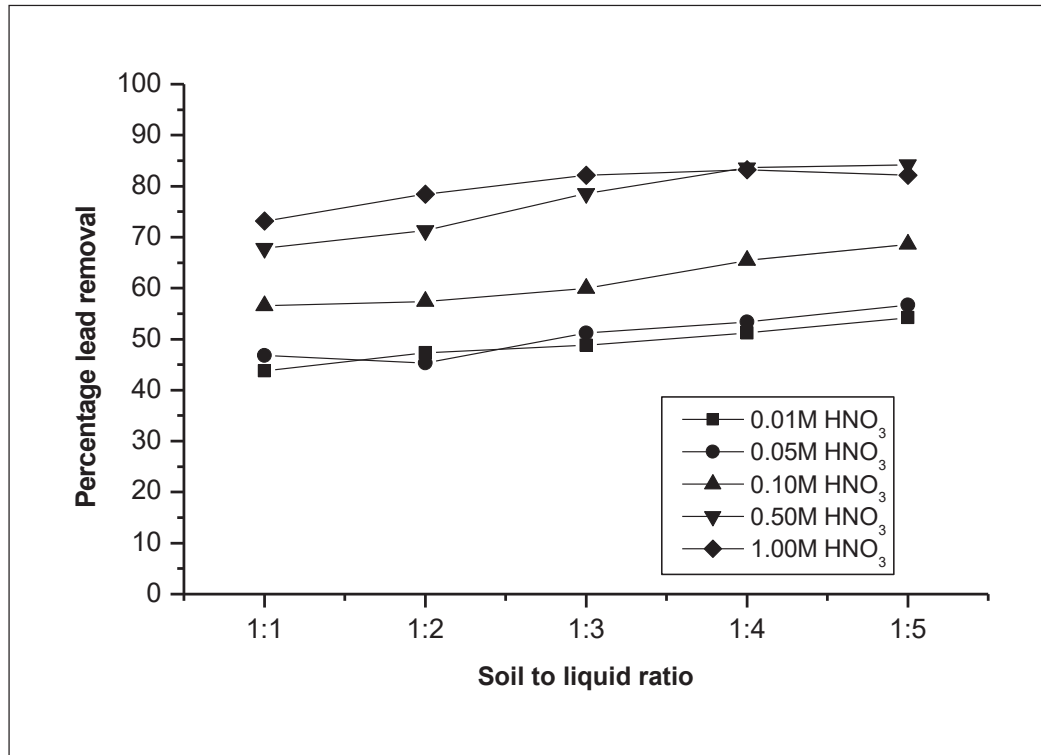
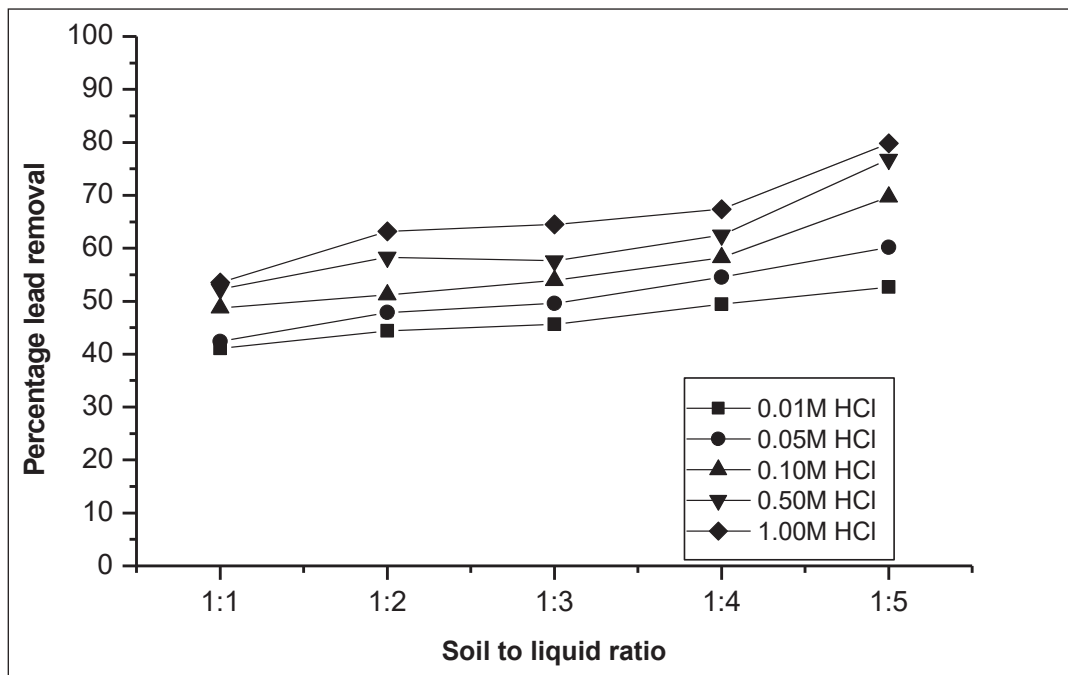Fig. 4: Effect of soil to HNO$_3$ ratio on percentage lead removal.

Fig. 5: Effect of soil to HCl solution ratio on percentage lead removal.
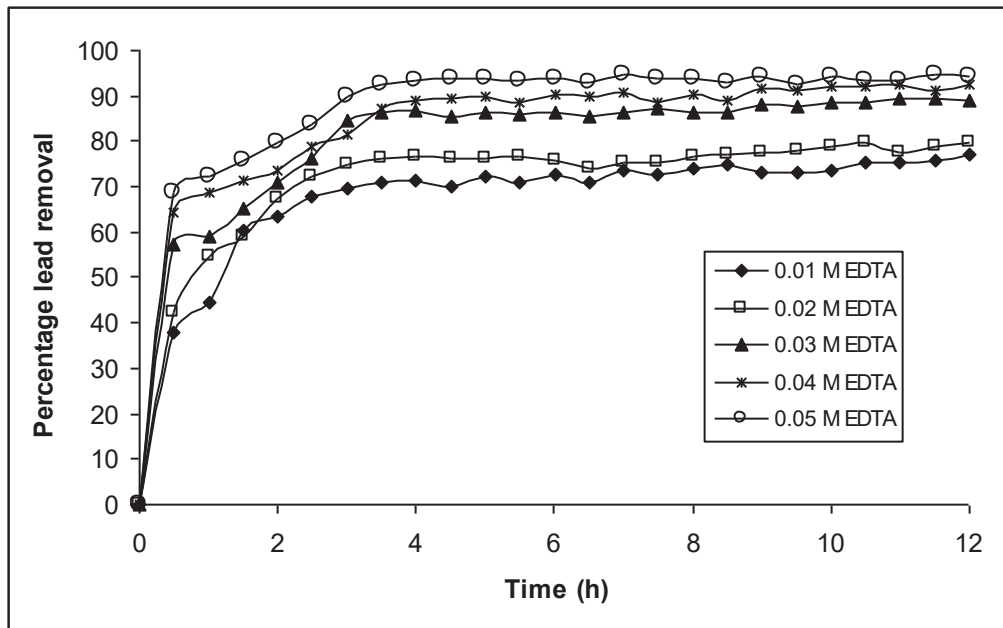
Fig. 6: Effect of contact time on percentage removal of lead using EDTA.

the equilibrium stage in each case was used for conducting other batch studies.

A close observation of Fig. 6 shows that the equilibrium period with EDTA is approximately 3.5 h, the corresponding percentage being 72.8%, 75.8%, 86.3%, 90.3% and 93.9% with 0.01 M, 0.02 M, 0.03 M, 0.04 M and 0.05 M EDTA, respectively. Moutsatsou et al. (2006) observed that 0.1 M Na_2EDTA was the most effective when the mixing period

was less than 1 h. They achieved a removal efficiency of 42% for the lead when the initial contamination level was as high as 64,195 mg.kg^{-1} (soil to liquid ratio = 1:33, shaking speed = 150 rpm).

When $CaCl_2$ was used as the chelating agent, the equilibrium period was about 6 h (Fig. 7). Rapid increase in percentage removal was observed in the first 6 h, and thereafter increase in percentage removal was only nominal
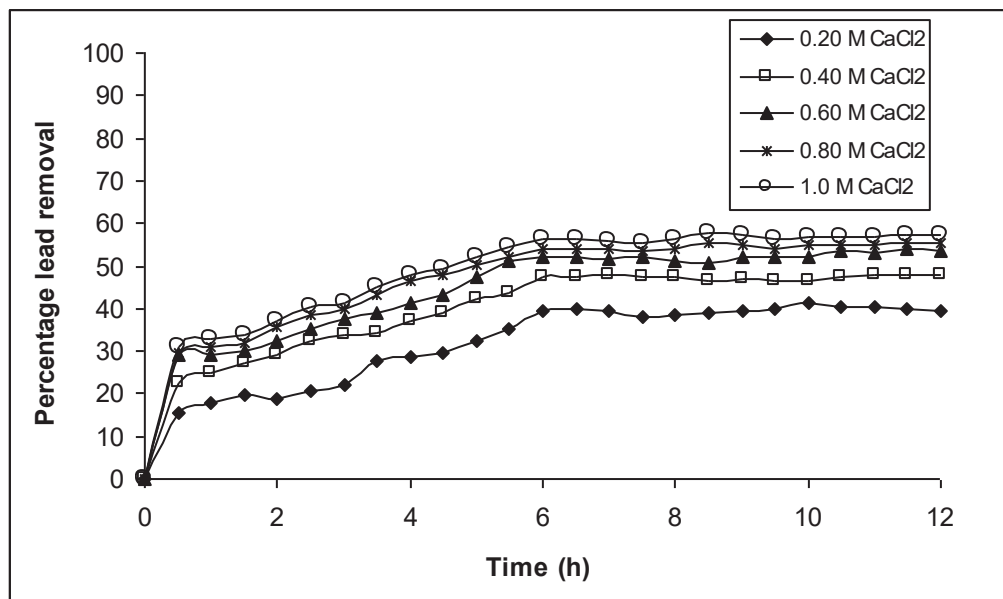

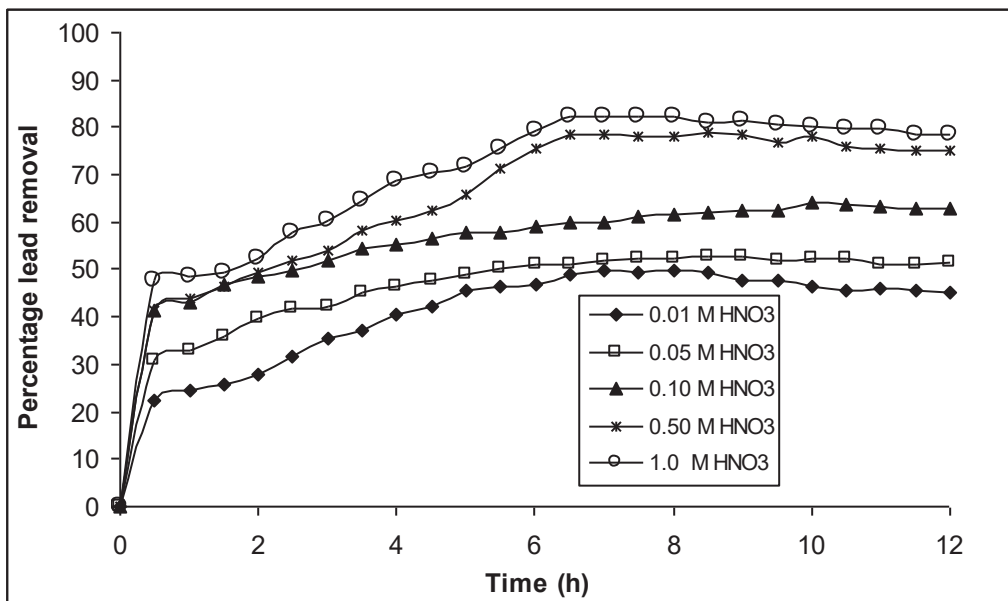Fig. 7: Effect of contact time on percentage removal of lead using $CaCl_2$.

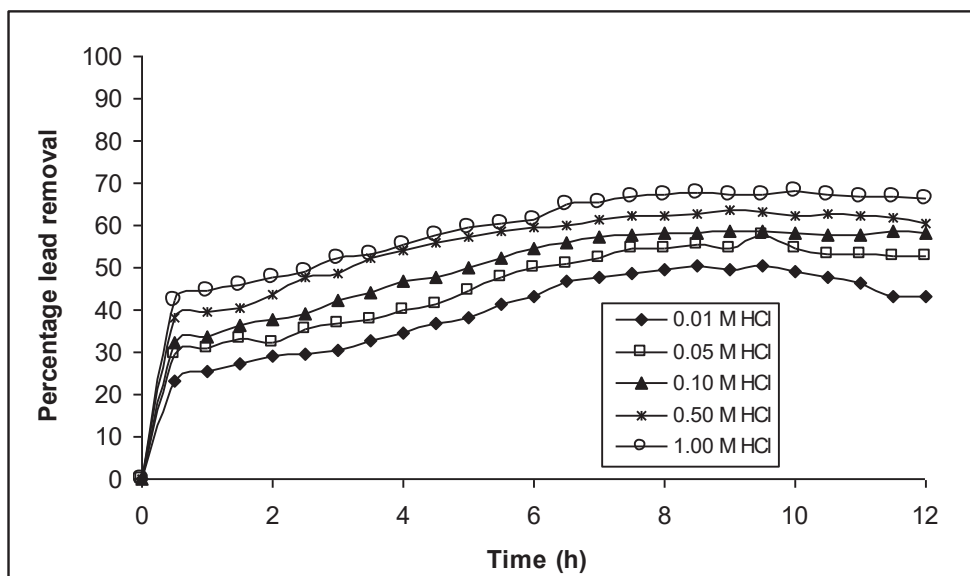Fig. 8: Effect of contact time on percentage removal of lead using HNO_3.

Fig. 9: Effect of contact time on percentage removal of lead using HCl.

at all concentrations. The percentage removal was 39.4%, 47.6%, 52.1%, 54.1%, and 56.3% with HCl concentrations of 0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1M, respectively. Makino et al. (2007) reported that the suitability of a chemical as a chelating agent increases as the contact period to reach equilibrium is reduced. Hence EDTA is a better chelant compared to $CaCl_2$.

When HNO_3 was used as the chelant, a steady state was reached at around 6.5 h, and this was taken as the equilibrium period (Fig. 8). The removal percentages were 48.8%, 51.2%, 59.9%, 78.6%, and 82.1% at 0.01 M, 0.05 M, 0.1 M, 0.5 M and 1.0 M concentrations of HNO_3, respectively. The batch studies with HCl exhibited a similar trend. The equilibrium time was 8 h (Fig. 9).

Strong acids extract only a very small portion of metal content from contaminated soil. In the current study, EDTA-based chelating agents performed better than HNO_3 and HCl. Similar observations were reported by Moutsatsou et al.
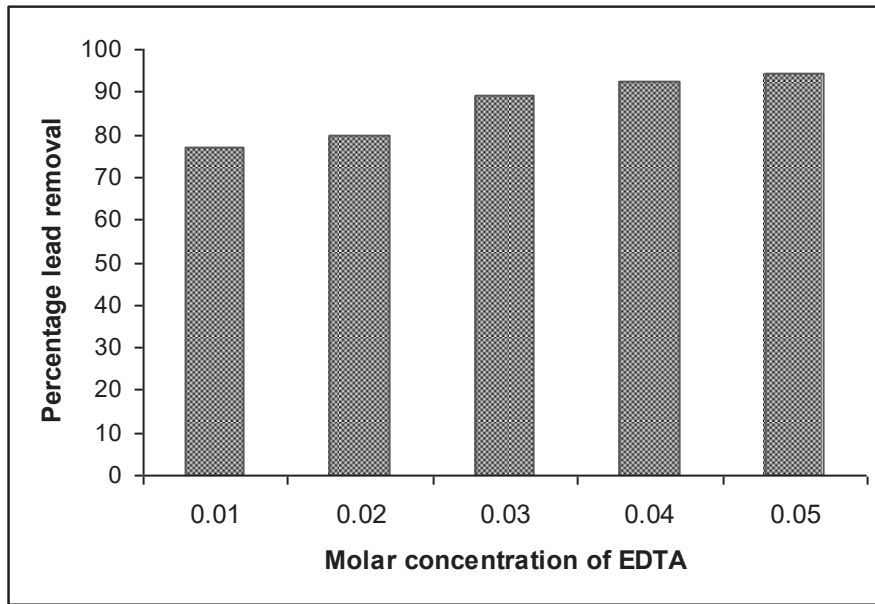
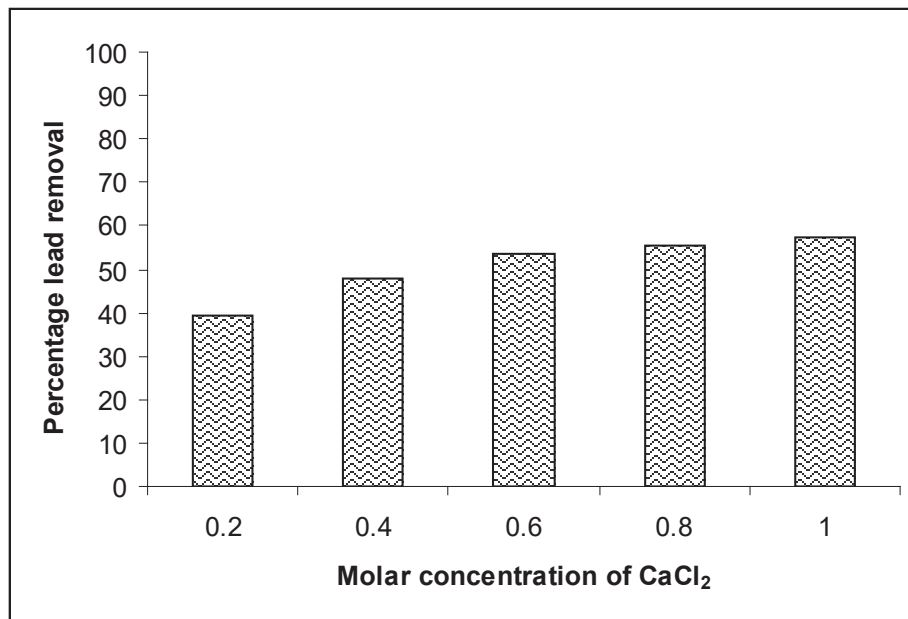Fig. 10: Effect of the molar concentration of EDTA on the removal of lead.

Fig. 11: Effect of the molar concentration of CaCl$_2$ on the removal of lead.

(2006) based on their investigations. HNO$_3$ exhibited high extraction capacities which may be occurring as a result of its strong oxidizing nature which results in the development of insoluble metal compounds.

Effect of Molar Concentration

There will be a high rate of recovery of metal when there is the presence of reagents that lead to the conversion of adsorbed metal ions into anion-dominated complexes. The ability of these agents to immobilize lead and other metals from soil matrix has been reported. EDTA is considered an effective agent which can extract some of the selected metals from soil (Finzgar & Lestan 2007). EDTA addition in small concentration could offer few advantages. Sometimes it leads to less clogging of the soil which normally occurs while washing with high strength of EDTA (Li & Shuman 1996).
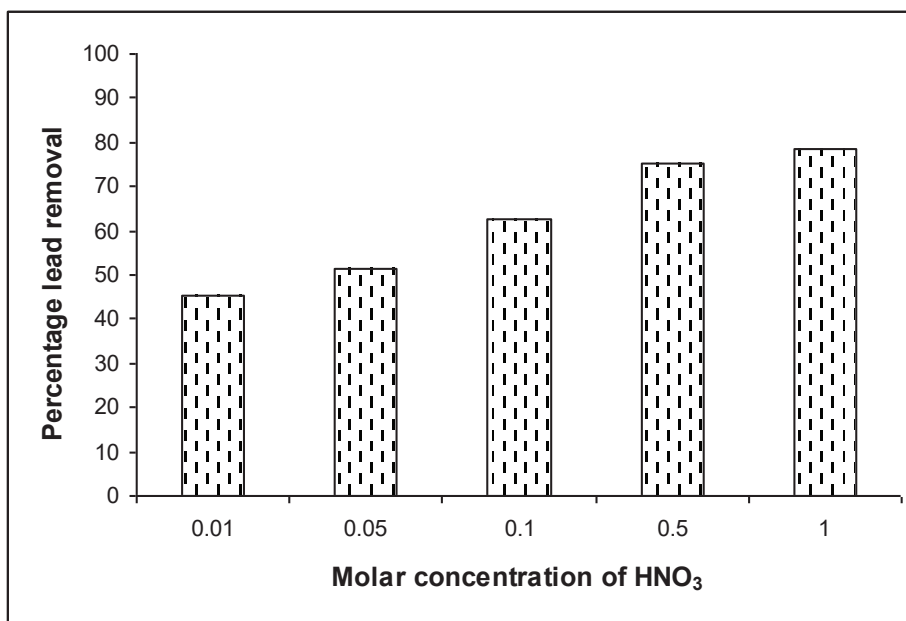
Fig. 12: Effect of the molar concentration of HNO_3 on the removal of lead.
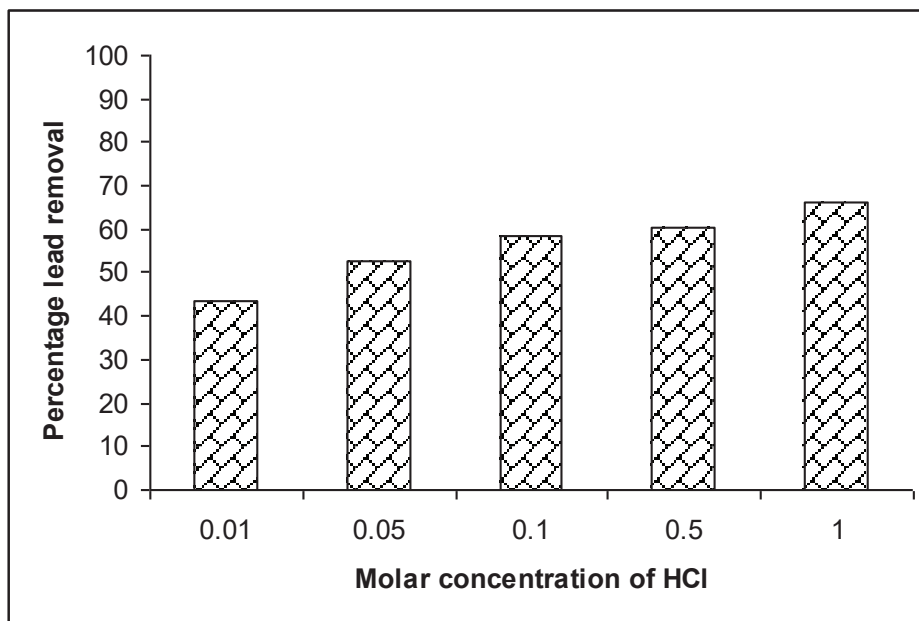

Fig. 13: Effect of the molar concentration of HCl on the removal of lead.

Elliott & Brown (1989) conducted a study using chelating agents such as EDTA and they observed that acids form strong water-soluble complexes.

The present study proved the molar concentration of the chelating chemicals influences contaminant removal considerably. This is evident from the results presented in Fig. 10 to Fig. 13. Increasing the chelant concentration resulted in higher lead solubilization. Using all chemicals, it was observed that the maximum percentage of lead removal was obtained at the maximum concentration of chemicals used for soil washing. With EDTA, the removal was maximum at 0.05 M concentration, and the corresponding percentage removal is 94.3%. The percentage removal was 77.1% at 0.01 M concentration.

With CaCl$_2$, the removal efficiency was maximum at 1.0 M concentration (57.5%). At lower concentrations (0.20 M), the percentage removal was only 39.4%. When HNO$_3$ was used, the percentage removal achieved was 45.3% and 78.3% at 0.01 M and 1.0 M concentrations, respectively. Similarly, with HCl, the percentage of lead removal was 66.4% at 1 M concentration and 43.4% at 0.01 M concentration. These results indicate that when a solution with a higher molar concentration of a finite amount was used, the atomic mass that came in contact with the contaminants was more, and hence, there was a higher opportunity to attach the contaminant with the chelant. As a result, the amount of contaminant removed from the soil mass increased.

CONCLUSION

The study has proved the effectiveness of chelating agents, Disodium EDTA (Na$_2$EDTA), calcium chloride (CaCl$_2$), nitric acid (HNO$_3$), and hydrochloric acid (HCl) in removing lead from soils. Based on the batch studies, it is observed that the strength of the liquid used for washing, the proportion of soil and solution, the solution pH, the period of agitation, etc., influence the removal of contaminants. For each soil-liquid system, a particular molar concentration of the chelant yielded better lead removal. The agitation period, which gave maximum removal, was unique for each system. While low pH enhanced the removal by EDTA and acids (nitric acid and hydrochloric acid), CaCl$_2$ showed better performance at moderately high pH. But sometimes acid percolation through soil may lead to extremely low pH conditions which necessitate further treatment. Also, there are chances of the production of toxic substances during soil washing. Results of column experiments show that the removal rate is very much affected by the flow rate and the bed depth. It is concluded that, while recommending soil washing using chelating agents for remediating lead-contaminated soils, it is essential to identify the influencing parameters and determine the optimum conditions so that higher removal can be achieved without any adverse effect.

ACKNOWLEDGEMENT

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