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A feasibility study on cleaning Pb-contaminated soil with chelating agents

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Abstract — In this paper, the complexing abilities of EDTA, TTHA and Cit. with lead in the Pb (2.59 mg/g) contaminated soil were compared in the laboratory. Possibilities for lead and the three agents to develop stable complexes increased proportionally to the growth of lead complexible form when the pH values ranged between 4 and 6. Under acid conditions, $\log B_{(Pb\text{-}TTHA)}$ valued as 28.1 was much higher than $\log B_{(Pb\text{-}EDTA)}$ as 18.0 depending on producing Pb_2-TTHA ($\log K_{Pb_2\text{-}TTHA}=11.0$) and Pb-HTTHA ($\log K_{Pb\text{-}HTTHA}=8.2$). Conclusively, the complexing ability of TTHA with Pb still exceeded that of EDTA by about 10% even when the amount of TTHA added was only equal to one fourth of that of EDTA. Due to the lower cost and less harm to crops, Cit. can still be taken as a better chelating agent in acid soil although its coordinative capability with Pb was weaker than EDTA and TTHA.

Keywords: soil contamination; Pb; clean up; chelating agents.

1 Introduction

The remedial methods used to treat contaminated soil may be broadly divided into two categories: methods aimed at preventing or restricting dispersion of the contamination to the immediate surroundings, and methods aimed at removing or destroying the contamination, also referred to as cleaning (Assink, 1986). The process of in situ remediation of heavy metal contaminated soil can be accomplished by the latter category in which the extracting and floating methods are the simplest and most effective, economical and available as well. In the first step of the extracting method, suitable chemical agents such as chelating compounds are added to contaminated soil and mixed intensively to increase the solubility of heavy metals. These agents should adhere selectively to the contaminated soil properties, and their function is to give hydrophobic or complexible capabilities to heavy metals adsorbed on the particle surfaces. After the washing processes, control and disposal of the leaching solution becomes a critical problem that must be solved to prevent groundwater pollution. The extracting agents and removed heavy metals are generally separated as a concentrated sludge which has to be disposed by incineration or by dumping at a suitable place. An extracting installation for the field application was set up in The Netherlands to clean the contaminated sandy soil of Pb of concentration 100 mg/kg with NaOH solution. The removal efficiency could reach 75 percent (Assink, 1986). The leaching technique also was used in Sweden to reclaim a former herbicide factory site over a 5 to 6 years period (Lars-Gunnar, 1980). Here washing water was applied through perforated pipes laid in a ditch throughout the contaminated area, then collected by drainage pipes and treated with activated carbon.

The aims of this paper are to compare coordinative capabilities and solubilities of the complexing compounds produced by Ethylenediaminetetraacetic acid (EDTA), citric acid (Cit.) and triethylenetetraaminehexaacetic acid (TTHA) with Pb in soil, and to provide an effective way to clean up Pb-contaminated soils in situ. Although EDTA is known as a strong ligand for metals, it is worthwhile to conduct a study on Cit. due to its advantages: lower cost and less harm to crops. Actually, Cit. is an indispensable constituent for crops, but TTHA has rarely been reported before in environmental studies. It is necessary to compare the three chelating agents in the Pb releasing processes.

2 Complex clean up method

2.1 Test method, agents and apparatus

The soil sample of loam in the test was collected from the terrace of the Yellow River in Lanzhou. Twenty five ml of 0.05 mol/L $Pb(NO_3)_2$ solution was sprayed on 100 g soil in a flask before soaking and stirring sufficiently, then the prepared sample was dried at a temperature of 105°C. Thus, Pb concentration of the artificially contaminated soil was managed at 2.59 mg/g. Having added a given amount of each chelating agent (TTHA, EDTA and Cit.) respectively into the flasks, the solutions were prepared and diluted with distilled water to 100 ml. Then two grams of the contaminated soil were put into each flask before pH values of the solutions were adjusted with HNO_3 or NaOH as necessary. The flasks were shaken at a room temperature (18°C) for 5 hours. After measuring the equilibrium pH, the solutions were filtered, and Pb concentrations were determined using a flame atomic adsorption spectrophotometer.

$Pb(NO_3)_2$, A. R.; EDTA, A. R.; sodium citrate (Cit.), A. R.; TTHA, A. R.; acidimeter (PHS-3C); shaker (THZ-82); flame atomic adsorption spectrophotometer (WFD-Y).

2.2 Coordination mechanism of TTHA

EDTA and Cit. were commonly used as the chelating agents for a long time, but little study dealt with TTHA for the purpose of environmental protection. A special introduction to TTHA is required. Multidentate complexing agents are often able to bind more than one metal ion. Depending on experimental conditions, compounds with a metal ligand ratio of either 1:1 or 2:1 may be formed. Here, the main consideration would focus on TTHA (H_6L). The reagent was introduced by Fröst, (Fröst, 1956) with the formula in Fig.1.

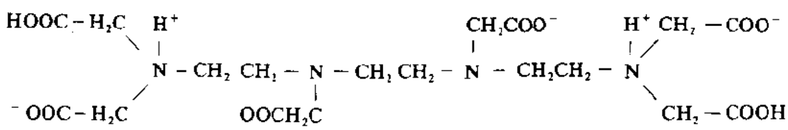

Fig. 1 Illustration of TTHA structure

As a hexahydric acid (H_6L), TTHA dissolves in an alkaline solvent although having little solubility in water. It can provide 10 dentates for metals in complexing processes, so that it produces the stable protonation chelates (MHL) and chelates of 2:1 (M_2L) etc. although it usually forms complexes higher or, at least, analogous to the stability of EDTA with the ratio of 1:1 (ML). The absolute stability constants of TTHA with Pb are listed in Table 1.

Table 1 Absolute stability constants of Cit., EDTA, TTHA-Pb complexes

(μ=0.1, temp.=25 ℃)

Cit.			EDTA		TTHA		
Log $K(PbH_2L)$	$K(PbHL)$	$K(PbL)$	$K(PbL)$	$K(PbHL)$	$K(PbHL)$	$K(Pb_2L)$	$B(Pb_nL)$
11.2	5.2	12.3	18.0	17.1	8.20	11.0	28.1

3 Results and discussion

3.1 Effect comparison of EDTA, Cit. and TTHA for cleaning up Pb

Depending on the properties of EDTA and other complexing agents which can combine with heavy metals to form stable and soluble chelates, EDTA was used to clean Pb contaminated soil in the past. There was a report by Kobayashi (Kobayashi, 1974) that EDTA was applied to remove Pb from a rice-paddy field contaminated by mining wastewater. In this paper, the dissolution effects of lead with EDTA, Cit. and TTHA in soil were compared. As the strong ligands, they react with Pb and other metals to produce stable chelates in soil. The pollutants could finally be eliminated from soil by water flow due to the decrease of soil adsorption. The results are displayed in Fig.2 that complexing capabilities of the three agents with Pb in soil increased in the order of Cit. < EDTA < TTHA.

Table 1 shows that the logarithm values of stability constants for Pb-Cit. and Pb-EDTA were 12.3 and 18.0 respectively, and Cit. displayed greater cleaning capacity even under condition of the lower pH values.

Classified as complexing agents, both TTHA and EDTA comprise amino-group and carboxyl group, which are strong functional groups capable of coordinating with a lot of metals to form stable complexes. Because of strong coordinative capability with metal ions. TTHA can form complexes, such as MHL or M_2L besides ML of 1:1. The tests confirmed that the chelating result of TTHA with Pb was still better than EDTA even if the addition of TTHA was equal to only one fourth that of EDTA in quantity under conditions of a wide range of pH values.

3.2 Effect of pH on chelating process

The existing forms of heavy metals in soil, to a great extent, were dominated by pH values. When soil pH values were decreased from 7.0 to 4.55, the proportion of the exchangeable form for Pb increased (Ellioit, 1989). Moreover, growth of pH values resulted in higher adsorption of heavy metals by the soil. The tests indicated that the soil had tremendous strong adsorptive capabilities for lead, and it was hard to measure the soluble form of Pb at an ordinary condition except for decreasing the pH value below 4.0. Only in this way a certain amount of soluble lead in soil could be evaluated.

This paper analyzed the chelating results of the three complexing compounds with Pb under different pH value conditions. It is seen from Fig.2 that chelating effect of Cit. was directly controlled by acidity, and the complexing capability declined apparently if pH values were more than 8.0. The changing curve is demonstrated in Fig.2.

But, EDTA was effective within a wider range of pH values between 4 and 10 because its complexing capability was much stronger than Cit. As a hexadentate ligand, EDTA could bind Pb firmly due to its 6 ligating groups to fill in all the available coordination sites of Pb ions. As to TTHA, the effective pH range seemed to be from 4 to 8. In a higher acidity, TTHA could form complexes of 1:1 Pb-TTHA and relatively stable Pb-HTTHA as well. As a result of hydrolysis of Pb, where OH^- is a ligand for producing metallic oxides, the chelating capability of TTHA with Pb would fall under alkaline conditions.

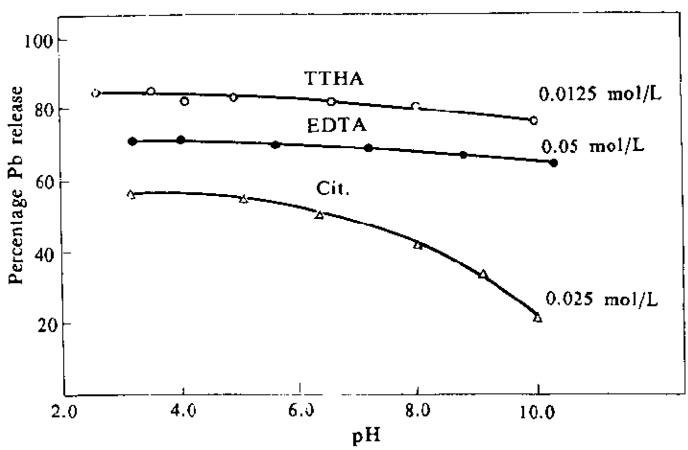

Fig.2 Effects of pH values for TTHA, EDTA and Cit. on Pb release from soil

The results denote that the extracting efficiency can increase from 70% to 90% when equivalent ratio of Pb to EDTA rises from 1:2 to 1:4, which can be seen in Fig.3. In the economic view, the ratio of 1:2 is acceptable in cleaning processes.

However, the extracting curve of Pb with TTHA at the equivalent ratio of 1:1 is the same to that at the ratio of 1:2. When the ratio of Pb to TTHA reaches 1:1, the amount of released Pb may achieve 84% because TTHA can produce a series of protonation chelats. The increases of extracting percentage of Pb with the different concentration of TTHA are demonstrated in Fig. 4. Definitely, the ratio of 1:1 for Pb to TTHA is a reasonable choice in application.

3.3 Pb-ligand and soil surface adsorption

Soil adsorption of trace metal elements was ruled by the pH value of the aqueous solution, quantity and properties of metals in the soil where adsorption of metal cations and hydrolysis commonly occurred, and as a result, pH values became the key factor. In general, the amount of metal cations adsorbed by soil surfaces was proportional to the pH value. When adding organic chelating agents, the adsorption effects of soil on metal cations were restrained significantly since metal cations reacted and formed stable large anions with ligands. The restraint was dependent on species of metal cation, properties of ligand and pH value of the aqueous solution in soil.

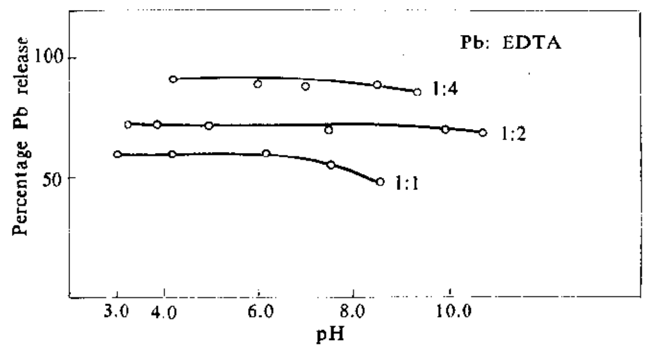

Fig. 3 Effects of the added EDTA amounts on release of Pb

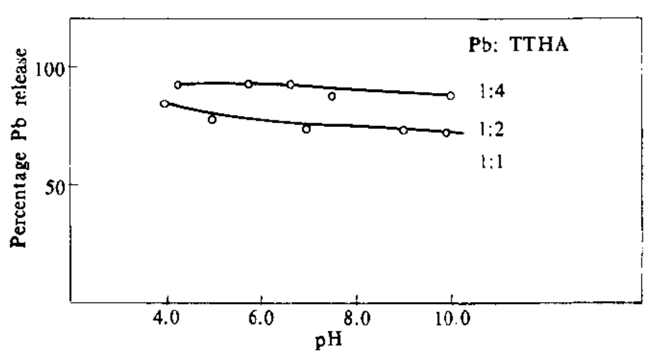

Fig. 4 Effects of the added TTHA amounts on release of Pb

The interaction between metal cations and ligands on soil surface was different from that in aqueous solution, and may depend on the orientation of the complex and, specifically, on which part of the molecule binds to the surface. In Fig. 2, the adsorbed complex is expressed as a generalized form (Me, L). Additionally, the adsorbed complex may be formed by a soluble complex adsorbed or metal and ligand ions sequentially absorbed. The real systems can be signified by the combination of the limiting cases, and adsorptive behavior of a known complex in a system would be governed by soil properties, organic content, electrolyte composition of the solution and electrical potential in soil and so on.

The complexing compounds of EDTA displayed restricting effects on adsorption in soil (Elliott, 1982), and the metal complexes of EDTA were not adsorbed by soil because of carrying the negative charges. This paper compared the influences of the above three chelating agents on soil surface adsorption. It was found that the recovery amount of Pb decreased with the increase of pH values, therefore, the three chelates were all metal-like complexes, i. e. the ligand concentration at a given pH would also directly influence Pb recovery besides pH value of solution (Benjamin, 1981).

In summary, augmentation of chelating agent concentration would enhance the solubility of Pb in soil. In the experiments, the concentration of chelating agents was to be equimolar with that of Pb (0.05 mol/L) which was supposed to be totally solubilized. In addition, the existence of a strong electrolyte was another important factor on Pb recovery. For example, offering $NaClO_3$ could enlarge Pb recovery by about 10% in EDTA system even though perchlorate did not coordinate with Pb because the added Na ions should promote displacement of adsorbed Pb ions and enhance solubility of Pb containing solid phases in the same manner as the EDTA system. Through the comparison of the three chelating agents, it is seen that Cit., as Pb cleaning agent, is competent in the acidic soils, and can even get satisfactory results in spite of the fact that its complexing capability appears weaker than EDTA and TTHA. Usually, EDTA has been considered an ideal chelating agent for removing heavy metals from soil. However, the best operable way and optimal conditions remain to be investigated because the cleaning methods with chelating agents are so high costly that they can not be widely utilized in practice by now.

4 Conclusions

The three chelating agents Cit., EDTA and TTHA can coordinate with Pb and form stable complexes. The stabilities increased in an order: Cit. $<$ EDTA $<$ TTHA. Utilization of the three chelating agents to treat contaminated soil under certain conditions could clean up 50% to 84% of Pb.

Pb release was directly affected soil acidity. Cit. was efficient in acidic soil (pH 4.0 – 7.0), but EDTA and TTHA in a wide range of soil pH values from 4.8 to 10.0 and from 4.0 to 8.0 respectively.

The optimum EDTA-Pb molar ratio for Pb recovery was 2, for TTHA-Pb was 1:1 or 1:2.

Adsorption capacity of soil of the complexes was controlled by soil pH values, ligand concentration, species of metal ions and other factors. The adsorption model of the above three chelating agents with metal could be accounted as a metal-like adsorption model.

Cit. was recommended to be used as an effective chelating agent for cleaning Pb up in acid soils due to its low cost although its coordinative capability was weaker than TTHA and EDTA.

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References

Assink JW. Extractive method for soil decontamination: a general survey and review of operational installations contaminated soil, Dordrecht, The Netherlands: Martinus Nijhoff Publishers, 1986

Benjamin MM, Leckie JO. J Environ Sci and Tech, 1981, 15(9):1050

Elliott HA, Denneny CM. J Environ Qual, 1982; 11(2):658

Elliott HA, Brown GA. Water Air and Soil Pollution, 1989; 45(5-6):361

Fröst AE. Nature, 1956; 178:322

Kobayashi J, Morii F, Muramato S. Trace Subst in Environ Health, 1974; 8:179

Lars-Gunnar, Lindfors. Proc of the conference on reclamation of contaminated land, London: Society of Chemical Industry, 1980

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