

Improving Cr (VI) Extraction through Electrodialysis

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A laboratory study has been carried out to determine the feasibility of in situ remediation of chromium (VI) contaminated soil using electrodialysis. In a classic setup, this technique implies the application of a low intensity direct current to the soil, which is separated from the electrode compartments by ion-exchange membranes. If the pollutants are ionic compounds, they can be forced to migrate to the oppositely charged electrode by electro-migration. Membranes selectively impede the flow of ions in the electrode compartments back to the soil. If a metal species is naturally present as an anion, mobilization from the soil at alkaline pH can be realized and, at the same time, the mobilization of other metal cations that occur at low pH can be minimized.

Experiments have been carried out with clayey soils (kaolinite clay and soil clay mixtures) that have been characterized and then contaminated by mixing with a potassium dichromate solution for several days. Initial Cr (VI) content ranges from 500 to 4000 mg/kg. Treatment tests were carried out in an acrylic laboratory cells consisting of a central soil compartment and two electrode compartments located at both ends of the column. Dimensionally stable titanium electrodes coated with mixed metal oxides were placed in the electrode compartments. 0.01M Na₂SO₄ electrolytes were recirculated through them from two 1-liter deposits using a peristaltic pump. Two commercial ion exchange membranes separated the anolyte and catholyte compartments from the soil in the standard configuration. A programmable DC: power supply was connected to the electrodes and a computer for data acquisition.

The study consisted of several runs under constant voltage or current conditions using different membrane combinations (0 membranes, 1 membrane or 2 membranes). Typical test duration was 7 or 14 days. Evolution of applied current/voltage to the cell as well as pH and conductivity of the electrolytes were periodically recorded. Electrolytes were also sampled for Cr content determination. At the end of the treatment period, soil cores of ca. 2g were taken at different positions in the cell for total Cr content and speciation analyses. Fractionation of chromium has been determined on soil samples before and after the remediation process using a standardized four step sequential extraction procedure (SEP) with acetic acid, hydroxylamine, hydrogen peroxide and aqua regia solutions. Chemical analysis of digested soil samples, electrolytes and extracting solutions were carried by spectroscopy (AAS and ICP).

The fractionation analyses show that initially most of the chromium in the soil is located in the most mobile fraction (81%) and similar amounts in the other 2 (7% and 10%) with little chromium in the residual fraction. In the standard 2 membrane configuration, pH of the electrolytes varies during the runs as a consequence of water electrolysis reactions at the electrodes and depending on the applied current and can reach values below 2 and above 12 at the anode and cathode respectively. The lower selectivity of the membrane for the H⁺ causes the acidification of the soil to pH around 3-4. Accumulation of chromium in the anode chamber shows that electromigration is the predominant driving force for the transport of ions.

As the electrodialysis treatment proceeds, the more labile soil fraction (soluble - exchangeable - carbonic) is depleted first and the amount of chromium in it decreases drastically to less than 7% as it is being removed from the soil into the anolyte solution. In some instances, changes in the total chromium distribution occur due to the treatment. Some of it is being transferred to other soil phases, which are more difficult to mobilize. Removal of chromium of 27% at 15 V and 57 % at 30 V have been achieved in one-week treatments. Higher voltages yield higher initial removals rates and higher amounts of chromium at the cost of being more energy inefficient. Operation with only the anion exchange membrane have also been carried out and higher extraction yields can be achieved and will be presented.

Keywords: Cr (VI), Extraction and Electrodialysis.