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Remediation of Polluted Soils Contaminated with Linear Alkylbenzenes Using Fenton´s Reagent

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ABSTRACT

Linear Alkyl Benzenes (LABs) are used as insulating oil for electric cables. When it happens a spill, LABs they are basically sorbed in the soil, because, these compounds have high hidrophobicity and low vapor pressure. The conventional methods of treatment of soils are not efficient. The Fenton's reaction (reaction between a solution of iron II and hydrogen peroxide) it generates hydroxyl radicals, not selective, and capable of oxidize a great variety of organic compounds. A study was conducted to evaluate the viability of use of the Fenton's reagents to promote the remediation of polluted soils with Linear Alkyl Benzenes. A column was especially projected for these experiments, packed with a sandy and other soil loamy. The pH of the soil was not altered. The obtained results demonstrated the technical viability of the process of injection of the Fenton's reagents for the treatment of polluted areas with LABs.

Key words: Soil Remediation; Fenton's Reagent; Linear Alkyl Benzene

INTRODUCTION

An organic pollutant when reaches the underground, can be in the following forms (Fig. 1): (i) Free phase - it is constituted in a veil non miscible on the top of the groundwater; (ii) Dissolved phase - part of the pollutant that is dissolved in the groundwater; (iii) Sorbed or residual phase - it consists of the dispersion between the source and the level of the groundwater and pollutants involving soil grain or discontinuity in the rock characterize it. It is the most important phase for viscous pollutants; (iv) Vapor phase - gaseous phase of the volatile compounds that occupies emptiness of the soil or of the rock.

The equilibrium among these phases is related with properties as the vapor pressure and the solubility in water, and it can be expressed by the *Raoult* and *Henry* laws. In the case of Linear Alkyl Benzenes (LABs), these are basically sorbed in the soil, because these compounds present low vapor pressure and it lowers solubility in water (Table 1). The LABs are used as precursors of the linear alkyl benzene sulfonic acid, main raw material of the detergents (Johnson et al., 2003) and as insulating oil of electric cables in underground (Johnson et al., 2002). These compounds possess in their molecular structure an aromatic ring and a linear chain from 9 to 15 atoms of carbon (Fig. 2). The presence of the aromatic ring turns these compounds very toxic to the microorganisms of a polluted place. The low density of these

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compounds avoids the migration below to the groundwater, and due to low solubility (table 1), the conventional methods of treatment (pump and treat, for example) are not efficient.
The use of active oxidation is a technique of soil remediation "*in situ*" that has been well studied lately. The Fenton reaction (Fenton, 1894) that consists of the reaction between a solution of iron II and hydrogen peroxide (Equation 1), generating hydroxyl radicals, which are strong oxidizers, not selective, and capable of oxidizing a great variety of organic compounds (Sun and Pignatello, 1992).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \qquad (1)$$

The Fenton reagent was excessively tested in the wastewaters treatment, until the more complexes, as wastewaters of high salinity (Moraes et al., 2004). Lately, the use of this reagent has been documented for the treatment of polluted areas with organic highly recalcitrant compounds (Tyre et al., 1991; EPA, 1998 and Siegrist et al., 2000). This work seeks to study the application of the Fenton reaction to promote the remediation of polluted soils with LABs.

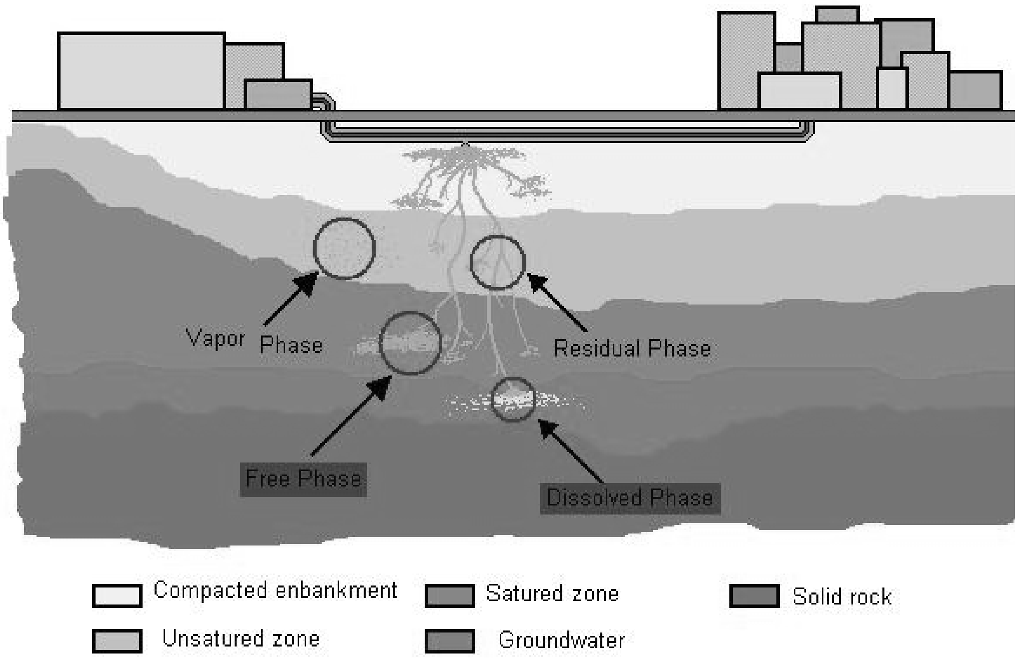


Figure 1 - Behavior of organic pollutants in underground. Main phases in which the pollutants are found (Costa et al., 1999).

Table 1 - Physical properties of commercial product - LABs (Johnson, 2000).

Physical Properties	
Density (20 ºC)	0.86 kg.L^{-1}
Boilling Point	726 ºC
Viscosity (20 ºC)	8.1 mm^2.s^{-1}
Solubility in water (25 ºC)	0.41 mg.l^{-1}
Vapor pressure (25 ºC)	4.9*10^{-4} mmHg
Henry Constant	0.071 torr.L.mol-^{1}
Partition Coefficient Octanol-water (K_{ow})	5.72 - 5.75

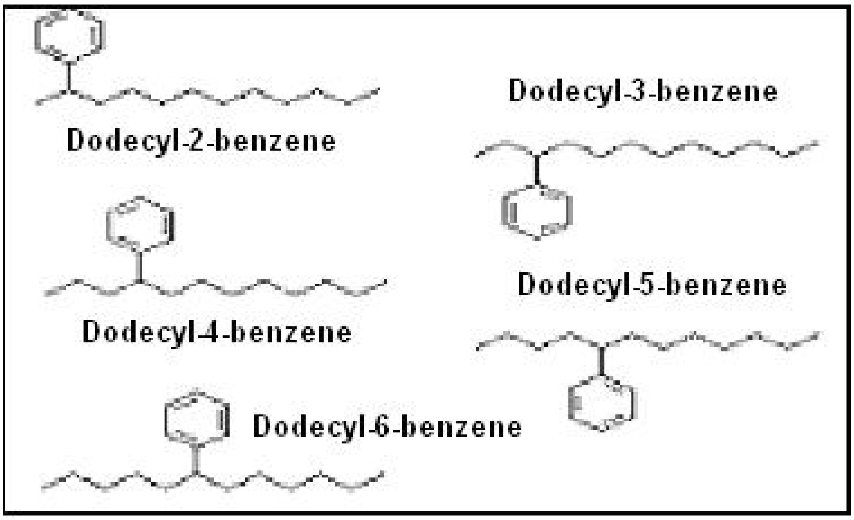


Figure 2 - Molecular structures of Linear Alkyl benzenes (dodecyl benzenes)

MATERIALS AND METHODS

Reagents

Analytical grade reagents: ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), hydrogen peroxide (H_2O_2, 30%), phenol and a commercial sample of LAB as pollutant were used.

For the analysis procedure, milli-Q water (18 ms) was used, besides methanol and acetonitrile HPLC grade.

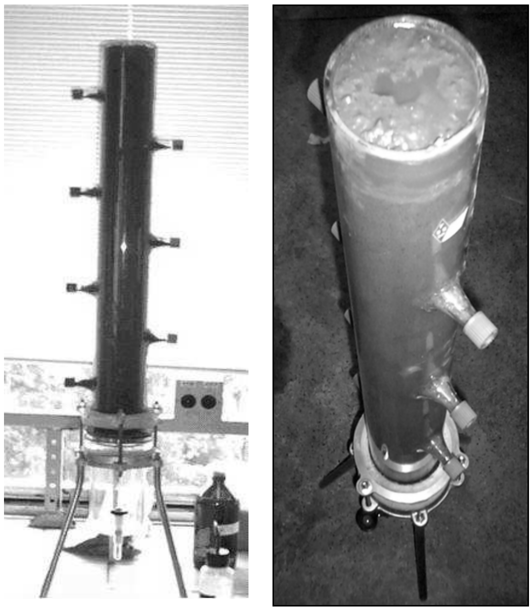
Methodology

The experiments were carried out in a column projected for this end, as show in Fig. 3. This column has 10 cm of diameter and 80 cm of height of soil column. The column has lateral holes (1 cm of diameter) at spacing of 10 cm, appropriate for the retreat of samples, reagents addition and temperature measure, for example. The soil was supported on a sieve of 100 mesh, that just allowed the passage of liquids, which was collected in a 1.5 L vessel.

Two samples of soils were used; sandy without any pollution (soil 1) and polluted with LAB (soil 2), and unpolluted loamy soil (soil 3). The loamy soil was triturated, in order to obtain a more uniform granulometry. For a model study, the sample of sandy soil was contaminated (soil 1) with phenol.

The phenol was mixed to the sandy soil, for vigorous agitation, in way obtaining a contamination of about 600 µg / g of dry soil. The loamy soil (soil 3) was contaminated with LAB (125 mg of LAB by gram of dry soil). The polluted soil was packed without pressure in the column. The Fenton's reagent was added in batch form, in the top of the column. For the soil 1, the concentrations of ferrous sulfate and hydrogen peroxide were 25 mM and 15% (4.4 M). For the other soils, concentrations of 2.5 mM of ferrous sulfate and 2.2 M of H_2O_2 were used. The added volumes were of 50 mL of each solution for each batch. In the soil 1, 500 mL of each solution and in the others 250 mL of each one of the reagents were added.

The analyses were accomplished in a HPLC (LC-10Advp, Shimadzu), coupled to UV/Visible detector (SPD-M10Avp, Shimadzu). To soil sample (10 grams), 20 grams of methanol and/or acetonitrile (extractor agent) were added and the mix was shaken vigorously. The mixture was left for 20 minutes and the supernatant obtained was used for HPLC analysis. The mobile phase was a mixture of water with methanol or acetonitrile, containing 0.25% of acetic acid. The gradient used was: 100% of water from 0 to 6 minutes, from 6 to 8 minutes, methanol or acetonitrile proportion increased to 80% and maintained for 30 minutes, being reduced to 0% until the 33 minutes and maintained in 0% up to 45 minutes. Methanol was used to extract phenol and acetonitrile to extract LAB. The chromatograms were obtained at 269 nm (phenol) and 202 nm (LAB). The extraction was accomplished before and after the treatment done with the Fenton's reagent.



(a) (b)

Figure 3 - Experimental column packed with clay contaminated artificially with the LAB. (a) Frontal seen. (b) Top after addition of the Fenton's reagent.

RESULTS E DISCUSSIONS

Figs. 4, 5 and 6 present the chromatograms of the extract obtained from the polluted soil with phenol (soil 1). Fig. 4, the chromatogram of the extract obtained of the polluted soil (before the treatment) is showed, the characteristic peak of the phenol, with retention time of 15.8 minutes. Fig. 5 presents the chromatogram of the extract obtained for the soil in the bottom of the column (after the treatment).

The phenol concentration was of 1.2 μg/g of dry soil. Fig. 6 shows the chromatogram of the aqueous phase collected from the vessel below the soil column. The phenol concentration in the aqueous sample was 12 mg/L. All the concentrations were measured with the helpful of calibration curves (not presented).

The chromatograms of Figs. 4, 5 and 6 show the efficiency of the Fenton's reaction in the degradation of aromatic compounds presents in the soil.

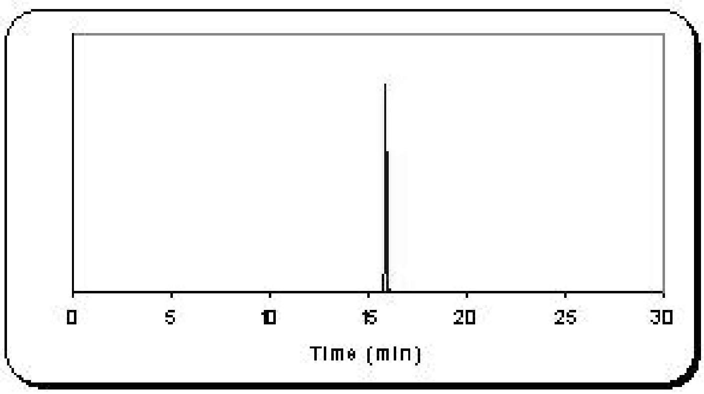


Figure 4 - Chromatogram of the methanol extract done from the polluted soil with phenol, before the treatment. λ =269 *nm*.

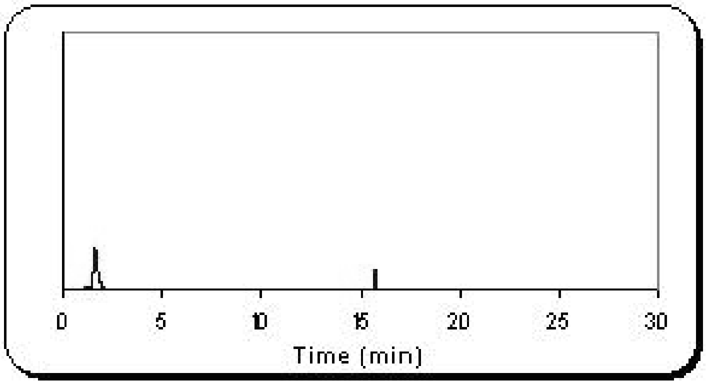


Figure 5 - Chromatogram of the methanol extract done from the polluted soil, after the treatment (bottom of the column). λ =269 *nm*.

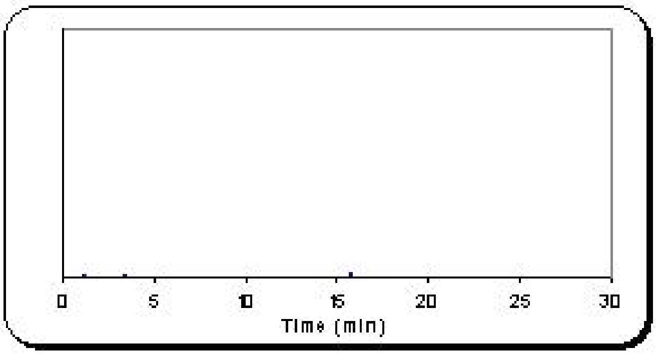


Figure 6 - Chromatogram of the aqueous phase picked up below the polluted soil column with phenol, after the treatment. λ =269 *nm*.

Figure 7 - Chromatogram of the acetonitrile extract done from the polluted soil with LAB, before the treatment. λ =202 *nm*.

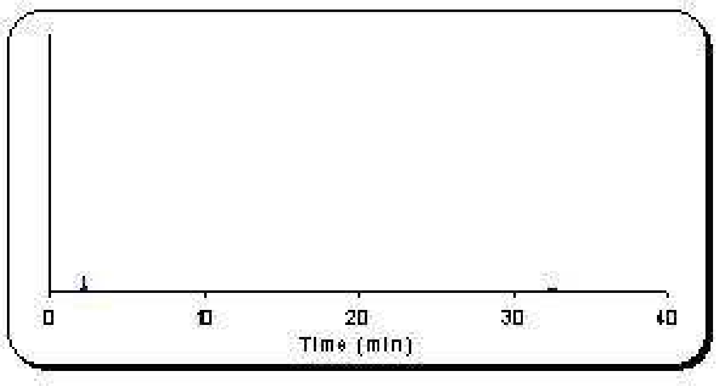


Figure 8 - Chromatogram of the acetonitrile extract done from the polluted soil with LAB, after the treatment. λ =202 *nm*.

The measure of the phenol concentration in the aqueous phase is important, because the aromatic compounds are very much soluble in water than aliphatic and others hydrophobic compounds, which can be dragged until the saturated zone, contaminating the groundwater. Fig. 6 shows that the phenol in the aqueous phase was degraded, as also turn by Moraes et al. (2001).

Figs. 7 and 8 present the chromatograms of the acetonitrile extract from the polluted sandy soil with the spill of LAB (soil 2), before and after the treatment, respectively. Due to the absence of appropriate patterns, it was impossible to quantify the representative compounds of the mixture; however, through information given by the producer, on the qualitative composition of these oils, we could identify several isomers of the linear alkyl benzenes, as also shown by Eganhouse et al. (1983) and Ishiwatari et al. (1983).

Comparing Figs. 7 and 8, we noticed that the hydroxyl radicals were generated oxidizing the representative compounds of LAB. The formation of vapors was observed, and, also, that leaves of the oil it was dragged to the water, however, this stayed insoluble, what facilitates your separation. The compounds that were dragged until the aqueous phase were very hydrophobic, and in the aqueous phase carboxylic acids in low concentration were probable detected which were result of the incomplete reaction of the hydroxyl radicals with the organic compounds present.

Analyzing the structure of LABs and knowledge of the reactivity of aromatic and aliphatic compounds with the hydroxyl radicals, it could be suggested that the phase not degraded dragged until the top of the aqueous phase it was composed basically of aliphatic compounds (present in the linear chain in the structure of the linear alkyl benzene), were more resistant the oxidation for hydroxyl radicals that the aromatic (Watts and Stanton, 1999). Fig. 9 shows sandy soil, before and after the treatment. The reduction of the black color indicated the degradation of the pollutant and the increase of intensity of the yellow color indicated a larger concentration of iron.

Fig. 10 shows the chromatograms of the extract obtained from the loamy soil (soil 3), using acetonitrile as extractor. A considerable reduction in the representative compounds of LAB observed at the places where the Fenton's reagents penetrated.

The chromatogram of the polluted sample before the treatment (not presented) was similar to the extracted sample of the middle of the column. Showed a section of the column, where the formation of preferential ways was observed due to the percolation difficulty and the liberation of heat from the reaction.

A considerable difference was noticed when the number of peaks of the chromatogram of the polluted soil with the spill was compared with the number of peaks of the artificially polluted soil with LAB. This difference could be explained by the fact that LAB of the sandy soil suffered natural transformations at the place of the spill, generating a series of compounds with small structural difference. This would also explain the large number of peaks and the proximity of the same ones, in the chromatogram of the Fig. 7.

The Fenton's reagent was extremely effective for the free and dissolved phases; however the sorbed phase was more difficult to be treated. The transport of the reagents in underground depends on the flow of water. Thus, at the places where the flow of water was null or very low, they present difficulty in remediation. The idea of injecting the reagent in high concentration did not provide solution for this problem, because the reaction of Fenton was very fast. Besides, the risk of accidents increase indeed when it was used these reagents in high concentration.

The reaction is very fast, therefore, an appropriate suggestion would be to work with low concentrations and a high volume, in periods of longer time, allowing the water to flow through most of pores possible. Another suggestion would be to inject the peroxide first (oxidizer) that would react, partly, with the salts of iron presents in the soil (Watts et al., 1999). The exceeding peroxide would react with Fe^{+2} (catalyst) injected later.

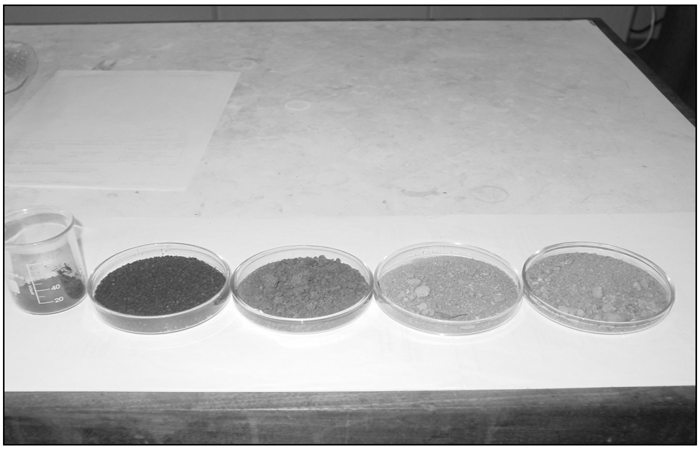


Figure 9 - Sandy soil after and before the treatment of Fenton's reagent. Of the left for the right in the petri plates: polluted original soil with LAB and soils after the treatment, of the bottom of the column, of the middle of the column of the top of the column, respectively.

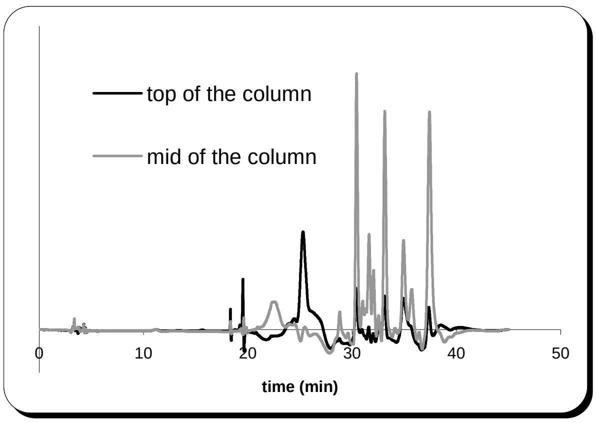


Figure 10 - Chromatogram of the polluted loamy soil with LAB. Extracts obtained in the middle and in the top of the column. λ =202 *nm*.

CONCLUSIONS

The results showed the viability of the Fenton process in the degradation of LAB's and its derivatives presents in the soil, in spite of the fact that the pollutant in the sorbed phase was more recalcitrant. An optimization of the concentrations of hydrogen peroxide and ferrous ions would be necessary to guarantee safety, avoiding the formation of "volcanos". The soils, in general, present great heterogeneity. The transport processes in undergrounds (advection, convection, diffusion, etc.) are responsible for the posing difficulties in remediation. The evaluation of these physical properties, such as, porosity, viscosity and permeability, now allow a better description of the transport mechanisms.

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RESUMO

Os Linear Alquilbenzenos (LABs) são usados como fluido refrigerante de cabos elétricos. Quando ocorre um vazamento, os LABs ficam basicamente adsorvidos no solo, pois, são compostos bastante hidrofóbicos e com baixa pressão de vapor. Os métodos convencionais de tratamento de solos não são eficientes. A reação de Fenton (solução de ferro II e peróxido de hidrogênio) gera radicais hidroxila, não seletivos, e capazes de oxidar uma grande variedade de compostos orgânicos, chegando a mineralização dos mesmos. Neste trabalho foi estudada a viabilidade de utilização dos reagentes de Fenton para promover a remediação de solos contaminados com LABs. Utilizou-se uma coluna especialmente projetada para estes experimentos, empacotada com um solo arenoso e outro argiloso. O pH do solo não foi alterado. Os resultados obtidos demonstram a viabilidade técnica do processo de injeção dos reagentes de Fenton para o tratamento de áreas contaminadas com LABs.

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