



Chelation extraction of lead from soil using pyridine-2,6-dicarboxylic acid

Edward Macauley, Andrew Hong*

Department of Civil Engineering, University of Utah, Salt Lake City, UT 84112, USA

Received 24 April 1994; accepted in revised form 12 August 1994

Abstract

Pyridine-2,6-dicarboxylic acid (PDA) was employed as a lead-complexing agent. Batch testing involving PDA extraction of lead from spiked soils showed PDA to be an effective lead solubilizing agent across a wide pH range. Lead extraction efficiency was independent of the total carbonate concentration, competing cations, or the soil aging period. In addition, PDA compared favorably with EDTA as a lead-complexing agent, while behaving more desirably than EDTA in releasing the extracted lead. PDA was effectively reclaimed and reused in four successive extraction procedures, achieving in each run a lead extraction efficiency that exceeded 80% recovery of the total lead present in the spiked soil. In recovery procedures, the complex solution was elevated to a pH of about 10, separating the lead as a hydroxide precipitate, and allowing for virtually complete recovery of the PDA in solution.

1. Introduction

Lead contamination of soil occurs in many areas of the world. Soil near a zinc smelting operation was reported to contain lead concentrations as high as 6475 mg/l [1]. Upper soil horizons at a former battery reclamation site in Florida contained up to 135 000 ppm lead [2]. Lead contamination was reported in dredged sludge at the port of Hamburg [3]. Once a soil becomes heavily contaminated with lead, the sorptive capacity of the soil is exceeded, and additional contaminants will disperse along the direction of groundwater flow. Continuous precipitation and dissolution (mobilization) of lead contaminants in groundwater lead to the formation of a contaminant plume, extending in the downstream flow direction, which adversely affects soil quality, and potentially threatens regional water supplies.

Methods have been advanced addressing heavy metal contamination of soils. Major categories of solutions include containment, removal, and treatment, or

* Corresponding author. Tel.: + 1 (801) 581-6931. Fax: + 1 (801) 585-5477.

various combinations of these. Currently, the US Environmental Protection Agency favors 'permanent treatment to the maximum extent practicable' over land disposal and containment [4]. Extraction is a major 'permanent' treatment strategy for heavy metal removal, and can be accomplished either in situ, or following excavation and crushing.

Metal extraction has been accomplished with various agents; the most widely used are chelating agents. Unlike caustics or strong acids, which can degrade soil particles while mobilizing contaminants, chelators mainly remove the available fraction of inorganic contaminants [5]. Thus, the use of chelating agents provides for a high level of abatement, while removing only the most leachable portions of a metal contaminant. Often used as a benchmark indicator of ligand strength, EDTA is one of the most popular and powerful chelating agents, and has been used by many researchers to extract lead from contaminated soils [6–11]. Although expensive, chelating agents are known to provide for excellent metal removal without the destructive effects toward soil that are often associated with other methods, such as caustic or acid washing. Because of the costs of chelating agents, the key to their use lies in the ability to regenerate and reuse the chelator. EDTA is difficult to regenerate, although several new strategies are currently being pursued [6, 7]. Other conveniently regenerable chelating agents have also been investigated recently [12–14]. This paper investigates the use of PDA in the chelation extraction of lead from spiked soils, the subsequent recovery of lead, and the regeneration and reuse of PDA.

2. Experimental

2.1. Reactor and reagents

Batch reactors are 125 ml glass Erlenmeyer flasks holding an initial suspension of 100 ml at room temperature ($22 \pm 1^\circ\text{C}$). Adjustment of pH was made by manually adding 6 N HNO₃ or 6 N NaOH. In all soil spike procedures the initial solution for preparing a suspension was obtained by diluting a 1000 mg/l Pb stock solution, prepared from Pb(NO₃)₂ (EM Science, 99.0%), with deionized water (18 M Ω -cm) obtained from a Milli-Q system (Millipore) according to ASTM Standard D 3559-90 [15]. Ionic strength (*I*) was held constant with NaClO₄ (Aldrich, 99%); the total carbonate content (*C_T*) was added with NaHCO₃ (Mallinckrodt). A typical lead-spike solution contained a total dissolved lead concentration (*Pb_T*) of 50 mg/l, *I* of 0.1 M, and *C_T* of 1 mM. All exceptions were noted (see Table 1 for a list of abbreviations and symbols used in this paper).

Clean soil was obtained from a single site in Salt Lake City, Utah, air-dried for 30 days, passed through a 2 mm sieve, and mixed prior to use. The soil was characterized to have: pH = 7.8 (in water), pH = 7.5 (in CaCl₂), pH_{zpc} = 8.1, specific gravity = 2.65, cation exchange capacity = 13.9 meq/100 g, and respective size fractions of 90.4%, 7.5%, and 2.1% as sand, silt, and clay [14]. The soil fraction < 0.15 mm contained an organic content (dry) of 10.3% [16].

Table 1
Abbreviations

C_T	Total carbonate concentration (M)
EDTA	Ethylenediaminetetraacetic acid
I	Ionic strength (M)
L_T	Total ligand concentration (including all conjugate acid–base forms) (M)
Me_T	Total dissolved metal concentration (M or mg/l)
PDA	Pyridine-2,6-dicarboxylic acid (M)
Pb_T	Total dissolved lead concentration (remaining in the aqueous phase) (M or mg/l); Cd_T , Cu_T , Ni_T , and Zn_T are defined likewise
$Pb_{T,0}$	Total lead added to the system (including dissolved, solid, surface forms) (M or mg/l); $Cd_{T,0}$, $Cu_{T,0}$, $Ni_{T,0}$, and $Zn_{T,0}$ are defined likewise
pH_F	Final pH (\neq)
q	Metal loading on soil (mg/g)

2.2. General procedure

All soil spike adsorption procedures were carried out as 24-h batch sorption processes according to ASTM Standard D 4646-87 [15]. Generally, $NaHCO_3$ and $NaClO_4$ were added to a standard Pb solution in a 2-l high density polyethylene container and diluted to a desired Pb_T . The solution pH was kept low to ensure that all of the lead was dissolved, and 100 ml of which was added into a 125-ml glass Erlenmeyer flask containing 1 g (dry) of soil. Test soils in all adsorption and extraction procedures were held in constant suspension by operating a gyratory shake table (New Brunswick Scientific Co., Model G-2) at 260 rpm.

The metal extraction procedure was initiated immediately following the conclusion of the soil-spike adsorption procedure. At the end of adsorption, a desired amount of pyridine-2,6-dicarboxylic acid (PDA) (Fluka Chemika, >98%) was added in powder form to the suspension. The mixture was agitated continuously for another 24-h period, then a sample was withdrawn for metal analysis. The pH was measured at least three times throughout the course of the adsorption and extraction procedures.

The separation of metals from the ligand was performed by increasing the pH with 6 N NaOH and allowing the precipitates to form quiescently. In some cases, $Ca(NO_3)_2$ (Aldrich, 99%) was added to aid the separation.

2.3. Analytical methods

Aqueous constituents were taken as those that passed through a 0.45 μm filter (Gelman Sciences sterile aerodisc). Aliquot samples were acidified with strong HNO_3 , stored for less than three days in sealed high density polyethylene test tubes, and analyzed according to ASTM Standard D 3559-90 [15] using an atomic absorption spectrometer (Perkin-Elmer Model 280). Measurements of pH were made with a glass electrode and pH meter (Corning Model 240 probe and Orion Model SA 720 pH meter).

The computer program Minteqa2 [17] was used to predict the speciation and solubility of lead under specified conditions similar to those used in experiments.

3. Results and discussion

3.1. Soil adsorption of lead

Fig. 1 presents the equilibrium adsorption of lead by soil. A Freundlich adsorption isotherm was used to describe the behavior. Most extraction experiments in this study were conducted with spiked soils having a metal loading (q) of 5 mg/g (or 5000 ppm). Fig. 2 shows that at $q = 5$ mg/g (achieved by equilibrating 100 ml of 50 ppm lead solution with 1 g of soil), lead from the spike solution was almost completely sorbed prior to the addition of PDA at the start of extraction. Fig. 2 also shows the ability of PDA to extract lead from soil batches containing various amounts of soils that were spiked to various metal loadings.

Although the exact modes of surface sorption and types of surface complexes are unknown, the sorbed lead is likely, in view of the presence of carbonate species and the

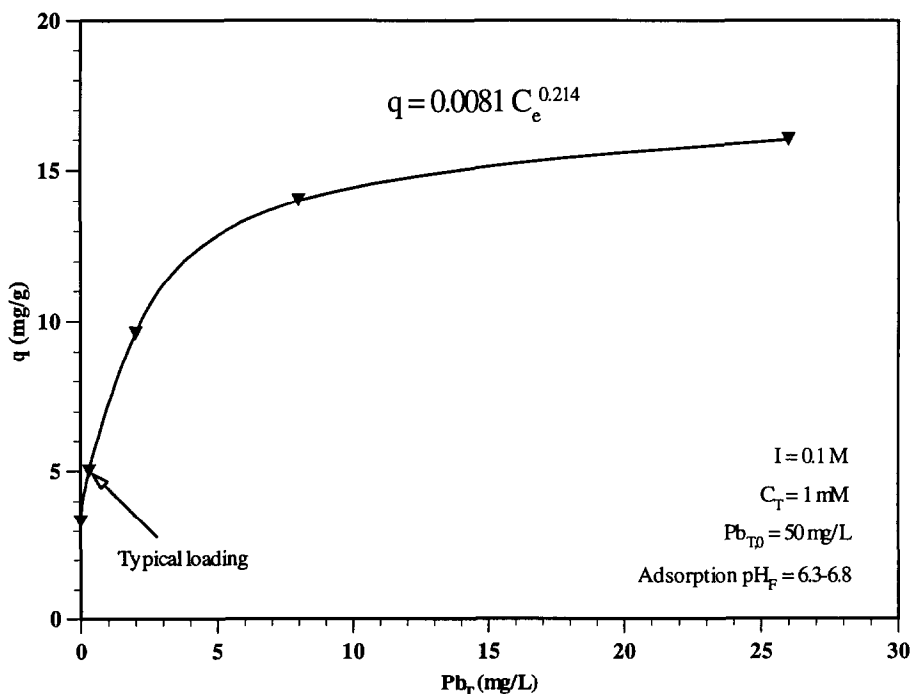


Fig. 1. Adsorption isotherm for lead on soil.

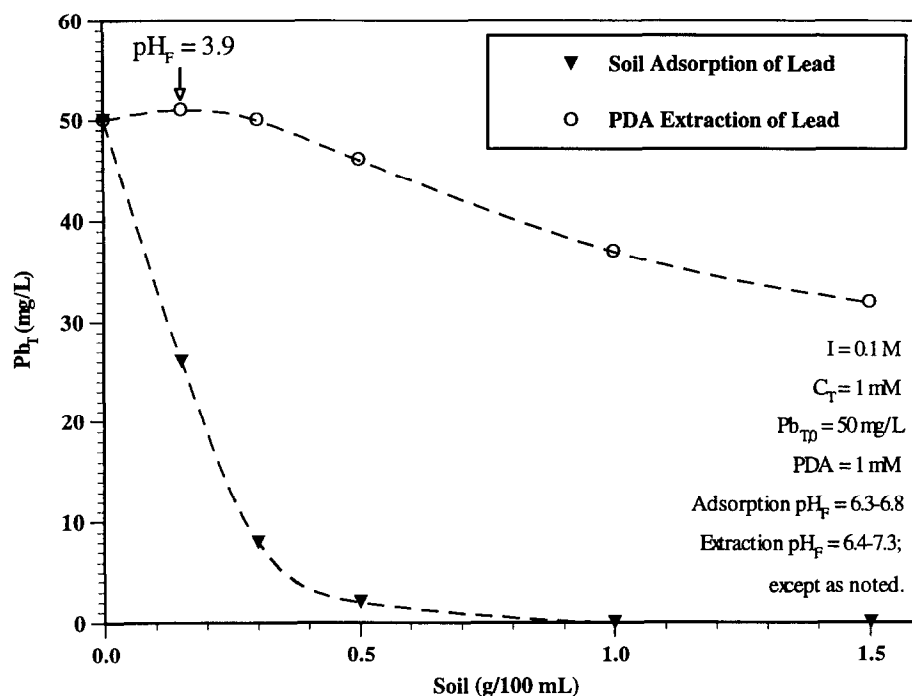


Fig. 2. Lead adsorption to soil, and extraction by PDA as a function of soil loading.

raised equilibrium pH brought about by the soil buffering capacity, to include lead carbonates, hydroxy-carbonates, and hydroxides physically entrapped by the soil particles.

A series of experiments was conducted to examine the effect of aging of the spiked soil. The batch adsorption procedure was prolonged and the spiked soil allowed to age ranging from 1.5 to 25 days before extraction. The extraction results obtained within a 25-day period showed no significant effect of aging on the extraction efficiency.

3.2. Metal extraction by PDA

Metal extraction from soil is accomplished by chelation of the metal with the multidentate ligand PDA, which forms soluble metal–ligand complexes. Chelation is defined as the process of cation bonding by coordinating bases belonging to the same base molecule, which results in the formation of a ring complex, generally with a central metal atom. Ligands are bases which complex with metal cations either through ionic or covalent bonding; chelating agents contain multiple ligand atoms, which bond metal cations at several coordinating sites. Therefore, chelation produces a complex more stable than that produced by complexation with any single ligand atom.

Extraction of a soil-surface bound metal ion likely involves an exchange reaction where a partner of the metal, such as a soil-surface hydroxyl group, is given up in exchange for a preferred partner, such as PDA. Fig. 3 shows the structural formula of PDA in a fully deprotonated state at neutral pH (for PDA: $pK_1 = 2.24$, $pK_2 = 5.07$ [18]). PDA is a base containing both a nitrogen donor atom and two side carboxyl groups. Therefore, it potentially binds a lead cation at three coordinating sites. The nitrogen donor atom of PDA enhances its complexation performance for soft sphere

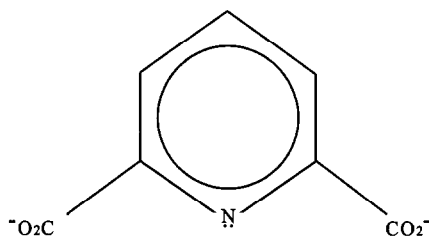


Fig. 3. Structural formula of pyridine-2,6-dicarboxylic acid (PDA), $C_7H_5O_4N$.

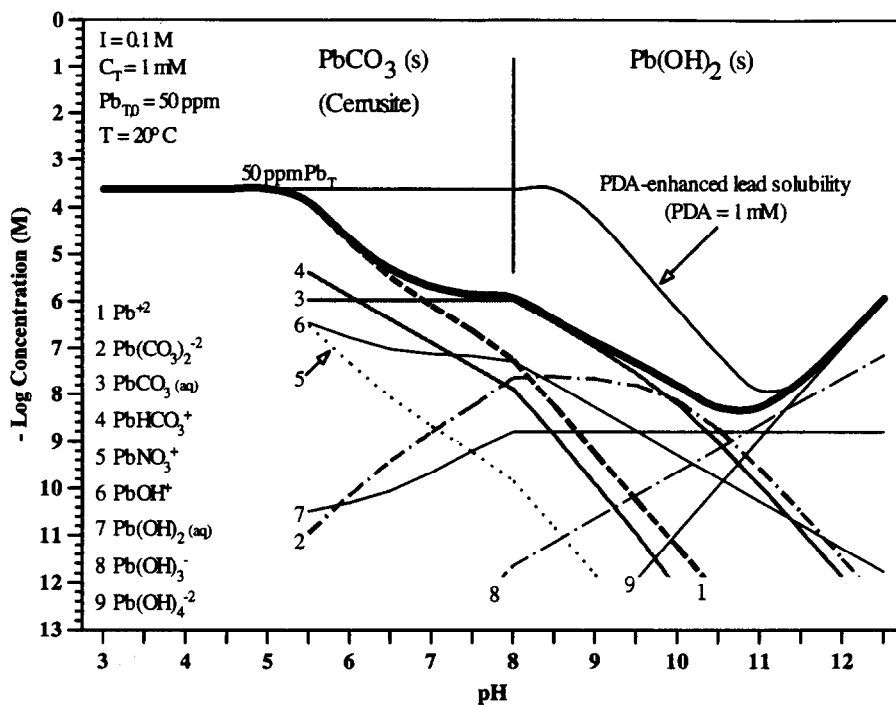


Fig. 4. Lead solubility and speciation as determined by predominant solids $PbCO_3$ (s) and $Pb(OH)_2$ (s) over a wide pH range. (As calculated by Minteqa2.)

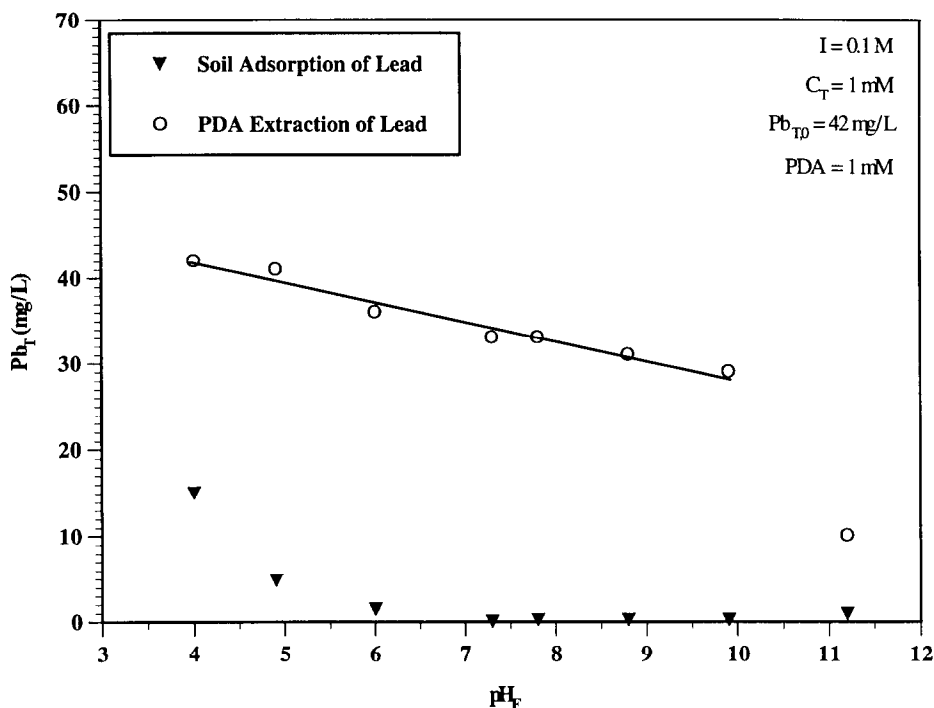


Fig. 5. PDA extraction of lead over a broad pH range.

metals such as lead of interest here [19]. A single PDA molecule or two PDA molecules can complex with one lead ion to form a mononuclear complex PbPDA , or $\text{Pb}(\text{PDA})_2^{2-}$, respectively.

In the middle pH range, lead solubility is increased by several orders of magnitude as a result of chelation with PDA. Fig. 4 shows that, theoretically, 50 ppm lead is completely solubilized by 1.0 mM PDA below pH 8.5 under typical experimental conditions. As shown in Fig. 5, lead solubilization by PDA was achieved across a broad pH range, with a modest decline in extraction efficiency with increasing pH. Fig. 6 shows that the presence of excess amounts of Al, Ca, and Fe effects only minor competition with Pb for PDA, with the Fe effecting the most. The slight increase in extraction efficiency with a large excess of competing cations present was probably only due to a small pH variation. Soil loading rates did not affect lead extraction, provided lead loading was held constant (Fig. 7). In experiments using spiked soils of various lead loadings, lead extraction efficiency increased with increased loading, and vice versa (Fig. 2). An optimal ligand-to-metal mole ratio (L_T/M_{e_T}) for the resolubilization of lead using PDA was determined from Fig. 8 to be approximately 3:1. At higher L_T/M_{e_T} ratios, a large increase in the ligand dosage provided only a modest increase in lead extraction; while at lower ratios, a slight decrease in the ligand dosage caused a large decrease in lead extraction.

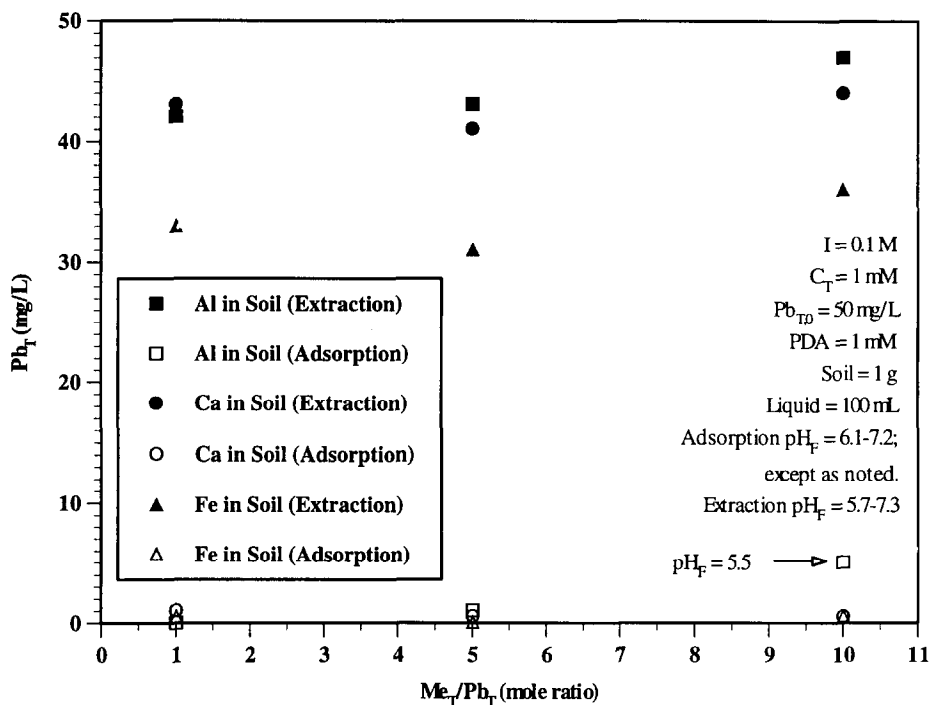


Fig. 6. PDA extraction of lead from soil in the presence of competing Al, Ca, and Fe cations.

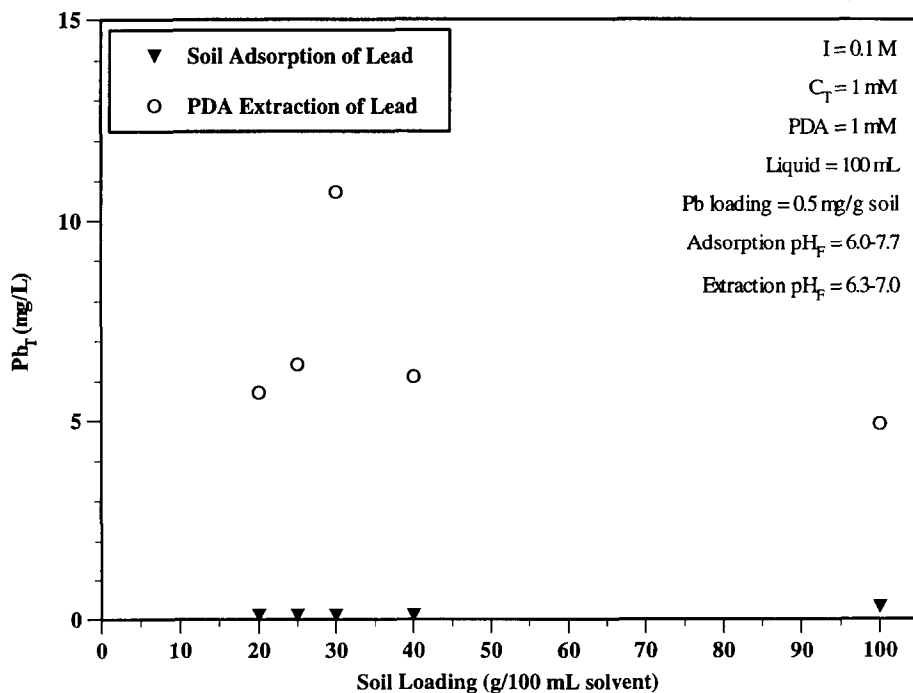


Fig. 7. Effect of soil loading on PDA extraction of lead.

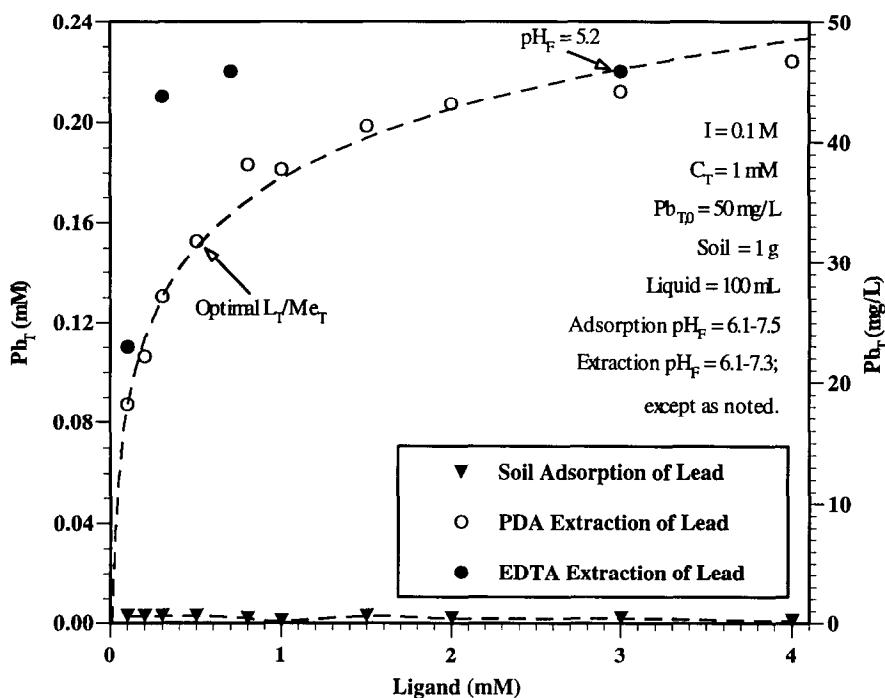


Fig. 8. Extraction of lead from soil by PDA and EDTA.

Other experiments were conducted which demonstrated that about 1 h was required to reach >95% extraction equilibrium; prolonging these same experiments resulted in no change over the next four days. Additional experiments were conducted with varying C_T (0 to 20 mM) which indicated little dependence of extraction efficiency on C_T . The extraction efficiency was slightly enhanced by NaClO_4 added for constant I (0.1 M).

The extraction efficiency of Pb by PDA was comparable with extraction by EDTA (Fig. 8). EDTA exhibited higher extraction efficiencies at low ligand concentrations because it has six ligand groups potentially available for coordination with a lead ion to form an octahedral complex. Conversely, PDA is only potentially a tridentate ligand; a minimum of two PDAs are required to bind all available coordination sites of the lead ion. This gives EDTA a 2:1 mole-ratio advantage over PDA, which explains higher EDTA extraction efficiencies at low molar concentrations. However, in the presence of excess ligand, e.g., above 2 mM in Fig. 8, the performance of EDTA is similar to that of PDA. Because above a 2:1 PDA/Pb mole ratio, there is sufficient PDA to allow full complexation of all the available lead. In addition, the advantage held by EDTA is further reduced when the extraction performance is evaluated on a per mass basis, as opposed to a per molar basis, as EDTA has a higher molecular weight than does PDA.

3.3. Complex separation

Under alkaline conditions, complexes of PDA with cadmium, copper, lead, nickel, and zinc rapidly decomposed into metal precipitates and PDA solute. The release of cadmium, copper, lead, and zinc was completed in less than 10 min at pH 11.0; complexed nickel was released slowly (Fig. 9). Precipitation of metals from a solution containing mixed metal-complexes occurred at different pH values for each metal. The order of metal precipitation (judging at pH 11.0) in a multimetal–PDA complex solution subject to stepwise increases in the basicity was: zinc, lead, cadmium, copper, and nickel (Fig. 10). This sequence agrees closely with theoretical computations based on the thermodynamic stability of constituent species which predicts that zinc will be the first metal to precipitate (pH 9.6), followed closely by copper, cadmium, and lead (pH 9.9–10.4), and finally by nickel (pH 11).

Separation of lead could be achieved under much less basic conditions when a large quantity of calcium ion (10 mM) was added: 90% separation was achieved at pH 8.6, while without calcium addition optimum lead precipitation was obtained at pH 10.3 (Fig. 11). A large amount of calcium ion will compete with lead for the PDA ligand especially at the oxygen ligand atoms of the carboxyl groups. The competition reduces PDA grip on lead, favoring hydroxide ions to form precipitate with the displaced lead cation.

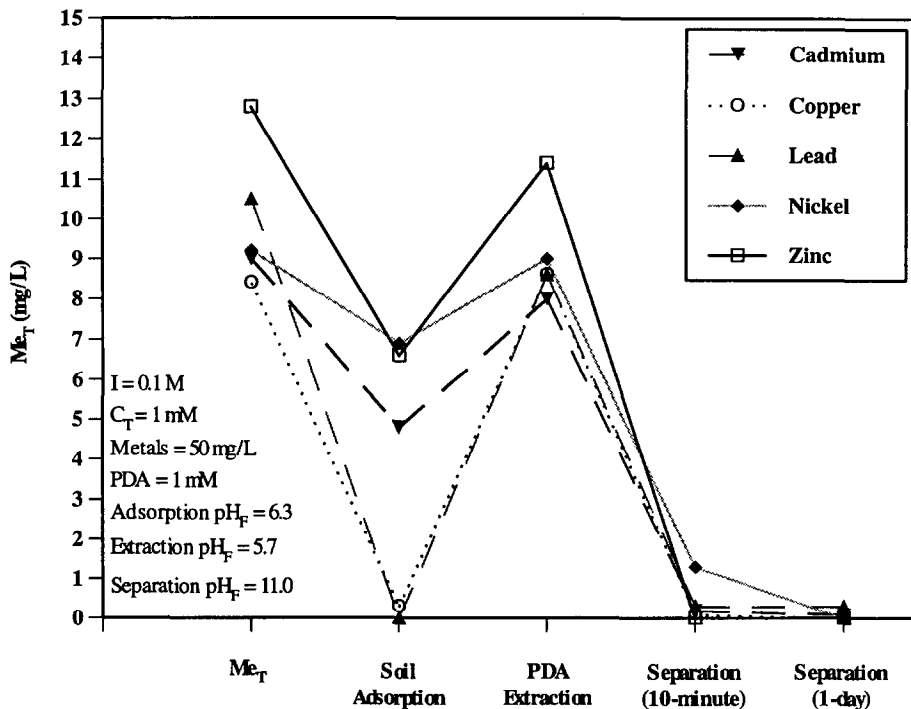


Fig. 9. Soil adsorption, PDA extraction, and separation of several heavy metals.

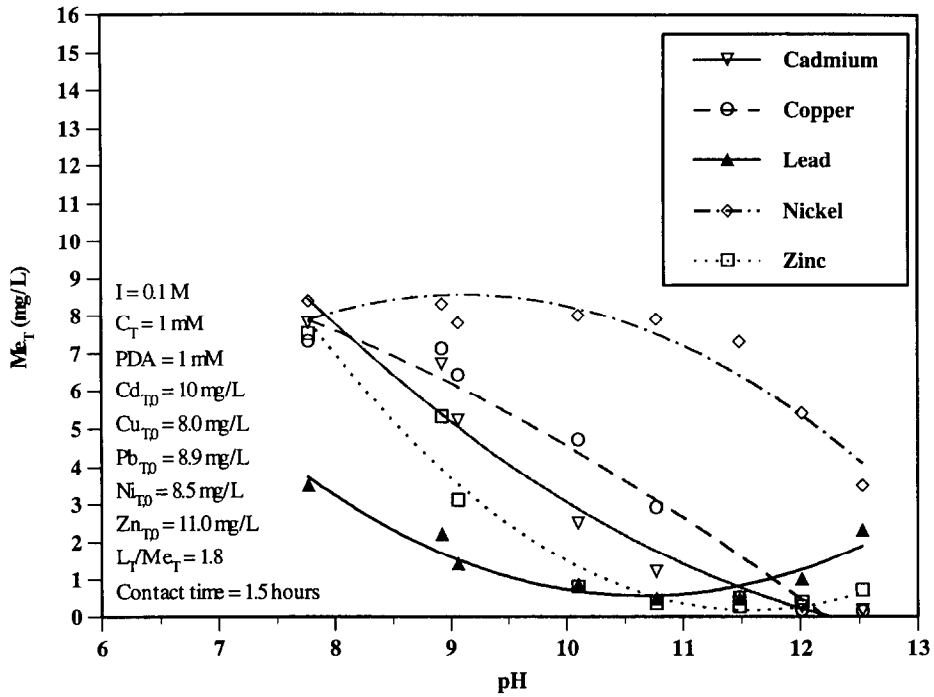


Fig. 10. Releases of metals by PDA upon stepwise increases of pH.

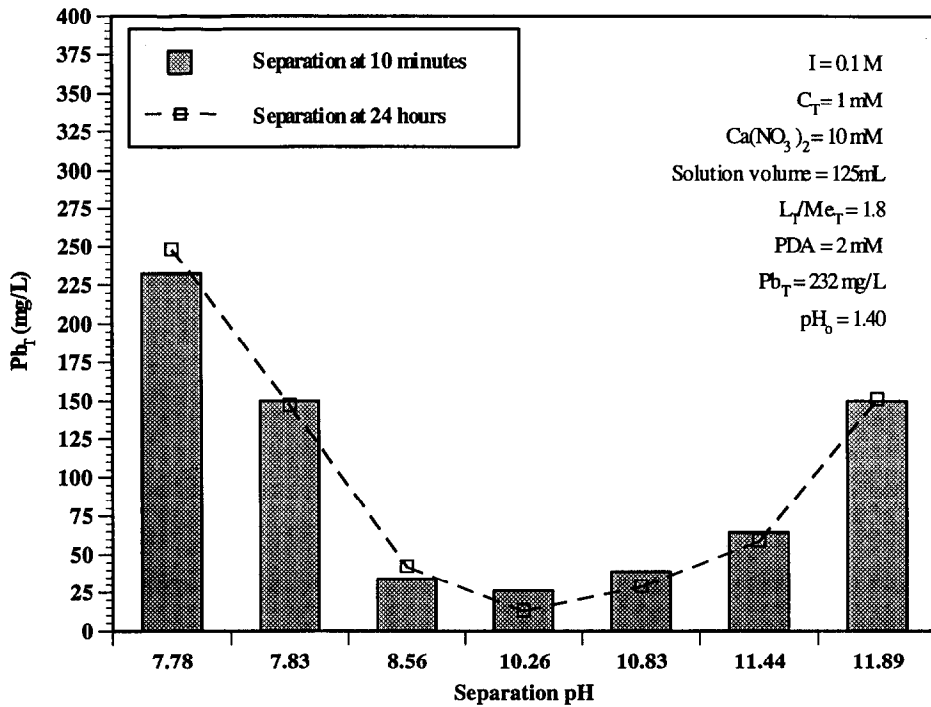


Fig. 11. Release of complexed lead by PDA as a precipitate at elevated pH.

In addition, Fig. 11 shows the occurrence of redissolution of lead compounds above pH 10.3, due to the amphoteric nature of the metal. This illustrates the importance of establishing the optimal separation pH for the specific conditions encountered in actual practice. An excessively high pH for separation results in reduced recovery efficiency, as well as greater costs for alkalization compounds.

3.4. Recovery and reuse

The task of treating the complex solution to separate the chelator from the metal is often difficult. A few methods regarding the Pb-EDTA complex have been reported recently. These methods are elaborate and they include: (i) the pre-extraction addition of divalent cations to the extraction solution, followed by the post-extraction alkalization of the chelate solution to a pH above 12.0 [7]; (ii) the recovery of EDTA using electrolysis [6]. This research demonstrates that by choosing the proper ligand, the separation of the Pb-PDA complex can be readily achieved by adjusting pH to values between 10 and 11.

In a series of successive extractions performed on freshly spiked soils, PDA was observed to maintain its full extraction potential throughout four consecutive extraction/separation procedures (Fig. 12). This suggests that near-complete ligand recovery

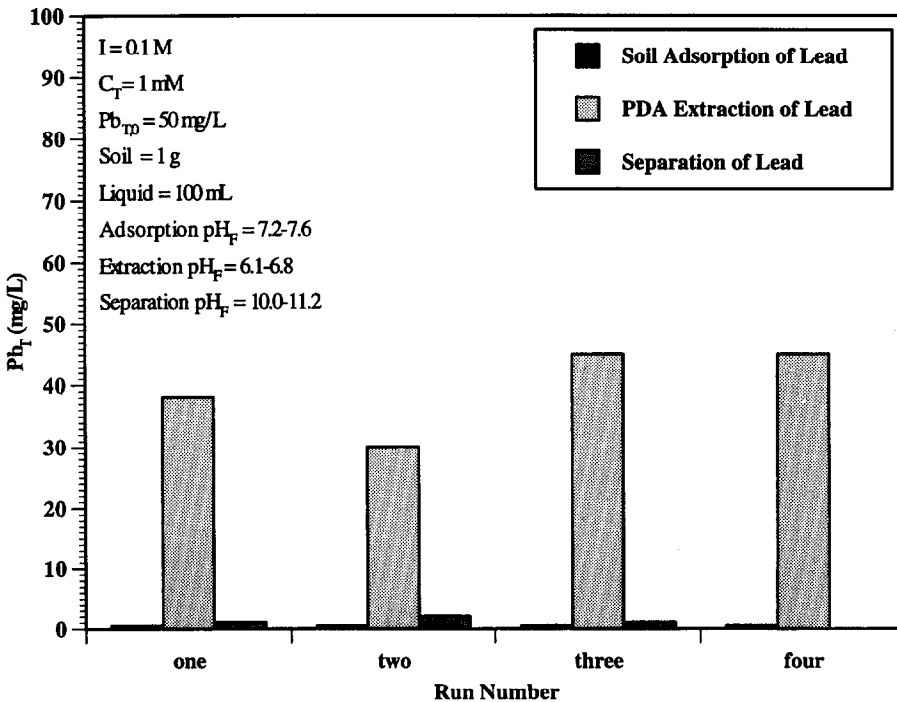


Fig. 12. Effectiveness of PDA extraction of lead from freshly spiked soils during successive tests.

is accomplished during the separation process and that separation was achieved solely by alkalization of the extraction solution with NaOH base. Attempts to separate the Pb–EDTA complex using similar procedures for Pb–PDA failed to recover the metal.

4. Conclusion

As predicted by equilibrium calculations, PDA is effective as a lead solubilizing agent. The effectiveness of PDA has been demonstrated for various conditions. PDA rapidly extracts a high percentage of the sorbed lead from a spiked soil across a broad pH range with little regards to the total carbonate concentration, competing cations, or the aging of the spiked soil. In addition, PDA compares favorably with EDTA as a lead-mobilizing agent, while remaining superior to EDTA in releasing the extracted lead. Finally, the reuse of PDA has been demonstrated.

References

- [1] J.A. Oyler, Remediation of metals-contaminated site near a smelter using sludge/fly ash amendments, in: Proc. 44th Purdue Industrial Waste Conf., Lewis, Chelsea, Michigan, 1990, pp. 75–82.
- [2] M. Trnovsky, J.P. Oxer, R.J. Rudy, M.J. Hanchak and B. Hartsfield, Site remediation of heavy metals contaminated soils and groundwater at a former battery reclamation site in Florida, in: R. Abbou (Ed.), *Hazardous Waste: Detection, Control, Treatment*, Elsevier, Amsterdam, 1988, pp. 1581–1590.
- [3] J.R. Werther, R. Hillgardt and H. Kröning, Sand from dredge sludge – development of processes for the mechanical treatment of dredged material, presented at the First Int. TNO Conf. on Contaminated Soil, Utrecht, The Netherlands, 1985, pp. 887–889.
- [4] E.W. Dienemann, Goldfarb and R.C. Ahlert, Evolution of the Superfund remedy selection process, including an assessment of implementation of permanent and alternative remedial technologies, *Environ. Prog.*, 11 (1992) 165–172.
- [5] J.W. Assink, Extractive methods for soil decontamination: a general survey and review of operational treatment installations, presented at the First Int. TNO Conf. on Contaminated Soil, Utrecht, The Netherlands, 1985, pp. 887–889.
- [6] H.E. Allen and P.H. Chen, Remediation of metal contaminated soil by EDTA incorporating electrochemical recovery of metal and EDTA, *Environ. Prog.*, 12 (1993) 284–293.
- [7] G.A. Brown and H.A. Elliott, Influence of electrolytes on EDTA extraction of Pb from polluted soil, *Water, Air, Soil Pollut.*, 62 (1992) 157–165.
- [8] H.A. Elliott and G.A. Brown, Comparative evaluation of NTA and EDTA for extractive decontamination of lead polluted soils, *Water, Air, Soil Pollut.*, 45 (1989) 361–369.
- [9] H.A. Elliott, J.H. Linn and G. Shields, Role of Fe in extractive decontamination of Pb-polluted soils, *Hazard. Waste Hazard. Mater.*, 6 (1989) 223–229.
- [10] R.W. Peters and L. Shem, Use of chelating agents for remediation of heavy metal contaminated soil, *Environmental Remediation*, American Chemical Society, 1992, pp. 70–84.
- [11] J. Slavek and W.F. Pickering, Extraction of metal ions sorbed on hydrous oxides of iron (III), *Water, Air, Soil Pollut.*, 28 (1986) 151–162.
- [12] A. Hong, T.C. Chen and R.W. Okey, Extraction of heavy metals from contaminated soils using selected chelates, in: Proc. 66th Ann. Conf. and Exposition of the Water Environment Federation, Vol. 5, Hazardous Wastes and Groundwater, Anaheim, California, 1993, pp. 171–182.

- [13] A. Hong, T.C. Chen and R.W. Okey, Chelating extraction of zinc from soils using n-(2-acet-amido)iminodiacetic acid, in: 1993 Special Symp., Vol. III, The 5th ACS Ann. Symp. on Emerging Technologies in Hazardous Waste Management, Atlanta, Georgia, 1993, pp. 788–791.
- [14] A. Hong, T.C. Chen and R.W. Okey, Chelating extraction of copper from soil using S-carboxymethyl-cysteine, *Water Environ. Res.*, 1994, in press.
- [15] American Society for Testing and Materials, Annual Book of ASTM Standards, ASTM, 1991.
- [16] USBR Procedure for determining moisture, ash, and organic content of soil, in: Earth Manual 1990, United States Department of the Interior Bureau of Reclamation, Denver, USBR 5430-89, 1989.
- [17] J.D. Allison, D.S. Brown and K.J. Novo-Gradac, Minteqa2/Prodefa2, a Geochemical Assessment Model for Environmental Systems: Version 3.0. User's Manual, EPA/600/3-91/021, 1991.
- [18] A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 1: Amino Acids, Plenum, New York, 1974, p. 377.
- [19] W. Stumm and J.J. Morgan, *Aquatic Chemistry*, Wiley, New York, 1981, pp. 341–345.