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Electroremediation of Mercury Polluted Soil Facilitated by Complexing Agents

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Electroremediation of mercury polluted soil, facilitated by the use of complexing agents, proved to be an attractive alternative treatment for the removal of mercury from polluted soil in mining areas located at Sierra Gorda in Querétaro, Mexico. Implementation of this remediation protocol is expected to improve the living conditions and general health of the population in this region. Experimental observations suggest that it is possible to remove up to 75 % of metal contaminants in mercury polluted soil samples by wetting them with 0.1M EDTA, placing them in an experimental cell equipped with Ti electrodes, and then applying a 5 V electric field for 6 hours. The efficient removal of mercury contaminants observed under these conditions is attributed to electromigration of the coordination complexes that form between the terminal hydroxyl groups in EDTA and divalent mercury (Hg^{+2}), which is probably strengthened by supramolecular interactions between unshared electrons at EDTA's tertiary amino nitrogens and Hg^{+2}. These interactions are particularly effective with the presence of potassium ions. This observation is supported by molecular modeling of several possible interactions in the proposed complex using the Density Functional Theory method (B3LYP LANL2DZ).

Keywords: Mercury, electroremediation, EDTA, DFT calculations.

1. INTRODUCTION

The mining district of San Joaquin is situated in the North of the State of Queretaro at the Southern tip of Sierra Gorda, Sierra Madre Oriental, Mexico. This mineral - rich area is apparently the consequence of hydrothermal processes that have operated in the region for millions of years, which in turn have their origin in the Tertiary magmatism that has been reported [1]. As a result of the use of cinnabar by pre-Hispanic and present day populations, a significant concentration of mercury pollutants are present in the surrounding environment [2].

The present study was specifically directed at remediation of the San Joaquin county, a region where mercury-based mining was probably the most important economic activity up to the 1970's. It was not until the end of 1990's that the mines were abandoned.

Mercury in the environment is a threat to human health because it is a metal with bioaccumulation ability, affecting the brain and central nervous system and resulting in mental impairment [3]. Thus, the need for mercury removal, both from soil and from solid wastes, is evident. In this regard, several accepted methodologies for mercury removal include thermal desorption, phytoextraction, phytovolatilization and, more recently, electroremediation [4 - 5].

Electroremediation has been successfully applied in a variety of soil restoration studies, this methodology having the advantage of exhibiting simultaneous chemical, hydraulic and electrical gradients. Indeed, for efficient mercury removal from a saturated soil with electroremediation, application of either an electric field or direct current through two electrodes (anode and cathode) is required. These are usually inserted in wells containing a supporting electrolyte made from inert salts, leading to improved electric field conductive properties [6 - 8].

Electroremediation has been successfully applied to samples contaminated with radioactive substances, as well as organic compounds such as phenols, trichloroethylene, paraffins, aromatics, naphthoaromatics, petroleum, and polycyclic aromatic hydrocarbons [9].

Furthermore, since electroremediation is a physicochemical technique based on ion transport, it is an excellent tool for the removal of inorganic species, such as As^{+3}, Cl^{-}, NO_3^{-}, SO_4^{-2}, CN^{-}, Zn^{+2}, Cd^{+2}, Ni^{+2}, Pb^{+2}, Cr^{+2}, Cu^{+2}, Fe^{+2}, Ag^{+2}, U^{+2} and Hg^{+2} [5-6], with removal efficiencies reaching 90-99 % in some cases [9].

The main advantages of electroremediation, as compared with other soil treatment procedures, are: [7-11]

(1) Electroosmotic flow is not dependent on either pore or particle size.
(2) Hydraulic gradient is enhanced by electromigration.
(3) Treatment can be applied *in situ*.
(4) It can be applied to low permeability soils.
(5) There is minimal disruption of normal activities at the site.
(6) The required investment is usually lower than that for other conventional treatments.
(7) It can be applied in conjunction with techniques such as pumping, vacuum extraction or bioremediation.

The processes taking place during electroremediation can be classified into two main categories:

a) *Processes occurring as a consequence of the applied electric potential*. These processes include electromigration (ion transport), electroosmosis (mass transport), and electrophoresis (charged particle transport).

b) *Processes occurring in the absence of an electric potential*.

This includes concentration induced processes like diffusion, sorption, complexation, precipitation and acid - base reactions [12].

Specifically, for mercury polluted soil electroremediation, the use of complexing agents like ethylendiaminetetraacetic acid (EDTA), KI, and NaCl under a constant potential gradient has been reported [13-14]. Based on the above precedents, it was decided to apply electroremediation aided by extracting agents for mercury removal from San Joaquin's Sierra Gorda soil samples.

2. METHODOLOGY

2.1. Materials, equipment, and reagents.

The reagents used in this study were high-purity reagents purchased from commercial suppliers and used without further purification. All solutions were prepared with deionized water (Milli-Q grade, with an electrical conductivity of $\cong$ 18 $M\Omega\cdot cm^{-1}$). During the electroanalytical protocol, inert atmosphere was generated using 99.9 % purity N_2. Electronics included a BAS-Epsilon potentiostat and a DC Power Supply as the current source.

2.2. Soil samples.

Soil samples were collected at two representative sites in the San Joaquin area, one far from an old mining site and the other near the site where mining activities took place. The latter presented a mercury concentration of 1800 ppm. The soil is derived from limestone of Upper Cretaceous periods and is classified as Chromic Luvisol [15]. Physical and chemical characteristics are: pH 7.18 (almost neutral), organic carbon content 5.96 % (high), clay loam texture, and 32.00 cmL mg of cation exchange capacity (medium).

2.3.Anodic redissolution voltamperometry mercury detection.

These experiments were carried out in a three electrode cell with a working electrode of glassy carbon (GC), a platinum counter electrode, and a Ag/AgCl electrode as a reference. The supporting electrolyte consisted of a 3 M KCl solution. The GC electrode was polished on a Buehler felt with 1.0, 0.3 and 0.05 μm Al_2O_3 suspensions, with deionized water rinses between each particle size. Following this procedure, residual alumina was removed by sonic cleaning of the GC for 5 min in Milli-Q water.

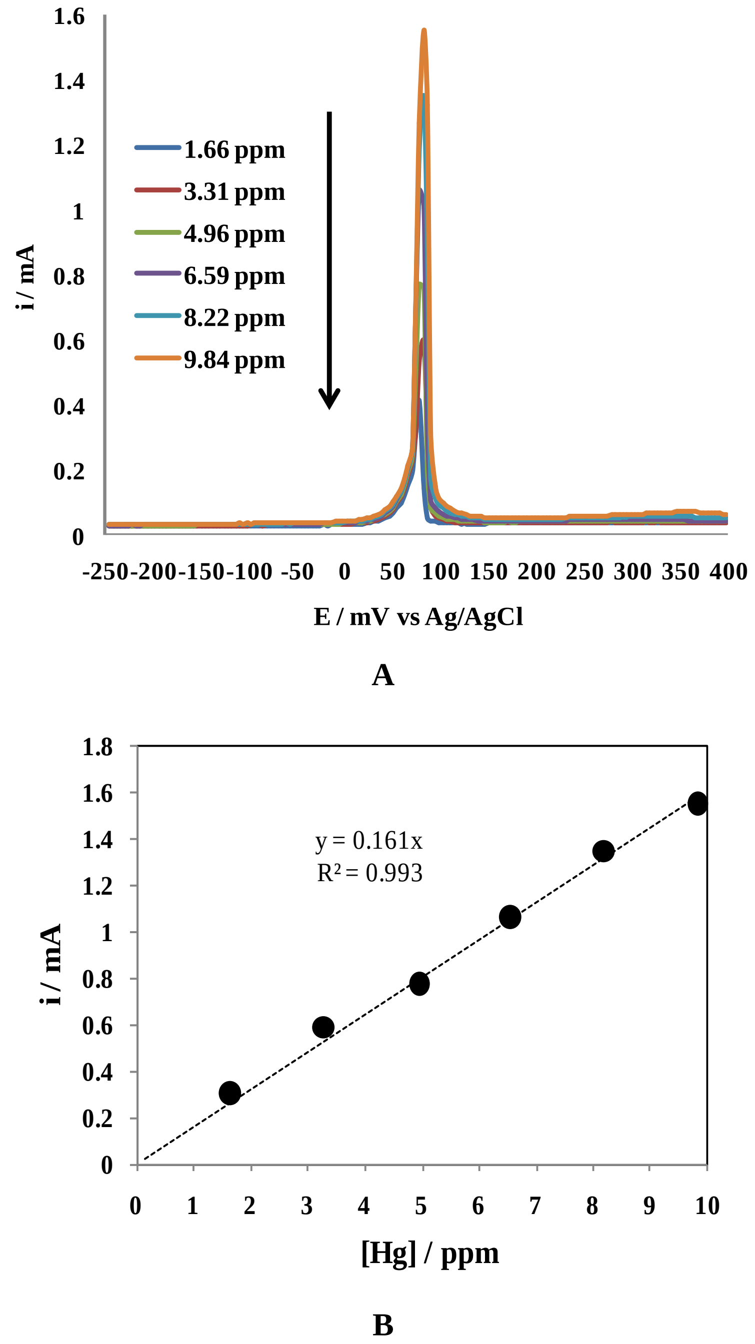


Figure 1. (A) Voltammetries obtained to construct calibration curves without anodic re-dissolution. (B) Calibration curves of Hg in 0.1 M HCl with pre-concentration for 3 min with a 30 s hold, Ep = -0.250 V and $\nu = 0.020$ V s^{-1}.

Anodic redissolution voltammetry was carried out in a 0.1 M HCl solution with a 3 min preconcentration of hexadistilled mercury and a 30 sec rest onto the GC electrode. The mercury signal was observed at –0.250 V using a scan rate of 0.020 V s^{-1} [16]. Results are shown in Figure 1A. A calibration curve for mercury was made with current data generated from each voltammogram (Figure 1B). It is important to point out that an internal standard of 666 ppm mercury was used, anticipating a detection limit of 18.5 ppb and a quantification detection limit of 61.6 ppm.

2.4. Remediation of mercury polluted soil by chemical extraction.

Mercury extraction from the soil samples was performed with several complexing agents according to published protocols [13 - 14] using 0.1 M solutions of KI, KCl, KOH, EDTA, and CTAB. Experimentally, a 0.2 g soil sample was treated with 2.5 mL of each solution and then left standing at room temperature for 72 h.

2.5. Mercury polluted soil electroremediation.

With the aim of achieving soil electroremediation, a 5 g sample was mixed with 2.5 mL of extractant solution containing the complexing agent and placed in the electrochemical cell. This cell consisted of two Ti electrodes acting as the anode and cathode. Several electrolyses were carried out at 5, 10, 15, 20, 25 and 30 V of potential for 20 min. At the end of each experiment, three 0.2 g samples were collected, one near the anode, another at the middle and the third near the cathode.

2.6. Molecular modeling.

For computational modeling, proposed interactions between Hg and KI or EDTA were studied with structural information extracted from crystallographic data obtained from the Crystallographic Cambridge Database. These complexes were subjected to DFT B3LYP LANL2DZ level of theory calculations using Gaussian 03W software [17]. To ensure the validity of the final structures, all proposed structures were subject to frequency analyses.

3. RESULTS AND DISCUSSION

3.1. Soil remediation by chemical extraction.

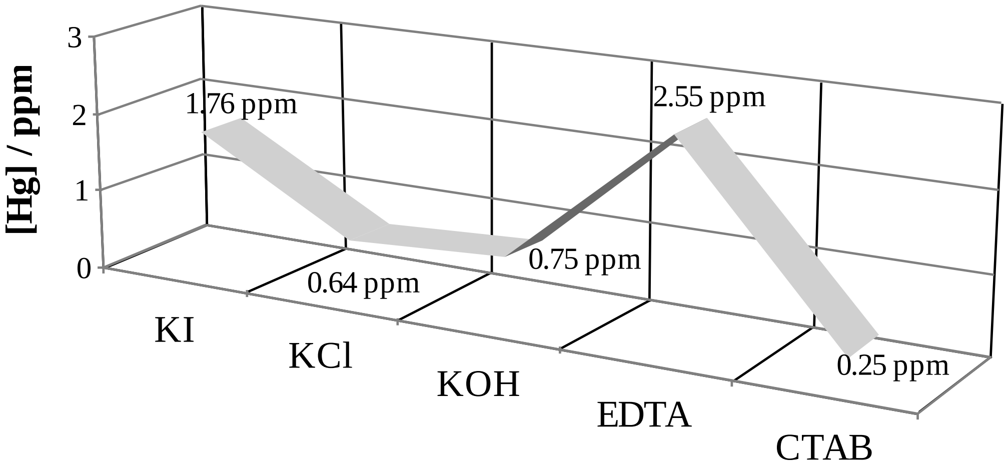


Figure 2. Graph of Hg removed from 0.2 g of soil with different extractant agents for 72 h at 278 K without stirring. The concentration of extractants was 0.1 M.

Figure 2 summarizes the degree of mercury removal achieved with a 0.1 M solution of each extractant. It can be seen that the complexing agents exhibiting greater efficiency are EDTA at 2.55 ppm, followed by KI at 1.76 ppm. This finding implies that EDTA extraction is approximately 57 % more effective than KI extraction under room temperature conditions without stirring. Less effective extractants are CTAB and KCl.

From molecular structural analysis, it can be inferred that EDTA is a good chelator for divalent cations (Hg^{+2}), likely because this ligand presents two tertiary amino groups as well as two carboxylic groups. In contrast, CTAB has only one tertiary amine and several terminal methyl groups, and with as bromide as a counterion, preventing molecular recognition between CTAB and ionic mercury (either Hg^{+} o Hg^{+2}). Thus, from molecular structural analysis it can be inferred that EDTA is a good chelator for divalent cations (Hg^{+2}), as it favors metal coordination with non-shared electron pairs from the tertiary amino groups, while affording coordinated complexes between mercury and the terminal carboxyl groups [18-19].

In this regard, the second best extractant (KI) possesses a counterion (I^{-}) which presents a greater effective ionic radius (206 pm), as compared with chloride (167 pm) and hydroxide (118 pm) [19]. Indeed, it may be argued that mercury ion complexation will be directly proportional to the increase in effective radius of the counterion [14], which validates that mercury was removed in greater quantity using KI than with KCl and KOH.

3.2. Mercury polluted soil electroremediation.

Based on the previous data, it was decided to use the best extractants (EDTA and KI) as supporting electrolytes for electroremediation experiments.

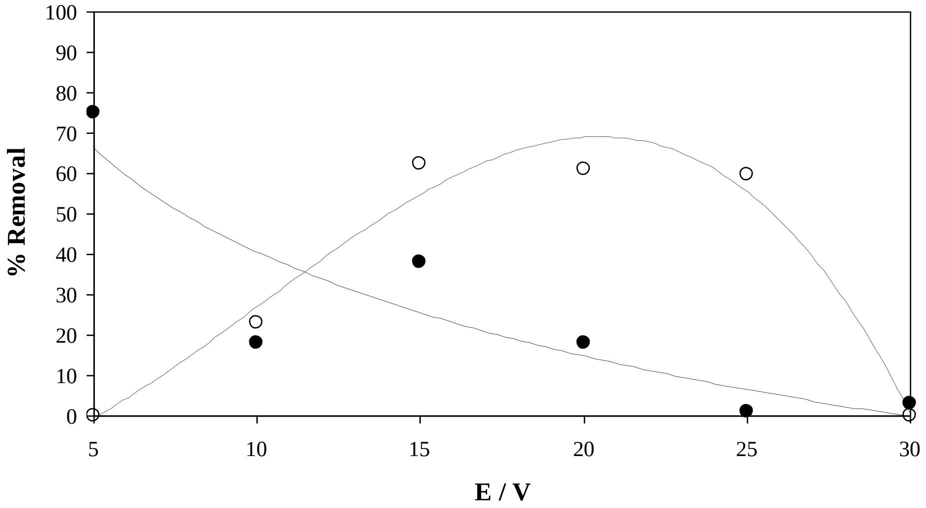


Figure 3. Graph of percentage of mercury removal during electroremediation at different potential values applied in the presence of KI (unfilled circles) and EDTA (filled circles) at 278 K.

The saturating solution was 0.1 M, as in the chemical extraction. A set of exploratory experiments involved the application of 5, 10, 15, 20, 25 and 30 V electric potential for 6 hours. Afterwards, mercury was extracted from the treated soil, and its residual concentration was compared as a function of the applied electric potential (Figure 3). It was observed that EDTA exhibited a better extraction efficiency (75 %) with a lower energy consumption (5 V), as compared to KI (62 %, 15 V).

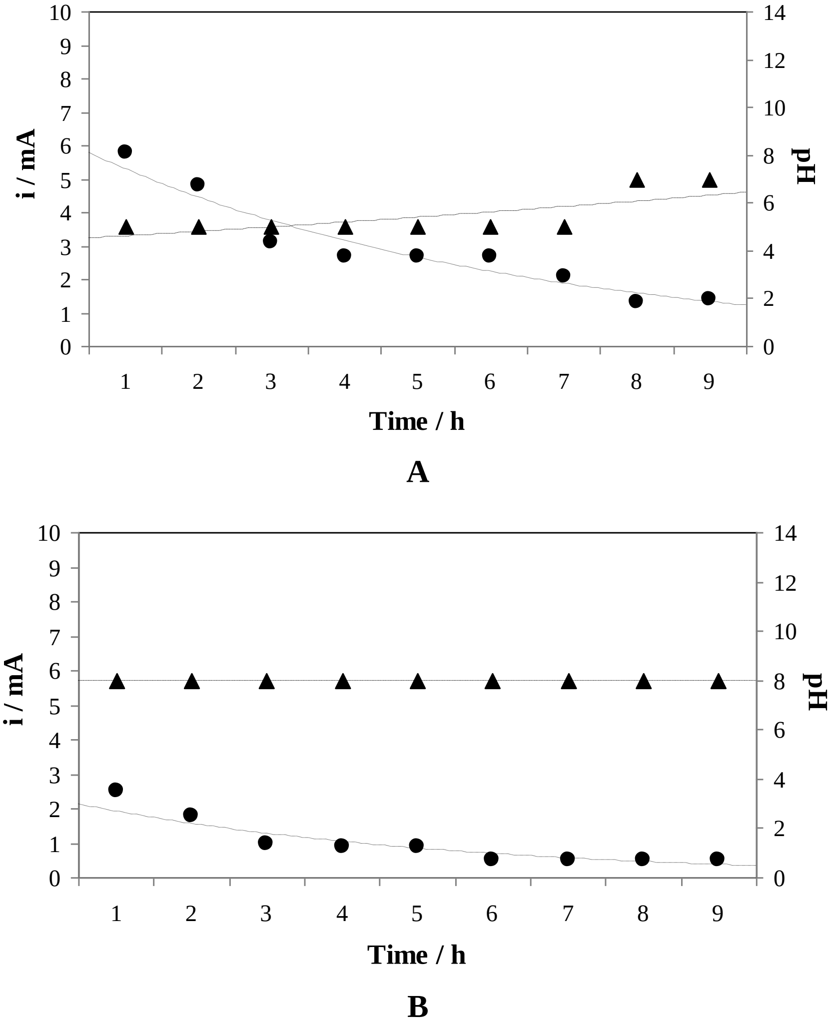


Figure 4. Graph of current (circles) and pH (triangles) in respect to time of electroremediation in the presence of 0.1 M KI (A) and EDTA (B).

The lower efficiency attained with KI is attributed to iodine instability, since iodine tends to be oxidized under the conditions created by the electrolysis reaction at the electrodes [19 - 21]. This becomes evident when the current diminishes under acidic conditions (Figure 4 A). In contrast, in the presence of EDTA, decrease in current is less significant than that observed with KI, resulting from the lower electric potential (5 V) and the fact that pH remains basic (about 8) during extraction (Figure 4 B). Therefore, electroremediation of mercury polluted soil is occurring through the electromigration of coordinate complexes and enhanced by supramolecular interactions between EDTA and Hg^{+2}.

In order to better understand the way Hg^{+2} interacts with KI and EDTA, molecular modeling was undertaken on the proposed interactions Hg^{+2} / 2 I$^-$, 2 Hg^{+2} 6 I$^-$ / 2 K$^+$, Hg^{+2} / EDTA, and 2 Hg^{+2} / 2 EDTA, with structural data based on experimental data [22-29]. According to the literature [26-30], the appropriate computational method for modeling systems involving organomercury compounds is a combination of the DFT method with the hybrid functional B3LYP [31] and the base LANL2DZ [32].

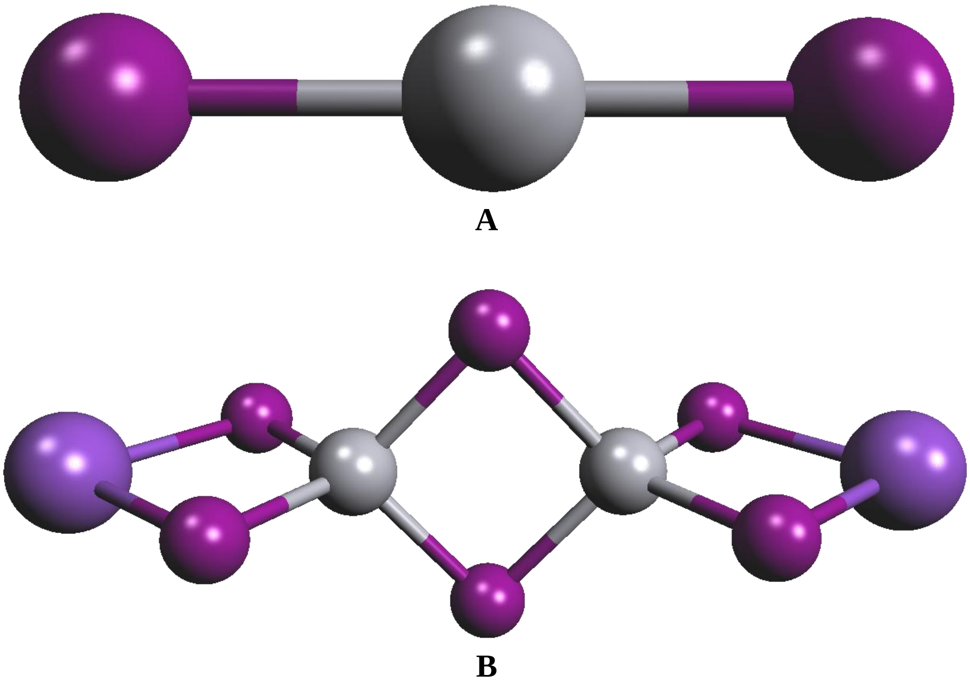


Figure 5. Optimized conformation and molecular structure of the proposed Hg^{+2} / 2 I$^-$ (A) and 2 Hg^{+2} / 6 I$^-$ / 2 K$^+$ (B) complexes (B3LYP LANL2DZ).

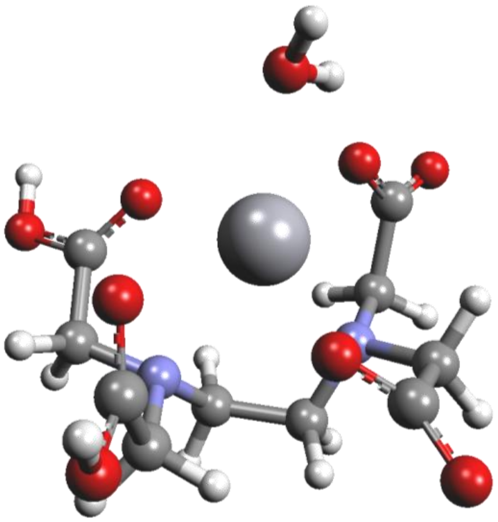
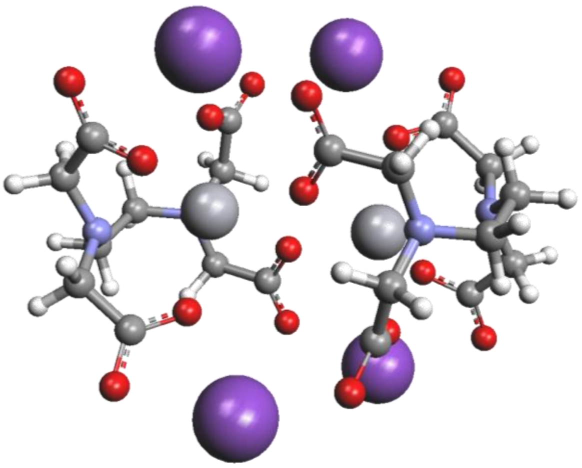


Figure 6. Optimized conformation and molecular structure of the proposed Hg^{+2} / EDTA complex (B3LYP LANL2DZ).

The information obtained by the model suggests that the lowest-energy structure for Hg^{+2} / 2 I^{-} is linear (see Figure 5 A), with the Hg^{+2} in its center (DFT, B3LYP LANL2DZ). Otherwise, for 2 Hg^{+2}6 I^{-} / 2 K^{+}, both Hg^{+2} ions are in the center of two tetrahedrons with the six I^{-} at the corners and the 2 K^{+} located at the complex termini (Figure 5 B, DFT, B3LYP LANL2DZ).

On the other hand, optimization of the Hg^{+2} / EDTA complex required an additional coordinating neutral molecule in order to stabilize the complex (Figure 6). In doing so, the metal is located at the center of the complex, participating in coordination with both oxygen (carbonyl) and nitrogen (amino groups) of the EDTA framework.



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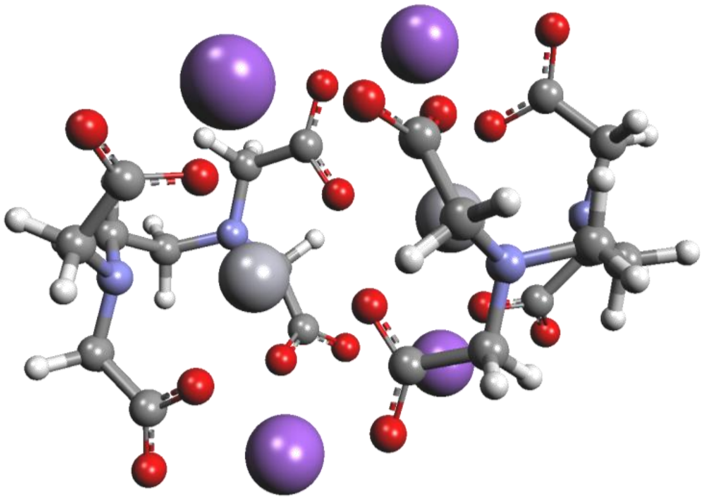

B

Figure 7. Optimized conformation and molecular structure of the proposed 2 Hg^{+2} / 2 EDTA / 4 K^{+} (A) and 2 Hg^{+2} / 2 EDTA / 4 Na^{+} (B) complexes (B3LYP LANL2DZ).

By the same token, the structure for the 2 Hg^{+2} / 2 EDTA complex required inclusion of four potassium ions, which form a bridge across EDTA molecules. Thus, a “cavity” is formed where Hg^{+2} is confined (Figure 7 A). In similar form, the calculated 2 Hg^{+2} / 2 EDTA / 4 Na^{+} complex suggests that the 4 Na^+ ions act like a bridge between EDTA molecules, forming a cavity where Hg^{+2} is retained (Figure 7 B). The resulting energy for the Na+ complex is higher than that estimated for the 2 Hg+2 / 2 EDTA / 4 K+ complex, suggesting that the K+ complex is more stable than the corresponding sodium analog Na+. Indeed, from these calculations, it may be anticipated that mercury removal should be more favorable with the potassium 2 Hg+2 / 2 EDTA / 4 K+ system than with the sodium system Hg+2 / 2 EDTA / 4 Na+. From the previous discussion, it can be inferred that EDTA in the presence of potassium ions is the better extractant for removal of Hg^{+2} from soil via electrochemical remediation.

4. CONCLUSIONS

Electroremediation of a mercury polluted soil from the San Joaquin mineralized area was attained with an efficiency of 75% when a 5 V electric potential was applied for 6 hours with an electrochemical cell of Ti electrodes in a soil wetted with 0.1 M EDTA.

The observed efficiency was apparently achieved by means of migration of coordinated complexes in the presence of an electric charge by electromigration and electrophoresis phenomena in electro-kinetic treatment. Molecular modeling studies suggest that coordination takes place between the terminal EDTA carbonyl and amino groups with divalent mercury (Hg^{+2}). Furthermore, calculations suggest that the supramolecular interactions between the non-shared electrons from the EDTA tertiary amines and mercury ion are aided by the presence of potassium ions.

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