R&D NOTE

Solvent Extraction of Chromium and Cadmium from Contaminated Soils

Roberto Mauri and Reuel Shinnar
Dept. of Chemical Engineering, The City College of CUNY, New York, NY 10031

Matteo d'Amore, Pierino Giordano, and Angela Volpe
Dept. of Food and Chemical Engineering, University of Salerno, Fisciano, Italy

The most important result of this work is to show that, when extracting metal ions from contaminated soils, water-insoluble chelators have the same yield when they are dissolved in a mostly aqueous, nontoxic solvent solution (e.g., a 99% water–1% ethanol mixture), as when more toxic systems (e.g., a 50% water–50% acetone mixture) are used. In addition, the solvent solution can be composed mainly of water, with only a very small amount (1% in our case) of solvent added to dissolve the complexing agent. These results extend and generalize those presented in Mauri et al. (1997).

One of the most promising methods of separating metal ions is to complex them to a molecule (a ligand or chelator) that exhibits specific binding affinity for a toxic metal, even in the presence of other more benign metals (see the review article by Peters, 1999, and references therein). Because the selectivity of the chelators is critical to the goal of removing the toxic metals from their less toxic counterparts, this approach consists of building a ligand framework that complements the unique characteristics of the toxic metal (size, charge, and shape) while minimizing interactions with nontoxic metals (Smith et al., 1996). Although environmentally benign wet extraction processes have been developed that use aqueous solvent solutions (Rogers et al., 1995; Huddleston et al., 1999), many chelators are water-insoluble, and therefore nonaqueous solvents are required.

Our work on soil remediation is based on the results of our research in the related area of extraction of biological compounds from fermentation broths. Our approach was based on first adding solvents that are soluble with water to extract the solutes, and then phase separating the resulting mixture into two phases by changing either the temperature (Ullmann et al., 1995) or the composition (Gupta et al., 1996) of the system. One of the main results of our research was to show that the extraction yield is much higher and the extraction faster than in conventional solvent extraction processes, due to the fact that the particles to be extracted are more effectively wetted by our water-soluble solvents than by the conventional, mostly water-insoluble ones. In fact, when the particles to be extracted are porous and preferentially wetted by water, conventional solvents cannot penetrate the pores well, resulting in very slow extraction (Gupta et al., 1996).

In this article, we intend to show that the experimental technique described in Gupta et al. (1996) can also be applied to soil remediation from metal ions, since, as most soils contain adsorbed water, their wettability by water-insoluble solvents is rather poor. In fact, to understand where the advantages of this approach lie, let us list some of the problems encountered in soil remediation by solvent extraction.

Most of the compounds that form stable complexes with metal ions are only weakly soluble in water, and preferentially adsorb on soil. The low solubility of both ions and complexing agents in water makes water an unsuitable extractant. Now, more powerful solvents can be used instead, that can better dissolve the complexing agents; however, as most of these solvents are insoluble in water, they do not wet the soil particles well, so their extraction yield is low. Water-insoluble solvents that, at the end of the extraction process, have remained in the soil must be removed. This can be very expensive in the treatment of excavated soils and sediments, and prohibitively difficult for *in situ* processes. On the other hand, water-soluble solvents can be easily removed through a water wash.

Experimental Results

In our process the contaminants were selectively extracted by contacting the soil with the carrier solvent in which the appropriate chelating agents had been dissolved. Our main innovation was the use of an environmentally acceptable, water-soluble carrier solvent, such as ethanol, showing that the

---

Correspondence concerning this article should be addressed to R. Mauri at this current address: Dept. of Chemical Engineering, DICCISM, University of Pisa, 56126 Pisa, Italy.

Table 1. Characterization of the Vesuvian Soil

pH (1/2.5 soil/water)	7.8
Composition (% by wt.)	
Organic carbon:	15.6
Silicon:	20
Aluminum:	10
Iron:	7
Size Distribution (% by wt.):	
Coarse (0.2–2 mm)	51.9
Fine (0.002–0.2 mm)	28.6
Silt (0.0002–0.002 mm)	9.7
Clay (< 0.0002 mm)	9.8

carrier solvents themselves do not have to be good solvents of the contaminants. In fact, their main purpose is to carry with them appropriate chelating agents that, being soluble in the solvent mixture, can first penetrate the pores in the soil, and then form complexes with the contaminants that thereby can be washed out of the soil.

Extraction of chromium

Chromium was extracted from a volcanic soil typical of the region near Salerno, Italy, which we will refer to as Vesuvian soil, and whose mineralogical analysis is reported in Table 1. Diphenylcarbazide was used as both chelating agent and photometric indicator. As indicated in Cheng et al. (1982), chromium, which in dilute water solutions forms the chromate anion $(CrO_4)^{2-}$, in the presence of diphenylcarbazide first reduces from Cr(VI) to Cr(III) and then reacts, forming a chelate cation. Since this intensely colored soluble Cr(III) chelate cation presents absorption spectra with a 550-nm peak, we used it to calibrate a spectrophotometer and determine the chromium concentration (see Mauri et al., 1997, for details).

At first, we used a solvent solution composed of 50% water and 50% acetone, in which we dissolved an appropriate amount of diphenylcarbazide, so that the number of moles of the extractant was, in every test, about five times larger than that of the chromium ions. Then we showed that more benign solvents, such as ethanol, can be used in very small amounts (i.e., less than 1%) without experiencing any reduction of the extraction yield, thereby showing that the role of the solvent mixture is simply to transport the chelator within the soil.

Experimental runs were performed through the following steps.

Soil Contamination. The soil was spiked by adding 50 mL of a water solution of potassium dichromate ($K_2Cr_2O_7$) containing 20 ppm of chromium to each gram of soil and mixing for 3 h. At the end of that time, the chromium concentration in water was measured, revealing that 23% of the chromium was absorbed, corresponding to a 46 ppm chromium contamination. This measurement was repeated five times, obtaining similar results within a 10% error.

Contaminant Extraction. After filtering the soil, we let it dry at ambient conditions, and performed a series of tests using a 50% water–50% acetone (in volume) mixture, containing a quantity of diphenylcarbazide so as to have approximately 5 moles of chelant per each mole of chromium. In Table 2 we report the results obtained by mixing one gram of contaminated soil for 2 h with 20 mL and 40 mL of the extracting solution, containing, respectively, 500 and 1000 ppm of diphenylcarbazide. The results are expressed in terms of the partition coefficient, P, defined as the ratio between the chromium concentration in the extracting solution and that in the soil particles at equilibrium, that is, $P = Cs/Cp$. Here, Cs is the ratio between the mass of the extracted chromium and that of the extracting solution, while Cp is the ratio between the mass of the chromium remaining in the soil and that of the soil itself. Clearly, Table 2 indicates that the partition coefficient is practically constant, equal to about 0.025, independent of the amount of the extracting solution used in the process. These tests were repeated five times, obtaining the same results within a 10% error.

Table 2. Chromium Extracted from 1 g of Dry Soil Using 20 and 40 mL of an Extracting Solution Composed of 50% Water and 50% Acetone, Containing 500 ppm of Diphenylcarbazide

	Cr in Soil Initially	Cr in Soil after Process	Cr Extracted	Cr Extracted	Partition Coeff.
20 mL	0.046 mg	0.0308 mg	0.0152 mg	33%	0.025
40 mL	0.046 mg	0.0234 mg	0.0226 mg	49%	0.024

Blank Extraction. The experiments were repeated, the contaminated soil washed with deionized water. With 20 mL of water added to each gram of contaminated soil, we saw that after mixing for 1 h, only 2% of the chromium was extracted.

Dry vs. Wet Soil. Another set of measurements was performed with wet soil, obtained by soaking each gram of dry contaminated soil with 1.3 mL of water for 1 h. Not surprisingly, we found that the extraction yield improved dramatically, with the partition coefficient increasing from 0.025 to 0.036 (see Table 3). Similar results were reported previously (Hug et al., 1997; Vitale et al., 1997).

Use of Benign Solvent Mixtures. At this point, we investigated how the composition of the solvent mixtures influences the extraction yield, using first a 50% water–50% ethanol, and then a 99% water–1% ethanol solvent solution (pure water is not a feasible solvent, since it does not dissolve diphenylcarbazide), with again a 5-to-1 molar ratio of chelant to chromium. In both cases, we obtained the same results as when using acetonitrile (see Table 3), showing that the role of the solvent solution is solely to carry the complexing agent inside the pores of the soil particles. This is an important result, since it shows that (1) the amount of solvent required to decontaminate the soil is very limited and (2) such solvent

Table 3. Chromium Extracted from 1 g of Wet Soil Using 20 mL of the Extracting Solutions*

	Cr in Soil Initially	Cr in Soil After Process	Cr Extracted	Cr Extracted	Partition Coeff.
(a)	0.046 mg	0.0266 mg	0.0194 mg	42%	0.036
(b)	0.046 mg	0.0264 mg	0.0196 mg	42%	0.036
(c)	0.046 mg	0.026 mg	0.020 mg	40%	0.035

*(a) Fifty % water–50% acetone; (b) 99% water–1% acetone; (c) 99% water–1% ethanol. All cases use a 5-to-1 molar ratio of diphenylcarbazide to chromium.

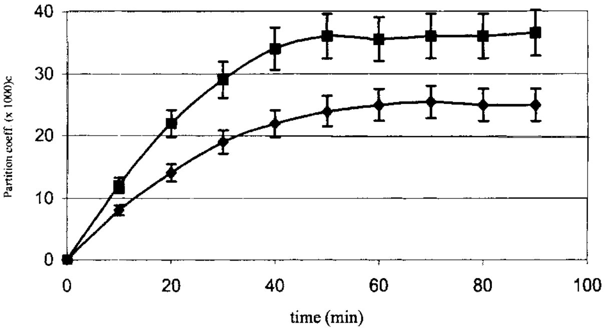

Figure 1. Amount of chromium extracted as a function of time from wet (top) and dry (bottom) soil.

Per each gram of soil, we have used 20 mL of a 99% water–1% ethanol solution, with a 5-to-1 diphenylcarbazide-to-chromium-ions molar ratio.

does not have to be a good solvent of the metal ions at all, and therefore a nontoxic one can be chosen. In fact, in a separate set of experiments we saw that the yield of the process starts to decrease only when the molar ratio between chelant and metal becomes less than 2.

Multiple-Stage Extraction Process. These measurements were repeated in an attempt to mimic a multiple-stage process. To do that, we repeated the extraction process using the soil that had been extracted the previous day and then let dry overnight at ambient conditions. Not surprisingly, we found that the partition coefficient was about the same as for the first extraction.

Kinetics of the Process. The percent of chromium extracted was measured as a function of time, using both dry and wet soil samples, with the extracting solution composed of 99% water and 1% ethanol, and with a 5-to-1 molar ratio of diphenylcarbazide to chromium. The results, plotted in Figure 1, show that, while for dry soils the equilibrium concentration was reached after 60 min, for wet soils the extraction process is somewhat faster. Again, each test was repeated five times, with identical results within a 10% error.

Extraction of cadmium

The extraction of cadmium was performed using an identical procedure as for the extraction of chromium. 1,5-Diphenylthiocarbazone was used as the chelating agent (Cheng et al., 1982), with a 5-to-1 molar ratio of chelant to metal, as before. First, samples of Vesuvian soil were spiked by adding 1 g of soil to 50 mL of a 2 ppm cadmium solution (here we used pure granulated cadmium). Note that, while chromium forms chromate anions, cadmium, like most metals, forms Cd^{2+} cations. After 3 h of stirring, we saw that about 29% of cadmium were absorbed by the soil, corresponding to an 18-ppm cadmium contamination. Then, after a blank extraction, we performed our extraction process using a mixture composed of 99% distilled water and 1% ethanol that contained 2 ppm of 1,5-diphenylthiocarbazone, and found a partition coefficient of about 0.048 for wet soil (see Table 4). As before, this result was unchanged when the percent of ethanol in the extracting mixture was increased to 50% and when ethanol was replaced with acetone.

Table 4. Cadmium Extracted from 1 g of Wet Soil in Two Successive Extractions*

Cd in Soil Initially	Cd in Soil After Process	Cd Extracted	Cd Extracted	Partition Coeff.
0.178 mg	0.089 mg	0.089 mg	50%	0.050
0.089 mg	0.045 mg	0.044 mg	49%	0.047

*Twenty mL of a 99% water–1% ethanol extracting solution, with a 5-to-1 molar ratio of 1,5-diphenylthiocarbazone to cadmium, were used.

Conclusions

Soils contaminated with chromium and cadmium can be remediated first by wetting them with water and then washing them with a 99% water–1% ethanol solution, which contains an appropriate chelator, namely diphenylcarbazide for chromium and 1,5-diphenylthiocarbazone for cadmium, with a 5-to-1 molar ratio between chelant and metal. The metal was extracted with a partition coefficient equal to 0.036 for chromium and 0.048 for cadmium.

The most important result of this work was to show that soil remediation can be accomplished using very "poor," rather benign (ethanol in our case) solvents, in which biodegradable and selective complexing agents have been dissolved. In addition, we showed that the solvent solution can be composed mainly of water, with only a very small amount (1% in our case) of solvent added to dissolve the complexing agent.

Our results can be explained by the fact that, as long as the solvent solutions are water soluble and can dissolve the chelators, their composition has no influence on the extraction yield, since their role is that of carriers of the chelators within the soil. As such, they must be water soluble to penetrate the pores of wet soil particles, but cannot be pure water, because the chelators, in our case, are not water soluble.

Literature Cited

Cheng, K. L., K. Ueno, and T. Imamura, *Handbook of Organic Analytical Reagents*, CRC Press, New York, pp. 253 and 277 (1982).

Gupta, R., R. Mauri, and R. Shinnar, "Liquid-Liquid Extraction Using the Composition-Induced Phase Separation Process," *Ind. Eng. Chem. Res.*, **35**, 2360 (1996).

Hickey, M. G., and Kittrick, J. A., "Chemical Partitioning of Cadmium, Copper, Nickel and Zinc in Soils and Sediments Containing High Levels of Heavy Metals," *J. Environ. Qual.*, **13**, 372 (1984).

Huddleston, J. G., S. T. Griffin, H. D. Willauer, and R. D. Rogers, "Metal Ion Separations in Aqueous Biphasic Systems and Using Aqueous Biphasic Extraction Chromatography," *Metal-Ion Separation and Preconcentration, Progress and Opportunities*, M. L. Dietz, A. H. Bond, and R. D. Rogers, eds., ACS Symposium Series 716, American Chemical Society, Washington, DC, p. 79 (1999).

Hug, S. J., H.-U. Laubscher, and B. R. James, "Iron (III) Catalyzed Photochemical Reduction of Chromium (VI) by Oxalate and Citrate in Aqueous Solutions," *Environ. Sci. Technol.*, **31**, 160 (1997).

Mauri, R., R. Shinnar, M. d'Amore, P. Giordano, and A. Volpe, "Solvent Extraction of Metal Ions from Contaminated Soils," *Proc. Annu. Meeting Air and Waste Management Association*, Toronto (1997).

Peters, R. W., "Chelant Extraction of Heavy Metals from Contaminated Soils," *J. Hazard Mater.*, **66**, 151 (1999).

Rogers, R. D., A. H. Bond, C. B. Bauer, J. Zhang, M. L. Jezl, D. M. Roden, S. D. Rein, and R. R. Chomko, "Metal Ion Separations in Polyethylene Glycol Based Aqueous Biphasic Systems," *Aqueous Biphasic Systems: Biomolecules to Metal Ions*, R. D. Rogers and M. A. Eiteman, eds., Plenum Press, New York, p. 1 (1995).

Smith, P., M. Barr, and R. Barrans, "Separation Chemistry of Toxic Metals," Los Alamos National Laboratory, NM, LA-UR-96-1007 (1996).

Vitale, R. J., G. R. Mussoline, K. A. Rinehimer, J. C. Petura, and B. R. James, "Extraction of Sparingly Soluble Chromate from Soils: Evaluation of Methods and E_h-pH Effects," *Environ. Sci. Technol.*, **31**, 390 (1997).

Ullmann, A., Z. Ludmer, and R. Shinnar, "Phase Transition Extraction Using Solvent Mixtures with a Critical Point of Miscibility," *AIChE J.*, **41**, 489 (1995).

Manuscript received Jan. 10, 2000, and revision received July 6, 2000.