



Chelating extraction of lead and copper from an authentic contaminated soil using N-(2-acetamido)iminodiacetic acid and S-carboxymethyl-L-cysteine

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Abstract

Heavy metal contamination of soil is common at many hazardous waste sites in many industrialized nations. Lead, chromium, cadmium, copper, zinc, and mercury are most often encountered at elevated concentrations. The extraction of heavy metals using selected chelating agents is seen as a remediation technique. In this study, we examined the chelating extraction and recovery of lead and copper from an authentic contaminated soil using S-carboxymethyl-L-cysteine (SCMC) and N-(2-acetamido)iminodiacetic acid (ADA) as a function of contact time, pH, ligand concentration, soil suspension, and number of consecutive runs. The results suggested that the chelators effectively extracted lead and copper from the contaminated soil, with ADA particularly effective for lead, the major contaminant of the soil. The chelators were recovered and reused over consecutive runs with no loss in performance. The extraction effectiveness depended on chelator concentration but not on pH or solid contents of the suspension. Major findings from this study of an authentic soil were consistent with our previous efforts in the extraction of heavy metals from spiked soils.

1. Introduction

Heavy metal contamination of soil is a common problem encountered at many hazardous waste sites in many countries of the industrialized world. Lead, chromium, cadmium, copper, zinc, and mercury are among the most frequently observed metal contaminants. In numerous National Priority List sites, they have been found to be at elevated concentrations. Activities contributing to heavy metal contamination of soil include vehicle emission, mining, smelting, metal plating/finishing, battery production recycling, agricultural/industrial chemical application, and incineration processes. Heavy metals are toxic to people and pose a great risk for safe groundwater supply.

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Once released into the soil matrix, most heavy metals are strongly retained. Thus, their adverse impact on environmental quality and on human health can and often does persist for substantial periods.

Chelating extraction of heavy metals from contaminated soils is seen as a treatment method. Although sorption studies of metals to mineral solid phases in the presence of synthetic or naturally occurring chelating agents have been conducted over the past two decades, the application of chelators in extracting heavy metals from contaminated soils as a treatment has been relatively recent. Only a few chelators, e.g., EDTA and NTA, have been studied for this application [1–7]. However, the choice of ligands for decontamination purpose appeared to be limited and somewhat haphazard; the separation of metals from the ligand after extraction was difficult and had not been adequately addressed. There is a need to assess the full potential of this technology in removing and/or recovering heavy metals from contaminated media, e.g., soils and mine tailings ponds. We had developed a methodology based on equilibrium chemical modeling to assess the application potential of chelating agents, and we reported the evaluation results of 200 chelating agents for the extraction of the six aforementioned heavy metals [8]. Based on these efforts, we chose three different ligands and successfully extracted and recovered cadmium, copper, lead, and zinc from spiked soils and were able to reclaim and reuse the ligands [9–12].

The extraction and recovery of lead and copper from an authentic contaminated soil using two selected chelators, N-(2-acetamido)iminodiacetic acid (ADA) and S-carboxymethyl-L-cysteine (SCMC), are reported here. This study illustrated that by choosing the proper ligand, heavy metals of interest could be extracted from contaminated soils and, more importantly, the metals could be readily recovered and the chelator reused. Furthermore, the chosen ligands appeared to preferentially complex with intended heavy metals over competing ambient cations. Lead and copper were recovered as metal hydroxides or hydroxy-carbonates upon raising the pH while the chelators remained in solution.

2. Experimental

2.1. Materials and analytical methods

S-Carboxymethyl-L-cysteine (SCMC), $C_3H_9NO_4S$, and N-(2-Acetamido)iminodiacetic acid (ADA), $C_6H_{10}N_2O_5$, were used as received (Fluka). Deionized water from a Milli-Q system (Millipore) was used throughout. Ionic strength (I) was maintained with $NaClO_4$ (Aldrich). Total carbonate content (C_T) was added with $NaHCO_3$ (Mallinckrodt). Calcium ion was added with $Ca(NO_3)_2 \cdot 4H_2O$ (Aldrich). Solution pH was adjusted with 3 N HNO_3 and 2 N $NaOH$ (Mallinckrodt). Batch reactors of 125 ml glass Erlenmeyer flasks were used in all extraction procedures. Glass flasks showed result no different from polyethylene flasks. All glassware and sampling bottles were cleaned by immersion in 6 N HNO_3 for 12 h and rinsed with deionized water prior to use. During sequential extraction procedures of metal analyses, KNO_3 , Na_2EDTA (disodium salt of EDTA), $NaOH$, and HNO_3 were used.

All experiments were conducted at the room temperature of 22 ± 1 °C. Aliquots were withdrawn from reaction mixtures, filtered through a 0.45 μm cellulose nitrate membrane filter (Micro filtration systems), acidified with HNO_3 , then analyzed for the total dissolved metal concentrations (as Me_T or Me_q). Metal analyses were performed with an atomic absorption (AA) spectrometer (Perkin Elmer model 280) using ASTM methods D1068, D1691, D1886, D1688, D3557, and D3559 for Fe, Zn, Ni, Cu, Cd, and Pb, respectively [13]. All equilibrium calculations were performed using the Minteqa2 computer program [14] with input equilibrium constants as listed in Tables 1 and 2.

2.2. Soil preparation and characterization

The heavy metals contaminated soil was collected from a polluted site, air-dried for one month, and passed through a 2-mm sieve. Experiments in quadruplicate were performed to analyze the metals: 5 g of soil was added to 100 ml of 3 N HNO_3 solution; the mixture was shaken for 24 h. Aliquots were taken and analyzed for Cd, Cu, Fe, Ni, Pb, and Zn contents. Lead, copper, and iron contents were found to be higher than 100 ppm (mg Me/kg Soil). A sequential extraction procedure was followed to determine the various forms of metals in the soil [15]. The organic content of the soil fraction that passed through a 0.147-mm sieve was determined [16]. The soil characteristics are summarized in Tables 3 and 4.

2.3. Metal extraction, recovery, and ligand reuse

Typically, metals extraction was conducted in a batch reactor containing 100 ml of a ligand solution (L_T) with $C_T = 1 \text{ mM}$, $I = 0.1 \text{ M}$. The pH was adjusted as necessary manually with 2 N NaOH or 3 N HNO_3 , then a desired amount of soil was added. The suspension was agitated with a gyratory shake table (New Brunswick scientific co., model G2) operating at 260 rpm. After a 12-h equilibration period, aliquots were withdrawn from the mixture and analyzed for dissolved metal contents. An extracted metal amount was expressed either as a total dissolved metal concentration (Me_T ; mg/l), or as a weight ratio to the soil (Me_q ; mg Me/kg soil). Following extraction and sampling, HNO_3 was added at 2 N to the suspension, then extraction was continued for 2 h before another aliquot was analyzed to determine the total metal loadings (Pb, Cu, and Fe) of the soil batch.

In studying metal recovery, the extract containing the metal–ligand complexes was separated from soil by centrifugation for 15 min at 3000 rpm. After determining the metal contents, the solution pH was gradually adjusted to a predetermined value. The solution was allowed to stand for 12 h before it was analyzed for various metal concentrations again.

Chelating agents were recovered and reused during consecutive extraction runs. The experimental procedure included metals extraction from soil, centrifugation for soil separation, pH adjustment for metal precipitate formation, vacuum filtration for precipitate separation, adjustment of ligand solution to pH 6, and application of the reclaimed ligand solution to a fresh soil batch. The procedure was repeated three more times.

Table 1
Equilibrium reactions of lead in a carbonate-bearing water [17]

Equilibrium reaction	log K, 25 °C, I = 0
$\text{PbO (s, red)} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.3
$0.5\text{Pb}_2\text{O(OH)}_2 \text{ (s)} + 0.5\text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-14.9
$\text{PbO (s, yellow)} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.1
$\text{PbCO}_3 \text{ (s)} = \text{Pb}^{2+} + \text{CO}_3^{2-}$	-13.13
$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 \text{ (s)} = 3\text{Pb}^{2+} + 2\text{OH}^- + 2\text{CO}_3^{2-}$	-43.8 ^a
$\text{Pb}_{10}(\text{CO}_3)_6(\text{OH})_6\text{O (s)} + 8\text{H}^+ = 10\text{Pb}^{2+} + 6\text{CO}_3^{2-} + 7\text{H}_2\text{O}$	-8.76
$\text{Pb}^{2+} + \text{OH}^- = \text{PbOH}^+$	6.4
$\text{Pb}^{2+} + 2\text{OH}^- = \text{Pb(OH)}_2^0$	10.9
$\text{Pb}^{2+} + 3\text{OH}^- = \text{Pb(OH)}_3^-$	13.9
$\text{Pb}^{2+} + 4\text{OH}^- = \text{Pb(OH)}_4^{2-}$	19.3
$2\text{Pb}^{2+} + \text{OH}^- = \text{Pb}_2\text{OH}^{3+}$	7.6
$3\text{Pb}^{2+} + 4\text{OH}^- = \text{Pb}_3(\text{OH})_4^+$	32.1
$4\text{Pb}^{2+} + 4\text{OH}^- = \text{Pb}_4(\text{OH})_4^+$	36.0
$6\text{Pb}^{2+} + 8\text{OH}^- = \text{Pb}_6(\text{OH})_8^+$	68.4
$\text{Pb}^{2+} + \text{CO}_3^{2-} = \text{PbCO}_3^0$	5.4 ^a
$\text{Pb}^{2+} + 2\text{CO}_3^{2-} = \text{Pb}(\text{CO}_3)_2^{2-}$	8.86 ^a
$\text{Pb}^{2+} + \text{HCO}_3^- = \text{PbHCO}_3^+$	2.9
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	14.0
$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.33
$\text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3^0$	6.35
$\text{H}^+ + \text{EDTA}^{4-} = \text{HEDTA}^{3-}$	11.01
$\text{H}^+ + \text{HEDTA}^{3-} = \text{H}_2\text{EDTA}^{2-}$	6.32
$\text{H}^+ + \text{H}_2\text{EDTA}^{2-} = \text{H}_3\text{EDTA}^-$	2.54 ^b
$\text{H}^+ + \text{H}_3\text{EDTA}^- = \text{H}_4\text{EDTA}^0$	2.2 ^b
$\text{H}^+ + \text{H}_4\text{EDTA}^0 = \text{H}_5\text{EDTA}^+$	1.5 ^b
$\text{H}^+ + \text{H}_5\text{EDTA}^+ = \text{H}_6\text{EDTA}^{2+}$	0.6
$\text{Pb}^{2+} + \text{EDTA}^{4-} = \text{PbEDTA}^{2-}$	18.0 ^b
$\text{PbEDTA}^{2-} + \text{H}^+ = \text{PbHEDTA}^-$	2.4 ^c
$\text{PbHEDTA}^- + \text{H}^+ = \text{PbH}_2\text{EDTA}^0$	1.7 ^c
$\text{PbH}_2\text{EDTA}^0 + \text{H}^+ = \text{PbH}_3\text{EDTA}^+$	1.2 ^c
$\text{H}^+ + \text{SCMC}^{2-} = \text{HSCMC}^-$	8.89 ^b
$\text{H}^+ + \text{HSCMC}^- = \text{H}_2\text{SCMC}^0$	3.36 ^b
$\text{H}^+ + \text{H}_2\text{SCMC}^0 = \text{H}_3\text{SCMC}^+$	1.99 ^b
$\text{Pb}^{2+} + \text{SCMC}^{2-} = \text{PbSCMC}^0$	5.78 ^c
$\text{PbSCMC}^0 + \text{H}^+ = \text{PbHSCMC}^+$	4.70 ^c
$\text{PbOHSCMC}^- + \text{H}^+ = \text{PbSCMC}^0 + \text{H}_2\text{O}$	9.60 ^c
$\text{H}^+ + \text{ADA}^{2-} = \text{HADA}^-$	6.84
$\text{H}^+ + \text{HADA}^- = \text{H}_2\text{ADA}^0$	2.3 ^b
$\text{Pb}^{2+} + \text{ADA}^{2-} = \text{PbADA}^0$	8.4 ^d
$\text{Pb}^{2+} + 2\text{ADA}^{2-} = \text{Pb(ADA)}_2^{2-}$	10.64 ^d

^a 25 °C, I = 0.3.

^b 25 °C, I = 0.1.

^c 25 °C, I = 1.0.

^d 20 °C, I = 0.1.

Table 2
Equilibrium reactions of copper in a carbonate-bearing water [17]

Equilibrium reaction	log K, 25 °C, I = 0
$\text{CuO (s)} + \text{H}_2\text{O} = \text{Cu}^{2+} + 2\text{OH}^-$	-20.35
$\text{Cu(OH)}_2 \text{ (s)} = \text{Cu}^{2+} + 2\text{OH}^-$	-19.32
$\text{CuCO}_3 \text{ (s)} = \text{Cu}^{2+} + \text{CO}_3^{2-}$	-11.5
$\text{Cu}_2(\text{OH})_2\text{CO}_3 \text{ (s)} = 2\text{Cu}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-}$	-33.3
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 \text{ (s)} = 3\text{Cu}^{2+} + 2\text{OH}^- + 2\text{CO}_3^{2-}$	-44.9
$\text{Cu}^{2+} + \text{OH}^- = \text{CuOH}^+$	6.3
$\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu(OH)}_2^0$	11.8
$\text{Cu}^{2+} + 3\text{OH}^- = \text{Cu(OH)}_3^-$	14.5 ^a
$\text{Cu}^{2+} + 4\text{OH}^- = \text{Cu(OH)}_4^{2-}$	15.6 ^a
$2\text{Cu}^{2+} + \text{OH}^- = \text{Cu}_2\text{OH}^{3+}$	8.2 ^b
$2\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}_2(\text{OH})_2^{2+}$	17.4
$3\text{Cu}^{2+} + 4\text{OH}^- = \text{Cu}_3(\text{OH})_4^{3+}$	35.2
$\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3^0$	6.77
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} = \text{Cu(CO}_3)_2^{2-}$	10.2
$\text{Cu}^{2+} + \text{HCO}_3^- = \text{CuHCO}_3^+$	1.8
$\text{Cu}^{2+} + \text{SCMC}^{2-} = \text{CuSCMC}^0$	8.15 ^c
$\text{CuSCMC}^0 + \text{H}^+ = \text{CuHSCMC}^+$	2.97 ^c
$\text{Cu}^{2+} + 2\text{SCMC}^{2-} = \text{Cu(SCMC)}_2^{2-}$	15.24 ^a
$\text{Cu}^{2+} + \text{ADA}^{2-} = \text{CuADA}^0$	9.70 ^c
$\text{Cu}^{2+} + 2\text{ADA}^{2-} = \text{Cu(ADA)}_2^{2-}$	12.8 ^c
$\text{Cu(H}_{-1}\text{ADA)}^- + \text{H}^+ = \text{Cu(ADA)}^0$	7.96 ^c
$\text{CuOH(H}_{-1}\text{ADA)}^{2-} + \text{H}^+ = \text{Cu(H}_{-1}\text{ADA)}^-$	10.08 ^c
$\text{Cu}^{2+} + \text{EDTA}^{4-} = \text{CuEDTA}^{2-}$	18.78 ^c
$\text{CuEDTA}^{2-} + \text{H}^+ = \text{CuHEDTA}^-$	3.1 ^c
$\text{CuHEDTA}^- + \text{H}^+ = \text{CuH}_2\text{EDTA}^0$	2.0 ^c
$\text{CuOHEDTA}^{3-} + \text{H}^+ = \text{CuEDTA}^{2-}$	11.4 ^c

^a 25 °C, I = 1.0.

^b 25 °C, I = 3.0.

^c 25 °C, I = 0.1.

Table 3
Characteristics of the authentic contaminated soil

Parameter	Value	Procedure
Soil pH	8.1 in water 7.3 in 0.01 M CaCl ₂	Ref. [18]
Organic content (<0.147 mm)	1.1%	Ref. [16]
Metals		3 N HNO ₃ ; 24 h
Pb _{q,tot}	6324 ± 3023 ppm	
Cu _{q,tot}	188 ± 137 ppm	
Fe _{q,tot}	5438 ± 420 ppm	
Zn _{q,tot}	74.5 ± 26.8 ppm	
Ni _{q,tot}	32.4 ± 11.4 ppm	
Cd _{q,tot}	4.7 ± 3.7 ppm	

Table 4
Various fractions of Pb, Cu, and Fe in the contaminated soil [15]

Fraction	Pb _{q, TOT} (ppm)	Cu _{q, TOT} (ppm)	Fe _{q, TOT} (ppm)
Exchangeable	18.2 ± 2.1	1.2 ± 0.4	2.7 ± 0.4
Adsorbed	71.6 ± 18.0	3.3 ± 1.0	11.2 ± 3.4
Organic	769.6 ± 154	12.6 ± 4.8	7.2 ± 1.0
Carbonated	720.6 ± 129	40.2 ± 8.9	44.5 ± 1.6
Residual/sulfide	906.5 ± 332	124.9 ± 132	9287.6 ± 3502
Total	2486.4 ± 497	182.2 ± 142.5	9353.2 ± 3503

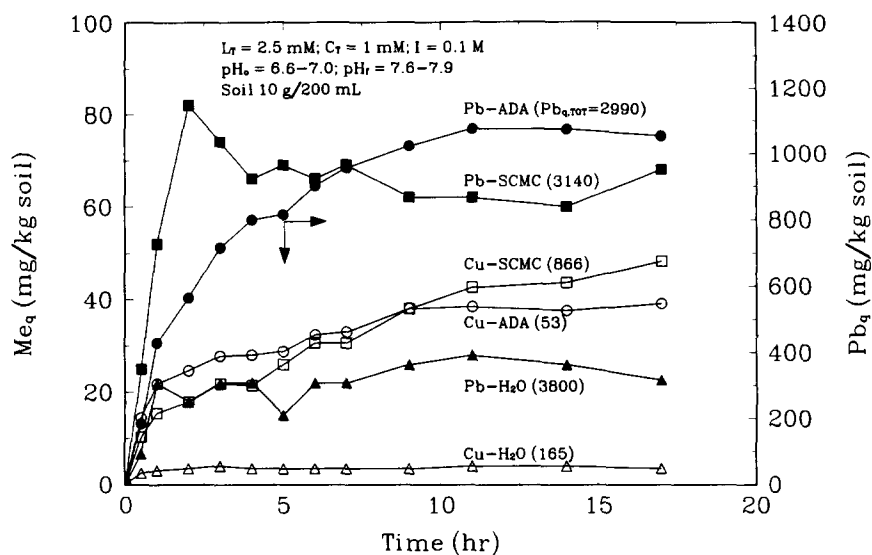


Fig. 1. Chelating extraction of lead and copper from the contaminated soil using ADA and SCMC as compared to water as a function of time.

3. Results and discussion

The extraction and recovery of lead and copper from the contaminated soil was studied according to contact time, pH, ligand concentration, soil suspension, number of consecutive runs. The extraction results were consistent with calculated solubilities of the metals at various pH, and calculated solubilities as enhanced by the presence of chelators.

Fig. 1 shows the concentration versus time profiles of lead and copper as they were extracted from the soil using either ADA, SCMC, or water only. All extractions were carried out at pH between 6.5 and 8. Washing the metal-contaminated soil with water is not effective as confirmed by the two lowest lying curves in the figure. ADA was

more effective than SCMC in extracting Pb by over one order of magnitude; while both chelators extracted copper about equally well. In one washing cycle, ADA was able to extract 30% of the total Pb from the contaminated soil, i.e., 1100 ppm out of 2990 ppm. The extraction reached equilibrium in about 12 h. At 17 h, HNO₃ was added at 2 N to extract the remaining metals in soil and these were taken as the total available amounts in the contaminated soil, indicated as Pb_{q,TOT}, or Cu_{q,TOT}. The large differences in Pb_{q,TOT} (or in Cu_{q,TOT}) were indicative of the heterogeneous nature of lead (or copper) distribution among individual 10-g samples, as each batch contained 10 g soil in 200 ml liquid.

After extraction equilibrium was established (about 12 h), the extract was analyzed for other metals. The Fe, Zn, Ni, and Cd contents were found to be 25, 10, 6.0, <0.1 mg Me/kg soil, respectively, for the ADA extract; and 11, 4.0, 6.0, <0.1 mg Me/kg soil, respectively, for the SCMC extract; and 5, 0.6, <0.01, <0.1 mg Me/kg soil, respectively, for water only.

Fig. 2 shows the extraction of lead as a function of pH and concentrations of chelators. The extractions were approximately equal with little influence by pH between 5 and 9. Very low initial pH values (e.g., 3.0) that were used in some cases did not increase extraction, because the high initial acidity was neutralized by the soil buffering capacity or the increase was small compared to the chelator-enhanced solubilization of metals. Fig. 2 also shows increased extraction according to increased chelator concentration as expected; however, ADA was superior to SCMC in lead extraction even at a lower ligand concentration.

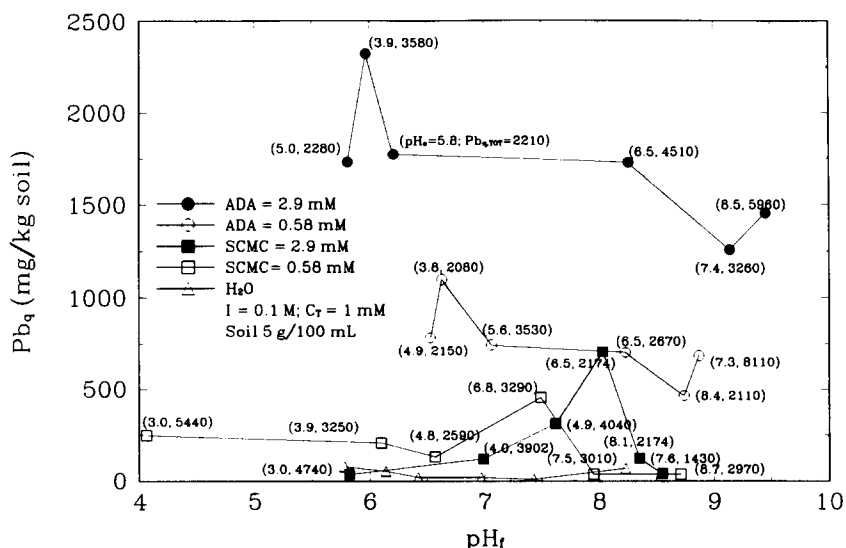


Fig. 2. Chelating extraction of lead using ADA and SCMC as a function of final pH and ligand concentration.

Fig. 3 shows the extraction of copper as a function of pH and concentrations of chelators. Increased extractions were observed for increased chelator concentrations as expected. ADA appeared to be slightly better than SCMC in copper extraction. The extraction remained essentially constant over a broad equilibrium pH despite very low initial pHs in some cases.

Table 5 shows the extraction results as the soil suspension was varied from light (5%) to heavy (50%). The extractions were equally effective for all solid loadings studied. The relative chelating strengths of ADA and SCMC toward Pb and Cu were consistent with those exhibited in previous figures.

Fig. 4 shows the separation of Pb and Cu from the complexes solution after soil extraction. The metals began to form precipitates and to separate from the chelators that remained in solution as the pH was increased. SCMC released lead at about pH 9.2 and copper at pH 11.5 while ADA only slightly released the extracted metals upon pH increase. The addition of Ca ion greatly enhanced the separation; at 10 mM Ca, both chelators allowed the release of metals to form hydroxide precipitates and to separate from solution. The readiness of a chelator to release an extracted metal and facilitate recovery depended on the chelator affinity for the metal. This means that the preference of ADA for Pb also makes it difficult to recover lead after extraction, but this drawback can be easily reversed by adding a benign competing Ca ion.

Fig. 5 demonstrates that the chelators can be recovered and reused over consecutive runs without deterioration in performance. No loss of extraction or recovery efficiency was observed for ADA extraction of lead over four consecutive runs. The enhanced extraction by SCMC might be only due to the heterogeneity among soil batches.

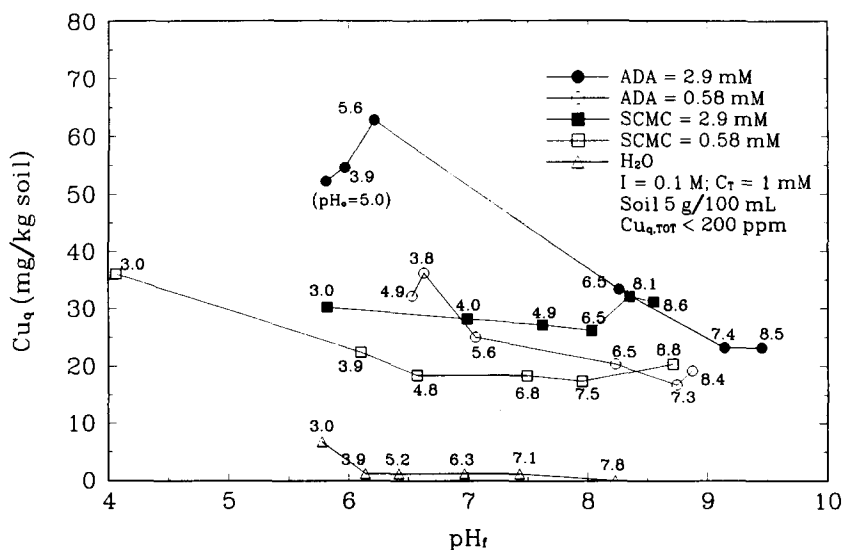


Fig. 3. Chelating extraction of copper using ADA and SCMC as a function of final pH and ligand concentration.

Table 5

Extraction efficiencies of lead and copper by ADA and SCMC as a function of soil suspension concentration

ADA = 3 mM; pH ₀ = 6.2							
Soil (g/100 ml)	5	10	15	20	25	50	
pH _f	6.3	6.9	7.1	7.0	7.4	7.8	
Pb _T (mg/l)	78.7	167.6	162.6	144.8	177.8	198.1	
Pb _q (mg/kg soil)	1574	1676	1084	724	711	396	
Pb _T /L _T (mole ratio)	0.13	0.27	0.26	0.23	0.29	0.32	
Cu _T (mg/l)	1.86	3.41	4.64	5.9	5.28	8.01	
Cu _q (mg/kg soil)	37.2	34.1	31.0	29.5	21.1	16.0	
Cu _T /L _T (mole ratio)	0.01	0.018	0.024	0.031	0.028	0.042	
SCMC = 3 mM; pH ₀ = 6.2							
Soil (g/100 ml)	5	10	15	20	25	50	
pH _f	7.4	7.7	7.9	7.9	7.9	7.9	
Pb _T (mg/l)	11.4	6.1	11.68	5.94	7.99	6.35	
Pb _q (mg/kg soil)	228	61	77.8	29.7	32.0	12.7	
Pb _T /L _T (mole ratio)	0.018	0.01	0.019	0.01	0.013	0.01	
Cu _T (mg/l)	1.38	2.38	4.84	5.26	5.2	9.6	
Cu _q (mg/kg soil)	27.6	23.8	32.3	26.3	20.8	19.2	
Cu _T /L _T (mole ratio)	0.007	0.012	0.025	0.028	0.027	0.05	

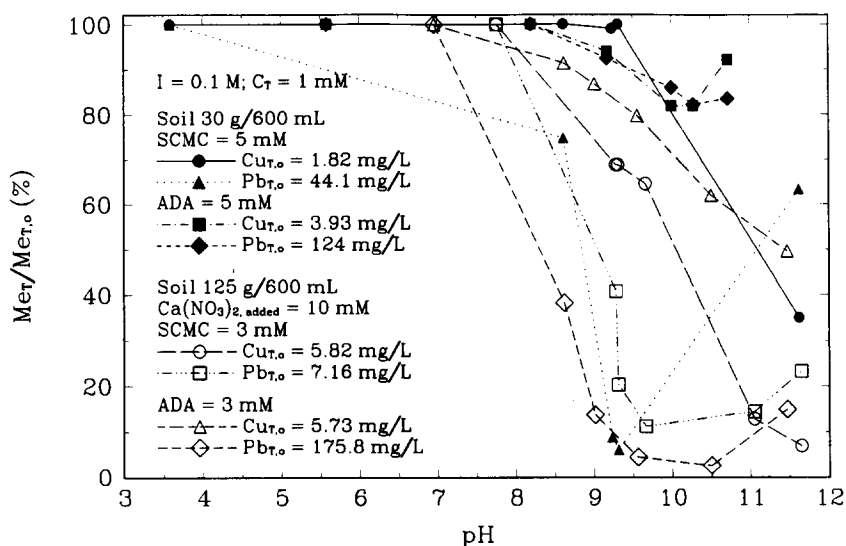


Fig. 4. Separation and recovery of extracted lead and copper from different amounts of ADA and SCMC as a function of pH, with and without the aid of calcium ion.

Fig. 6 shows the computed results of the total lead solubility and lead speciation over a wide pH range; it also shows a comparison of the total lead solubilities as enhanced by the presence of chelators, including ADA, SCMC, and EDTA. The

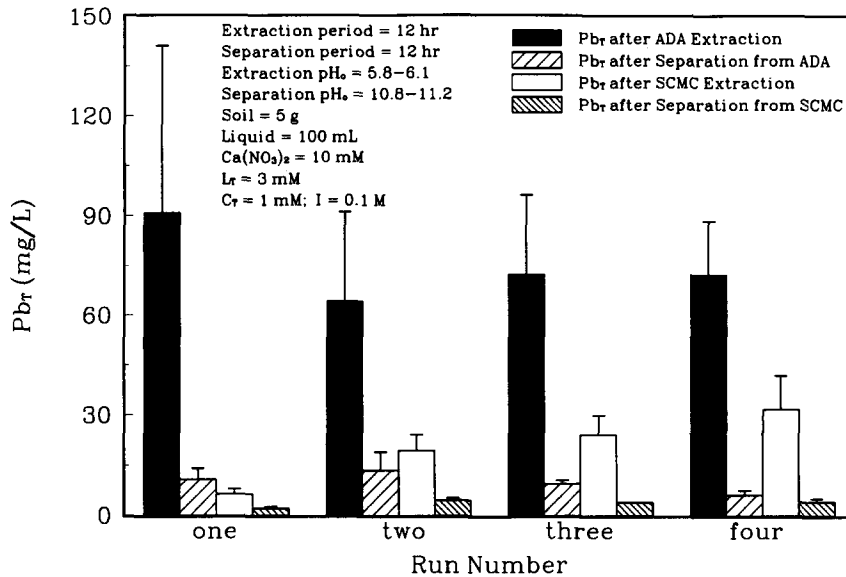


Fig. 5. Extraction of lead from contaminated soil batches using recovered ADA and SCMC during consecutive runs.

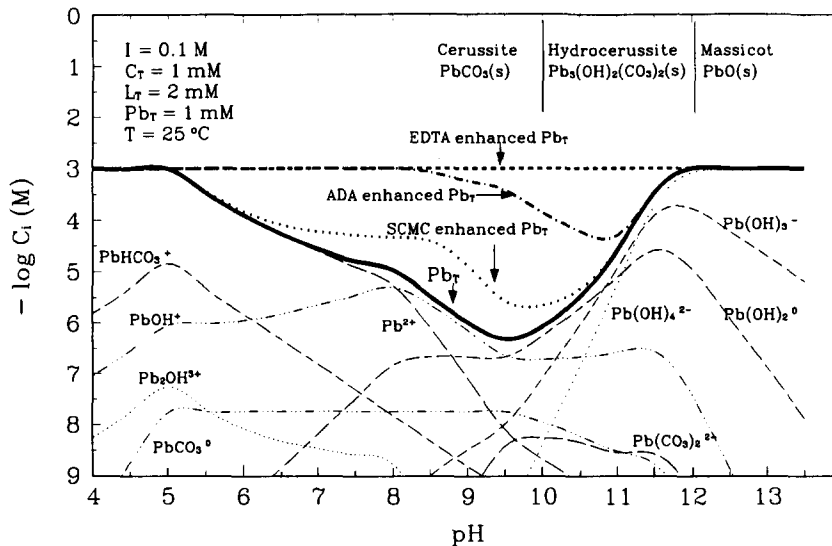


Fig. 6. Speciation and solubility of lead as enhanced by ADA, SCMC, and EDTA over a wide pH range.

calculation was performed with the Minteqa2 computer program using equilibrium constants of Table 1. Fig. 7 shows similar information for the copper system. These figures show that without the help of any chelating agent the solubilities of lead and

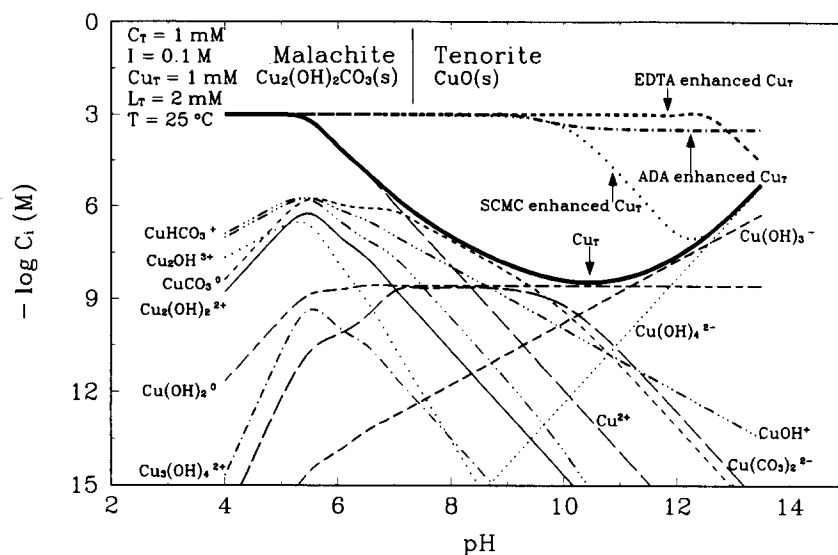


Fig. 7. Speciation and solubility of copper as enhanced by ADA, SCMC, and EDTA over a wide pH range.

copper in natural waters are very low. From Figs. 6 and 7, the Pb_T is between 25 mg/l (or $10^{-3.9} M$) at pH 6 and 0.2 mg/l (or $10^{-6} M$) at pH 9; whereas the Cu_T is between 13 mg/l (or $10^{-3.7} M$) at pH 6 and $1 \mu g$ ($10^{-7.8} M$) at pH 9. This is consistent with water being an ineffective washing medium.

Figs. 6 and 7 compare the relative strengths of EDTA, ADA, and SCMC in solubilizing Pb and Cu. EDTA is the strongest, followed by ADA and then by SCMC. Being most effective, EDTA forms very stable metal-ligand complexes with Pb and Cu. The stabilities of these complexes cannot be suppressed even at high pH, which explains the difficulty and elaborate methods often required for metals recovery in EDTA extraction.

Fig. 6 predicts that ADA solubilizes Pb below pH 8, but this ability quickly diminishes and the chelator will release Pb when pH is raised (e.g., to 9.2). This explains the easy recovery of Pb from the complex solution upon a pH increase. Fig. 6 also predicts that SCMC is less effective than ADA in extracting lead, the SCMC-enhanced Pb_T curve is only slightly higher than the Pb_T curve (with water only).

Fig. 7 predicts that both ADA and SCMC effectively solubilize Cu below pH 9; however, unlike for Pb, the ADA-enhanced Cu_T and SCMC-enhanced Cu_T curves are not suppressed, especially for ADA, until a much higher pH is reached. This explains the experimental observations (Fig. 4) that a higher pH was necessary and less complete metal separation was obtained for copper. The calculation results suggest that SCMC is a better chelating agent for copper extraction application since the subsequent recovery of the metal and the chelator is easier.

3.1. Metal selectivity of chelators

Selectivity of a chelating agent toward the heavy metal is important for heavy metal removal and recovery from soil. The preferential extraction of Pb over other ambient metal such as Fe from the contaminated soil has been consistent with our previous results using soils spiked with Pb and with excess Fe, Al, and Ca [11]. In the present study, both ADA and SCMC prefer complexing with Pb and Cu over indigenous Fe. The selectivity is attributed to the sulfur ligand atom and the nitrogen ligand atom of SCMC and ADA, respectively. It is well known that sulfur- and nitrogen-containing ligands form more stable complexes with soft (heavy) metals than with hard (alkali) metals. The screening and determination of suitable chelating agents for heavy metals remediation have been discussed previously [8-10].

3.2. Pilot-scale operation consideration

The bench-scale chelating extraction of lead and copper from the contaminated soil has been very encouraging that a pilot-scale soil remediation system should be tested. It is anticipated that a countercurrent column, or a stirred tank followed by a countercurrent column would best serve the purpose. Tuin and Tels [19] detailed the process design of extracting metals from contaminated soils in a stirred tank, countercurrent column, and a combination of the two using 0.1 to 0.3 N HCl. The process can be modified for chelating extraction reported in this study by adding metal-chelator separation and chelator recirculation components. Process parameters during extraction are pH, contact time, soil suspension, and chelator concentration. The results indicated that pH and soil suspension were less critical, but an optimum contact time should be determined for a particular soil under treatment. A high chelator concentration is likely desirable for extraction; the maximum concentration may be controlled by the chelator solubility. Therefore, the mass flow rates of the counterflowing extracting liquid and the soil, respectively, must be determined according to the level of contamination, the maximum solubility of the chelator, and the extraction kinetics of the soil batch. During metal-chelator separation, important parameters include pH, residence time, and Ca concentration. Feasible values of some operating parameters can be synthesized from extraction and separation results are reported in this paper.

4. Conclusions

This work has shown that (1) lead and copper could be extracted from contaminated soils using chelating agents ADA and SCMC; (2) the metals could be readily separated and recovered as metal precipitates by simply raising the solution pH; (3) the chelators that remained in solution after separation were successfully reused for further extraction during consecutive runs. The results suggest that ADA is particularly effective for extraction of Pb while SCMC is especially effective for Cu.

The extent of extraction depends on contact time and chelator concentration, but does not depend on extraction pH or soil suspension. The extraction results have been consistent with equilibrium calculations using published thermodynamic constants.

Nomenclature

ADA	N-(2-acetamido)iminodiacetic acid, $C_6H_{10}N_2O_5$
EDTA	ethylenediaminetetraacetic acid, $C_{10}H_{16}O_8N_2$
SCMC	S-carboxymethyl-L-cysteine, $C_5H_9NO_4S$
C_T	total carbonate concentration (M)
I	ionic strength (M)
L_T	total ligand concentration (including all conjugate acid-base forms) (M)
Me	a metal contaminant, e.g., Pb, or Cu, etc.
Me_T	total dissolved metal concentration (M or mg/l)
$Me_{T,0}$	total dissolved metal concentration prior to the start of a process (M or mg/l)
Me_q	total dissolved metal concentration (mg Me/kg soil). For example, in a 5 g/200 ml soil suspension, $Me_q = 600$ mg/kg soil is equivalent to $Me_T = 600 \times 5 \times 10^{-3} / (200 \times 10^{-3}) = 15$ mg/l
$Me_{q,TOT}$	total metal available in the contaminated soil (mg Me/kg soil)
pH_0, pH_F	initial pH, final pH, respectively (#)

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