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Electrochemical oxidation of soils contaminated with organic pollutants

Abstract

Electrochemical oxidation, or electrooxidation, is a branch of Direct Current Technologies (DCTs), which are innovative techniques for contaminated soil remediation, in which electrical fields are created in the polluted media by applying low-voltage direct currents (DC) to electrodes placed in the ground.

In recent years, DCTs have proven to be effective for the remediation of many organic and inorganic pollutants from soils and sediments. The main electrochemically induced phenomena include water electrolysis, electroosmosis, electromigration, electrophoresis, changes in soil pH and geochemical reactions. In particular, the electric fields can enhance oxidation and reduction reactions, able to mineralize the organic pollutants occurring in the target media. Moreover, in soils the presence of microconductors can promote redox reactions diffusively in the treated matrix and the production of hydrogen peroxide. Once hydrogen peroxide has been created, the soil natural iron content can catalyze the production of hydroxyl radicals, which are strong non-selective oxidant agents, capable of degrading most of organic pollutants. These recovery techniques seem particularly effective in saturated low permeability soils (like clays and silts), which are often very difficult to treat with conventional methods, because of their low permeability and their high sorption capacity. However, it is still not clear what processes play the most important roles in organic mineralization, and what factors can affect the treatment results.

The main objectives of this study were to evaluate the efficiency of electrochemical oxidation for the remediation of different organic contaminants from various types of fine-grain soils and sediments. The research also aimed at assessing the best design parameters and the most important factors that can influence the system efficiency, as the applied voltage, the treatment duration and the soil mineralogy. A better knowledge of these processes will help to design more efficient and more effective remediation actions.

For these purposes, two one-dimensional experimental setups for bench-scale testing were assembled and several laboratory tests were performed. Each experimental device included a PVC electrochemical cell, a pair of plate stainless steel

electrodes, a stabilized DC power supply, a multimeter for voltage and current monitoring and tanks for the pore fluid collection at the electrode compartments. During each experiment, the contaminant removal was evaluated under a constant voltage gradient, ranging from 0.5 to 6 V/cm, for a fixed period of time, which arrived up to 4 weeks. No conditioning fluids were dosed to improve the soil conductivity or to enhance the contaminant transport. Several parameters were investigated, including contaminant concentrations, changes in soil pH, electroosmotic flux, soil humidity and soil mineralogy. Moreover, at the end of each trial, the contaminant content in the soil sample was evaluated at different distances from the electrodes.

A systematic study was performed to assess the effectiveness of electrooxidation on fine-grain soils contaminated with diesel fuel. Diesel fuel is a mixture of aliphatic and aromatic hydrocarbons and was chosen to represent the environmental pollution due to spills of oil and other petroleum products, which are a frequent source of soil contamination and pose important environmental concerns. Two types of soils were considered in the study: a silty clay, mainly composed of kaolin, and a bentonite clay, mainly composed of montmorillonite, in order to assess the influence of different soil mineralogical compositions on the electrochemical processes. In addition, different feasibility studies were conducted to assess the applicability of electrooxidation for the remediation of river sediments contaminated by polycyclic aromatic hydrocarbons (PAHs), silty soils contaminated by organolead compounds, and clayey soils contaminated by landfill leachate.

According to the results achieved, electrochemical oxidation proved to be effective for the remediation of various types of aliphatic and aromatic hydrocarbons, as well as for ammonia and leachate organic contaminants, while a limited removal was encountered for the organolead compounds. The tests performed on diesel-contaminated soils resulted in about 46-69% TOC (Total Organic Carbon) removal and in 66-87% TPH (Total Petroleum Hydrocarbons) removal after four-week treatments. Significant degradations of both TOC and ammonia (about 60%) were achieved in the leachate-contaminated clay after electrochemical processes of a few days. The results also showed that a very efficient remediation of PAH-contaminated sediments could be attained via electrochemical methods, with total PAH removals above 90%. These contaminant degradation efficiencies can be considered very satisfactory, since the remediation of fine-grain soils and sediments contaminated with hydrophobic and sorbed organic pollutants is very difficult to attain and represents up to now a challenging technical task.

Among the main influence factors, the applied voltage seems to have a limited influence on the system efficiency, good results being achieved with specific voltages as low as 1 V/cm. Contaminant removals proved to significantly increase with process duration, with higher removal efficiencies being attained for treatments lasting for a few weeks, rather than for a few days. Final contaminant concentrations were found to be evenly distributed across the treated sample. This indicated that the oxidation reactions occurred homogeneously within all the treated volume and not only nearby the electrodes. Moreover, the electrokinetic transport of the target pollutants was negligible during the tests performed, which were unenhanced. The occurrence of the electroosmotic flux does not seem to be necessary to attain the pollutant mineralization and the processes seem to require low energy expenditures, being the current densities applied very low, about 0.01-1 mA/cm². The buffer capacity of the soil affected the soil pH changes, by determining the tendency of the treated medium towards acidification or basification, though the remediation efficiency did not seem to be influenced by changes in the soil pH. On the opposite, the soil mineralogy, and in particular the iron content, seems to affect significantly the degradation process, the best results being achieved for soils with high metal concentrations. In this framework, the diffuse indirect oxidation is assumed to be the main mineralization pathway. The process occurs at the pore scale and includes the electrochemical production of hydrogen peroxide and the subsequent generation of hydroxyl radicals through Fenton-like reactions.

On the whole, electrochemical oxidation seems to be effectively and amenably applicable for the mineralization of many organics with low energy expenditures, especially in finest soils, like silts and clays, with significant iron contents.