



# Removal of hexachlorobenzene from soil by electrokinetically enhanced chemical oxidation

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## ABSTRACT

This study investigates the feasibility of enhanced electrokinetic Fenton process for the remediation of hexachlorobenzene (HCB) in low permeable soil. Laboratory scale experiments were carried out in two different type of experimental setup to evaluate the influence of electrode positions in the system. Kaolin was artificially contaminated with HCB and treated by electrokinetic Fenton process.  $\beta$ -Cyclodextrin was used to enhance the solubility of HCB in pore fluid. Results show that the position of electrodes in the system and the way in which Fenton's reagent was added to the system has a significant influence on the treatment efficiency.

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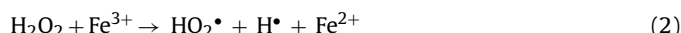
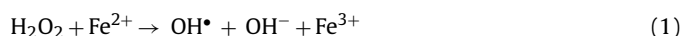
## 1. Introduction

The global nature of persistent organic pollutants (POPs) contamination has created a growing concern over the chronic toxicity and their impacts on human health and environment. One of the properties of POPs that make them difficult to treat is their low aqueous solubility. Though various conventional physical, chemical and biological techniques are available for the treatment of contaminated sites, they have proved unsuccessful to remediate soils of low permeability contaminated with compounds of low water solubility like POPs.

Recent research has shown that electrokinetic remediation is one of the promising technologies for the remediation of low permeable soil. In this process, separation of contaminants is brought about by the application of electric field between two electrodes inserted in the contaminated mass. Application of electric field initiates certain transport mechanisms such as electromigration, electro-osmosis and electrophoresis in the soil that involve the movement of ions, pore fluid and charged particles, respectively in the medium [1–5]. When treating soil contaminated with POPs, the influence of electromigration and electrophoresis can be neglected because of the non-polar nature of POPs. Therefore electro-osmosis is the major mechanism by which POPs are

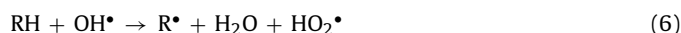
transported through the soil matrix during their treatment. The hydrophobic nature of POPs makes them difficult to be removed from soil. The contaminants sorbed to the soil particles can be moved by electro-osmosis only if they are soluble in the pore fluid. Thus the use of a surfactant or cosolvent to enhance the process is necessary for increasing the solubility and enhancing the mobility of these contaminants in the pore fluid [1]. But, this causes only the movement of contaminants from one point of the soil section to another and the waste stream collected from the electrode chambers of the electrokinetic system requires further treatment.

Among various treatment methods, oxidation by Fenton's reagent was found to be very effective for highly biorefractory contaminants [6]. The primary reactions in the Fenton's process are



where  $\text{OH}^\bullet$  is the hydroxyl radical and  $\text{HO}_2^\bullet$  is the perhydroxyl radical.

In the presence of organic substrate the reactions include:



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**Table 1**  
Kaolin characteristics

Properties	Values
Mineralogy	
Kaolin	100%
Particle size distribution	
Gravel (%)	0
Sand (%)	7
Silt (%)	17
Clay (%)	76
Specific gravity	0.508
Carbonate content (%)	5.5
pH	5.2
Electrical conductivity ( $\mu\text{S}$ )	189.2
Cation exchange capacity (mmol/100 g)	3



where  $\text{R}^\bullet$  is the organic radical.

Thus Fenton's oxidation is an effective mechanism for the decomposition of toxic organic compounds. However, when applied alone, Fenton's process fails to treat low permeable soil. Also, hydroxyl radicals generated by Fenton's reaction have limited capability to oxidize the contaminants sorbed to the soil [7]. This drawback can be overcome by integrating enhanced electrokinetics with Fenton's process. In Electrokinetic Fenton process, hydrogen peroxide passes through low permeable soil from anode to cathode by electro-osmosis and produces hydroxyl radicals in the presence of iron in soil. Finally hydroxyl radicals oxidize or decompose organic wastes. Some researchers have successfully integrated electrokinetics with Fenton's process to treat various organic compounds [8–11]. But little research has been done on electrokinetic Fenton process enhanced by surfactants or cosolvents for the treatment of low permeable soil contaminated with POPs.

Therefore, in this study, the performance of enhanced electrokinetic Fenton process for the treatment of low permeable contaminated soil is investigated by selecting HCB as the model compound. Though HCB is no longer manufactured commercially, it is still being produced as a byproduct during the manufacture of other chlorinated solvents. Kaolin was artificially contaminated with HCB and laboratory scale electrokinetic Fenton experiments were carried out in two different types of experimental setup.  $\beta$ -Cyclodextrin was used for the enhancement of HCB mobility in the soil system. The influence of electrode position in electrokinetic Fenton system is also analyzed by selecting two different apparatus for conducting the experiments.

## 2. Materials and methods

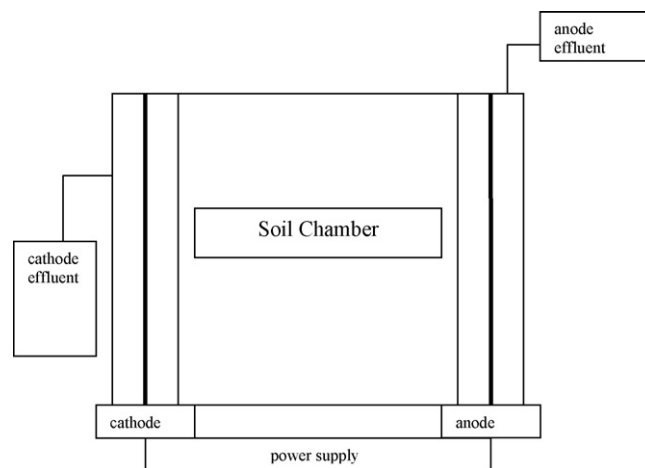
The model soil selected for the study was Kaolin. Laboratory grade Kaolin was obtained from VWR International (Finland).

A preliminary analysis of soil was done based on the methods prescribed by soil science methods and applications [12] physical and chemical properties of kaolin are shown in Table 1.

HCB was selected as the representative POP in this study and was purchased from VWR International (Finland). HCB is practically insoluble in water (0.0062 mg/L at 25 °C) and has a log octanol partition coefficient of 5.73 [13].

Thirty percentage hydrogen peroxide was supplied by J.T. Baker and ferrous sulphate (99% ferrous sulphate heptahydrate) from Fluka.

Test specimen was prepared by artificially contaminating kaolin by the following method: weighed quantity of kaolin was first homogeneously mixed with HCB-hexane solution. Then the wet



**Fig. 1.** Schematic diagram of electrokinetic apparatus used.

mass was left open in the fume hood till all the hexane evaporated and a totally dry soil mass was obtained.

### 2.1. Electrokinetic Fenton reactor

The electrokinetic apparatus used for test 1 is shown in Fig. 1. The apparatus was made of glass and consisted of three parts: two electrode chambers and a soil chamber in between. The dimensions of electrode chamber were 12 cm × 20 cm × 20 cm and that of soil chamber were 13 cm × 20 cm × 20 cm. Inert electrodes made of titanium and coated with platinum were used for all experiments. Filter cloths were inserted on either sides of soil chamber to prevent soil from getting mixed with anode and cathode solutions. The chambers were closed using a removable lid with openings to insert electrodes which also served as gas vents.

Contaminated soil was uniformly stacked into the soil chamber and the electrode chambers were filled with respective solutions. Then the electrodes were inserted into the chambers and connected to the power supply.

Test 2 was carried out in an open pan with no separate chambers for electrodes. The dimensions of the cell were 28 cm × 22 cm × 10 cm. Both the apparatus were designed by keeping in mind the practical implementations of the process in field.

### 2.2. Operating conditions

For test 1, the contaminated soil was directly stacked into the soil chamber of the electrokinetic apparatus. The anode chamber was filled with 1.5 L ferrous sulphate solution so that Fe:substrate ratio is 1:10 and 1% (by weight)  $\beta$ -cyclodextrin. The cathode chamber was filled with deionized water. Electrodes were then inserted into the respective chambers and connected to the power supply. After 48 h when current developed, 15% hydrogen peroxide was supplied from the anode chamber.

For test 2, before stacking into the apparatus, the contaminated soil was soaked with ferrous sulphate solution, so that Fe:substrate ratio is 1:10, and 1% (by weight)  $\beta$ -cyclodextrin. The electrodes were then directly immersed into the soil and connected to the power supply.

A constant voltage of 30 V was applied during the entire period of both the tests. Moisture content of the soil in test 2 was maintained at around 35% by adding deionized water. Fifteen percentage hydrogen peroxide was periodically added from the anode part for both the tests. Blank tests were also run in order to estimate the contaminant loss by evaporation.

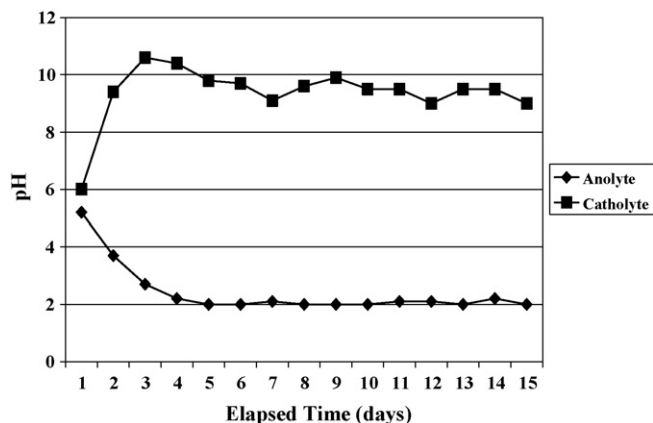


Fig. 2. Electrolyte pH: pH profile of anolyte and catholyte for test 1.

### 2.3. Chemical analyses

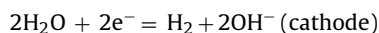
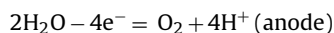
Soil samples were taken periodically and analyzed for HCB. pH and zeta potential of soil samples were monitored continuously. pH was measured by using a pH meter (pH 730 inoLab WTW series). The zeta potential of the soil samples were measured by Zeta sizer Nano-series (Malvern instrument), equipped with a microprocessor unit. A maximum of approximately 2 g of soil samples were taken without disturbing the system. Samples along the anode and cathode portions were taken from a distance of about 2 cm from the walls of the chamber.

HCB was extracted from the soil sample by ultrasonication based on a method adopted from Yuan et al. [14]. The extract so obtained was analyzed using a gas chromatograph coupled to an inert mass selective detector (Agilent 5975). The column used was HP-5 capillary column (30 mm × 0.32 mm ID) with a 0.25- $\mu$ m film thickness. Helium at constant flow rate (25 cm/s) was used as carrier gas. The oven temperature was programmed from 40 to 270 °C at 10 °C/min. The injector temperature used was 250 °C and the injection volume was 1  $\mu$ L. All the analyses were done in duplicate soil samples.

## 3. Results and discussions

### 3.1. Electrolyte and soil pH

The initial pH of anolyte was 5.2 and catholyte was 6. After 3 days of operation, the anolyte pH decreased to 2 and remained almost constant for the rest of the days (Fig. 2). The catholyte pH increased to 10.6 after 2 days of operation and then remained constant in the range 9–9.8 for the entire period of the test. This shows the general trend of pH distribution during electrolysis. This is because, due to the applied electric field, electrolysis takes place and  $H^+$  and  $OH^-$  ions are generated at anode and cathode, respectively which results in a low pH at the anode and high pH at the cathode [15]. The reactions taking place at the electrodes are



The acidic and basic fronts developed near anode and cathode migrate slowly to the soil and thus change the pH of soil.

The soil pH with elapsed time for test 1 and test 2 is shown in Fig. 3. During test 1, the soil pH at the anode and at the cathode decreased. The ionic mobility of  $H^+$  is 1.75 times greater than that of  $OH^-$  ion [16]. Therefore, the acid front generated at the anode advanced through the soil specimen and thus lowered the pH. This

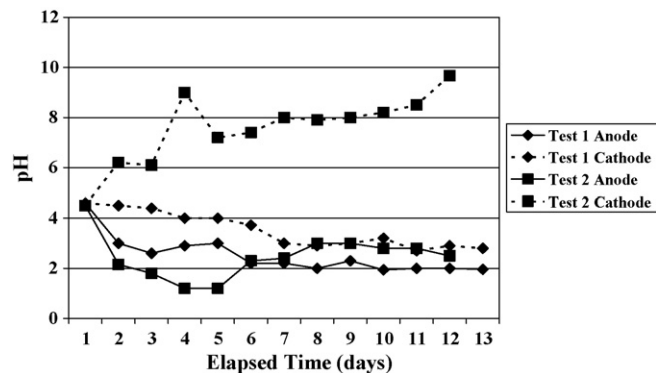
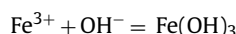
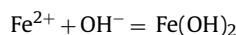


Fig. 3. Soil pH: pH profile of soil for tests 1 and 2.

decrease in the soil pH in the cathode part was not observed in test 2. The soil pH near cathode in test 2 gradually increased and was 9.6 at the end of the test. This is because, in test 2, electrodes were directly immersed into the soil and therefore the alkaline front was developed in the soil itself. Also the precipitation of stable ferrous or ferric hydroxide from ferrous or ferric ions at higher pH which existed near cathode contributed to the increase in soil pH near cathode.



### 3.2. Current

The current developed with elapsed time in test 1 and test 2 for a constant applied voltage of 30 V is shown in Fig. 4. In test 1, current was initially 0 mA and after 2 days of operation reached a maximum value of 10 mA which then stabilized and remained constant for the entire period of test. The delay in developing the current might have occurred due to the time taken by ions to migrate into the soil from the electrode chambers. The Fenton's reagent was supplied from the anode chamber and as it reached the soil, the ionic strength of the pore water increased and thus caused current to increase. After a while, with elapsed time, a steady state would have reached which stabilized the current. Whereas in test 2, at the beginning, current was higher than in test 1 and after 2 days of operation it decreased and then remained nearly constant for the entire period of test. Since the soil in test 2 was soaked in ferrous sulphate before the start of the experiment, initially ferrous ions in solution increased the electrolyte concentration in pore solution. Then the fluctuation

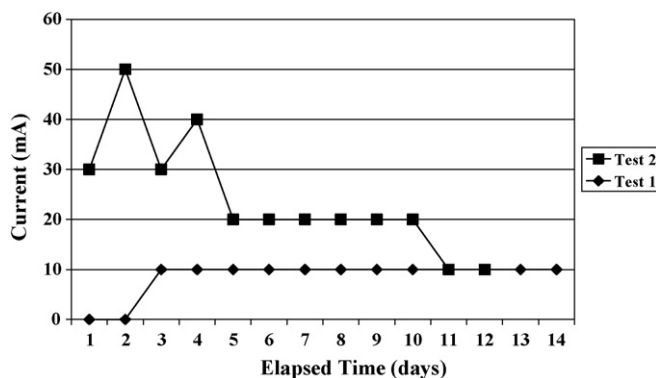


Fig. 4. Current: electric current developed with elapsed time during tests 1 and 2.

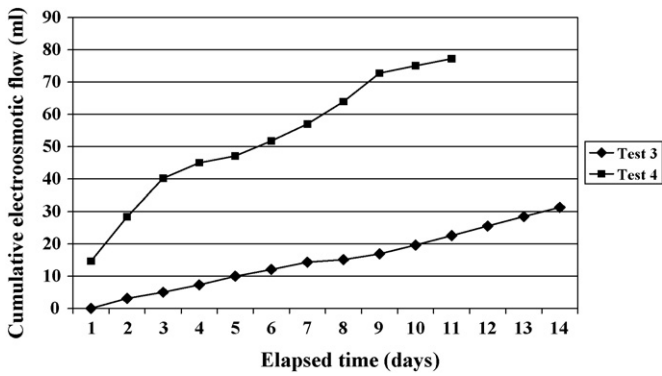


Fig. 5. Electro-osmotic flow: average electro-osmotic flow with elapsed time for tests 1 and 2.

and gradual decrease in current might have occurred due to the generation of  $H^+$  and  $OH^-$  ions and the subsequent precipitation of ions in the solution and migration of these ions to the electrodes [17].

3.3. Electro-osmotic flow

Contaminant transport is greatly influenced by electro-osmotic flow as increased electro-osmotic flow means better interaction between the soil-contaminant particles and the pore fluid.

Results show that the cumulative average electro-osmotic flow was maximum in test 2 when compared to test 1 (Fig. 5). Electro-osmotic flow for all the tests was in the same direction from anode to cathode. Results indicate that electro-osmotic flow had a significant effect on the way in which Fenton's reagent was added to the system. Higher flow in test 2 could be attributed to the higher current developed during the test. A difference in current occurs due to the physico-chemical processes such as electromigration of ionic species and electrolysis reactions which could affect the surface charges of soil and hence the electro-osmotic flow [18]. Studies by Hamed and Bhadra [19] showed that increased current leads to higher electro-osmotic flow which results in decreased processing time.

3.4. Contaminant removal

Fig. 6 shows the cumulative contaminant removal during tests 1 and 2. An overall removal efficiency of 64% was observed for test 1 which lasted for 14 days. The overall removal efficiency for test 2 which lasted for 12 days was 62%. The rate of contaminant removal was higher in test 2 when compared to test

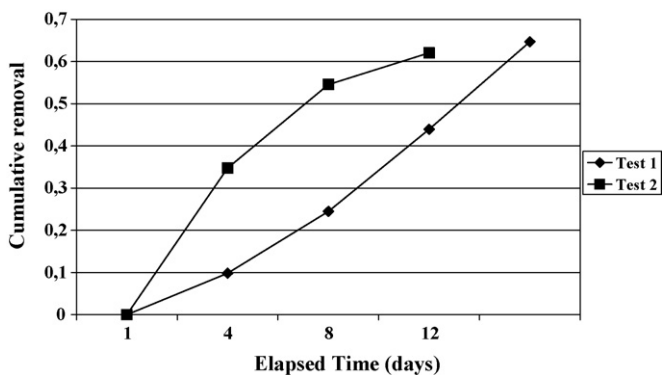


Fig. 6. Contaminant removal: cumulative rate of contaminant removal for tests 1 and 2.

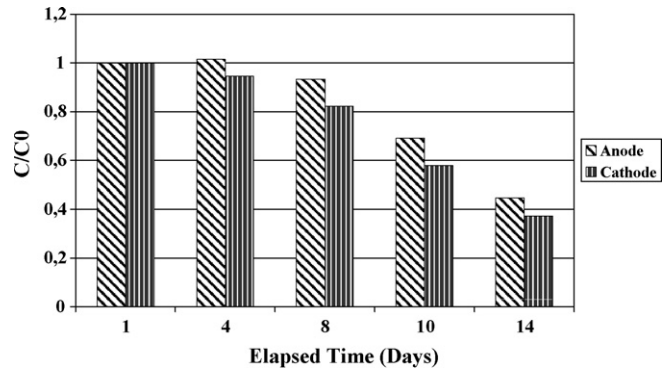


Fig. 7. Contaminant distribution: distribution of HCB in soil with elapsed time during test 1.

1. This is because of higher electro-osmotic flow that developed in test 2. The increased electro-osmotic flow resulted in better interaction between the soil contaminant particles and the pore fluid which caused faster desorption of HCB from the soil. There was a steady increase in the removal rate with time, which indicates that further removal is possible with time.

The final average concentration of HCB in soil for both tests is nearly the same. But the degradation of HCB depends also on its position. Figs. 7 and 8 show the distribution of HCB in soil along the anode and cathode portions of soil for test 1 and test 2, respectively (mass concentration,  $C$  divided by initial mass concentration,  $C_0$ ). Though there was a significant reduction in the contaminant concentration, from the figure it is evident that in test 1, removal was slower in the anode part. 66% of HCB present initially was removed from the anode portion and 67% from the cathode portion. A higher removal was observed along the cathode portion. This could be because of the comparatively higher electro-osmotic flow which developed at the cathode portion due to the relatively higher pH in that region which resulted in better soil-solution contaminant interaction than in the portion near anode.

But in test 2, HCB which accumulated in the cathode part did not undergo significant degradation. This was because of the high pH developed in the cathode part which was not suitable for the Fenton's reaction to take place. The final concentration of HCB in the anode part in test 2 was 0.141, which shows that there was 86% removal in the anode part. This indicates that higher contaminant removal is possible in test 2 if pH at the cathode could be controlled.

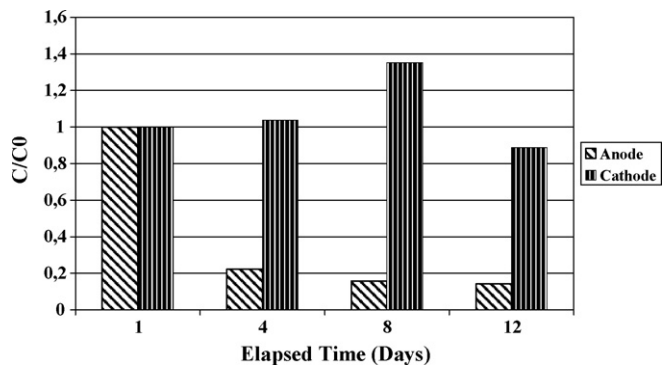


Fig. 8. Contaminant distribution: distribution of HCB in soil with elapsed time during test 2.

**Table 2**  
Energy consumption

Test	Voltage (V)	Energy consumption (kWh)	Removal efficiency (%)	Removal efficiency per energy consumption
1	30	0.0936	64	683.76
2	30	0.2232	62	277.77

### 3.5. Energy consumption

The energy consumption for the tests was calculated [20] and is presented in Table 2. During test 1 which lasted for 14 days, the energy consumed was 0.0936 kWh and that for test 2 which lasted for 12 days was 0.2232 kWh. The removal efficiency per energy consumption for test 1 was found to be 2.46 times higher than that in test 2. The relatively higher energy consumption in test 2 has occurred because of the high current developed during the test. Energy consumption is considered to be one of the major factors for a reasonable choice of remediation methods.

### 4. Conclusions

From the studies carried out, the following can be concluded:

- Enhanced electrokinetic process is a feasible method for treating low permeable soil contaminated with HCB.
- $\beta$ -Cyclodextrin was observed to be effective in enhancing the mobility of HCB in the system.
- An overall removal efficiency of 64% was observed “almost” uniformly across the soil during the electrokinetic Fenton test 1 (electrodes in chamber) which lasted for 14 days.
- An overall removal efficiency of 62% was observed during electrokinetic Fenton test 2 (electrodes in soil) which lasted for 12 days. But the removal was uneven across the soil due to the high pH developed at the cathode region. The performance of electrokinetic Fenton test 2 (electrodes in soil) could be improved if the pH level can be controlled at the cathode region.

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