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Laboratory Experiments on the Electrochemical Remediation of the Environment. Part 9: Microscale Recovery of a Soil Metal Pollutant and Its Extractant

Jorge G. Ibanez,*,[†] Patricia Balderas-Hernandez,[‡] Elizabeth Garcia-Pintor,[†] Sandy Nohemi Barba-Gonzalez,[§] Ma. del Carmen Doria-Serrano,[†] Lorena Hernaiz-Arce,[†] Armando Diaz-Perez,[†] and Ana Lozano-Cusi[†]

[†]Centro Mexicano de Quimica Verde y Microescala, Departamento de Ingenieria y Ciencias Quimicas, Universidad Iberoamericana, Prol. Reforma 880, 01219 Mexico, D. F. Mexico

[‡]Facultad de Quimica, Centro Conjunto de Investigacion en Quimica Sustentable UAEM-UNAM, Universidad Autonoma del Estado de Mexico, Carretera Toluca-Atlacomulco, Km 14.5, Toluca, Estado de Mexico, Mexico

[§]Departamento de Quimica, CUCEI, Universidad de Guadalajara, Boulevard Marcelino Garcia Barragan #1451, 44430 Guadalajara, Mexico

S Supporting Information

ABSTRACT: Many soils throughout the world are contaminated with metal salts of diverse toxicity. We have developed an experiment to demonstrate the removal of a metal from an insoluble surrogate soil pollutant, $CuCO_3 \cdot Cu(OH)_2$, by complexation followed by the simultaneous electrochemical recovery of the ligand (i.e., EDTA) and of the metal in its elemental form (i.e., Cu^0). We have calculated speciation diagrams to predict appropriate conditions and to interpret the results.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Environmental Chemistry, Inorganic Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Aqueous Solution Chemistry, Coordination Compounds, Electrochemistry, Microscale Lab

Soils are frequently the depositories of a wide range of wastes[1,2] including atmospheric deposition. Prevention strategies can undoubtedly ameliorate this problem; however, remediation technologies are of immediate urgency in many instances. For example, a site located in a former battery recycling plant contained over 5×10^4 mg Pb/kg of soil.[3]

There are a wide variety of soil remediation technologies based on physical, chemical, electrochemical, or biochemical principles.[4−6] Physicochemical remediation of metal-polluted soils is fundamentally based on two principles:[1−4,7] (i) immobilization of the metal via retention increase by the soil matrix and (ii) removal of the metal from the soil matrix, which involves transfer of metal ions into a washing solution by desorption from the soil followed by dissolution. These washing solutions are frequently composed of acids (mainly hydrochloric, nitric, and sulfuric).[7] High removal yields can be obtained because metal ions tend to be more soluble at low pH values; unfortunately, the soil becomes acidified and this can introduce major alterations in its chemical, physical, and biological properties.

A modern alternative is metal complexation, based on the idea that metal complexes with chelating agents are frequently soluble and generally quite strong (i.e., they possess high stability constants) due to the chelate effect.[8] Even though this complexation approach has less impact on the soil properties than acid washing, it has its own challenges.[9,10] For example, synthetic chelating agents can be difficult to biodegrade and may also remove essential components and nutrients from the soil.[11,12] Ongoing research focuses on the possibility of using natural, biodegradable chelating agents from weak organic acids and their salts (e.g., citrates) that have a lower tendency to form strong chelates with Ca, Mg, and Fe and thus have less impact on soil composition.[13] Once the metal ions are extracted, the next step is to recover the metal and the extracting agent, although this is seldom achieved by *chemical* means. A promising alternative consists of the paired *electrochemical* recovery of both components by the simultaneous electrodeposition of the metal and the liberation of the chelating agent.[3,14]

Because metal carbonates and other derivatives are known to pollute soils,[11] in this qualitative experiment, the metal part of a pollutant (Cu^{2+}) will be extracted from one of its relatively insoluble salts, copper(II) hydroxide carbonate, mixed with silica gel to simulate the siliceous matrices commonly found in natural soil environments. This mixture is treated with either (i) pure water or (ii) a chelating agent (e.g., EDTA) to compare its behavior in both media. Then, Cu^0 (from the resulting CuEDTA solution) is deposited on the cathode of an electrochemical cell, and simultaneously, the EDTA contained in the remaining

Figure 1. U-tube electrochemical cell.

Figure 2. Species distribution diagram for the system: $Cu(II)-CO_3-EDTA-H_2O$ at $[Cu(II)] = 0.030$ M (pCu = 1.52), $[CO_3] = 0.015$ M, (pCO$_3$ = 1.82) and $[EDTA] = 0.50$ M (pEDTA = 0.29). (Note that no carbonated species predominate here.)

solution is precipitated from the anolyte due to its electrochemical acidification (its tetraprotonated form, H_4EDTA is insoluble). This experiment has been used in an applied inorganic chemistry laboratory and is also suitable for introductory environmental chemistry and electrochemistry laboratories; it can be successfully completed in a 1-h lab session.

■ EXPERIMENT AND RESULTS

A solid mixture of $CuCO_3 \cdot Cu(OH)_2$ and SiO_2 (in the form of fine silica gel) is placed in two small beakers: deionized water is added to one and an EDTA solution to the other. These additions form a suspension in both cases, but Cu^{2+} is only dissolved in the second case by formation of an EDTA complex. This latter suspension is filtered. The blue filtrate containing a Cu–EDTA soluble complex is used for the electrochemical recovery of Cu and EDTA in a small U-tube equipped with a Pt wire in one arm (anode) and a graphite rod in the other arm (cathode)[15] (Figure 1). The electrodes are connected through alligator clips to a dc power source (9–18 V). Electrolysis is allowed to proceed for a few minutes until the cathode starts changing color as a result of metal deposition, and a white powder appears at the bottom of the U-tube on the anodic side. At the same time, gas is produced at the anode and the surrounding solution (i.e., the anolyte) becomes acidic. In the solution surrounding the cathode (i.e., the catholyte), a gas (hydrogen) is also produced as a side product; the solution becomes increasingly basic and the blue color becomes paler.

■ HAZARDS

$CuCO_3 \cdot Cu(OH)_2$ is harmful if swallowed and causes irritation to skin, eyes, and respiratory tract. The concentrated acids and bases are corrosive. Chromium(III) sulfate is harmful if swallowed or inhaled and causes irritation to skin, eyes, and respiratory tract.

■ DISCUSSION

The silica gel is insoluble both in water and in the EDTA solution. The subsequent dissolution and reprecipitation phenomena observed in the solution containing Cu(II) and EDTA are better understood in light of the corresponding species distribution diagrams,[16] calculated with the freeware MEDUSA.[17] The lack of solubility of $CuCO_3 \cdot Cu(OH)_2$ in water is due to the fact that under circumneutral conditions its predominant form (see its diagram in the accompanying Supporting Information) is insoluble. Upon EDTA addition, the soluble species $[CuEDTA]^{2-}$ is produced because it
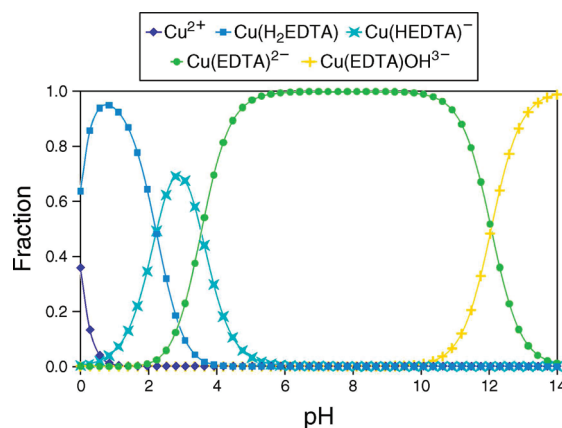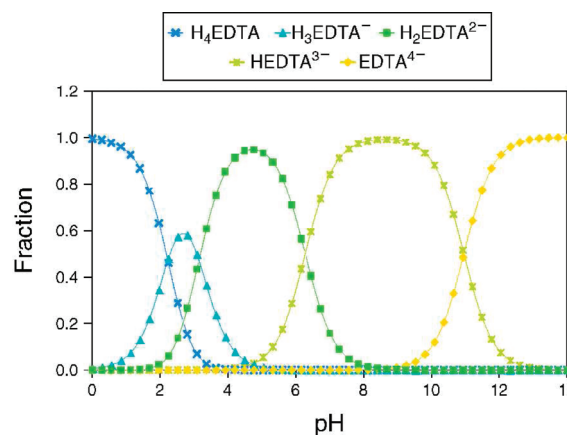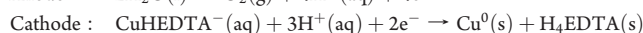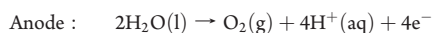

Figure 3. The EDTA distribution diagram.

predominates over a wide pH range (up to ca. 12, see Figure 2). Because this complex is nonelectroactive,[3] the pH must be lowered (to 3–3.5) to have the electroactive monoprotonated chelate $[CuHEDTA]^-$.

The recovery of Cu^0 metal from the solution by cathodic deposition is obvious by visual inspection. This can be explained with the corresponding Pourbaix diagram (see the Supporting Information),[18] whereby the $[CuHEDTA]^-$ is cathodically converted into Cu^0 at pH = 3. At the other side, the anodic oxidation of water produces local acidification and the EDTA (liberated from the Cu–EDTA complex as a result of the removal of Cu^0 by deposition) comes in contact with the protons; this forms the rather insoluble tetraprotonated form (i.e., H_4EDTA, as shown in the species distribution diagram of Figure 3), which precipitates out as a white powder.[19] Part of the EDTA inevitably becomes oxidized.[3] If the solution is removed from the U-tube, a qualitative test involving addition of Cr(III) to the remaining white powder confirms the presence of EDTA by production of the typical Cr–EDTA violet complex.

The crucial electrochemical reactions are thought to be:[20]

Anode : $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode : $CuHEDTA^-(aq) + 3H^+(aq) + 2e^- \rightarrow Cu^0(s) + H_4EDTA(s)$

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The procedure described herein produces a small Cu and EDTA recovery. If a higher recovery were desired, a longer electrolysis time must be allowed.[7,21−23]

CONCLUSIONS

Metal extraction by chelation from a simulated soil pollutant can be performed at the microscale level in a regular laboratory session with an EDTA washing solution. The resulting complex solution is subject to an electrochemical treatment to recover the metal (in its elemental form), as well as the chelating agent (in its tetraprotonated form). Both products are evident by visual inspection. The prediction of the working conditions and the interpretation of results are based on the corresponding predominance and speciation diagrams.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedure; $CuCO_3 \cdot Cu(OH)_2$ species distribution diagram; Cu-EDTA-CO_3 Pourbaix diagram. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jorge.ibanez@uia.mx.

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