
Combined electrokinetic soil flushing and bioremediation for the treatment of spiked soils polluted with organics

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The work aims at studying the feasibility of the electrokinetic enhanced bioremediation. This is an emerging group of technologies that tries to combine the advantages of the electrokinetic soil flushing technology (EKSF) and biological soil remediation processes. Results demonstrate that combination of both technologies is not easy due to their very different characteristics. Results of direct combination are not completely positive because EKSF produces great changes in the pH and temperature, which affects negatively to the microbial viability. To overcome these drawbacks, different alternatives have been tested in this work in order to improve the efficiency of the combined biological and electrokinetic treatment. This work summarizes the main results obtained in each of them. The best results were obtained using a combination of EKSF with permeable reactive biobarriers in which the microorganisms were supported on gravel (EKSF-PRB). The position of the biobarrier was away from the extreme pH sections, and in this zone the supply of inorganic nutrients was ensured. Experimental results corroborated that the pollutant degradation efficiency is much higher using the combined EKSF-PBR technology (26.8% removal in a 14-day long treatment with an electric energy consumption below 100 kWh m⁻³) than using the simple biological treatment or the EKSF (11.8% removal in the same 14-day long treatment period).

1. Introduction

Many different technologies can be applied for the remediation of polluted soils (Gan et al., 2009; Mulligan et al., 2001; Yeung and Gu, 2011). These technologies are classified into in-situ or ex-situ techniques. In-situ technologies are applied in the same place where polluted soil is located without any soil digging works. Ex-situ technologies requires digging, dredging or any other process in order to stir the polluted soil before the treatment, which can be done in the same place (on site) or away from it (off site). Depending on the nature of the treatment applied, both, in-situ and ex-situ technologies can be classified into biological, physical-chemical and thermal treatments. All of them have different advantages and disadvantages for their application. Because of this, nowadays it is aimed the synergistic integration of different technologies looking for a higher efficiency in the soil remediation. One promising soil remediation technology for been applied coupled with many other treatments is the electrokinetic remediation technology (Yeung and Gu, 2011). Its combination with bioremediation, so-called electro-bioremediation, is a hot topic nowadays.

Basically, the electrokinetic enhanced bioremediation technologies are based on increasing the biological removal rate of pollutants by electricity-driven transport processes such as electro-migration, which has been used for supplying inorganic nutrients in soil bio-remediation processes (Cunningham et al., 2001; Peyton, 1996; Schmidt et al., 2007; Xu et al., 2010), electrophoresis, which has been suggested for the transport of microorganisms to increase the rate of the biological degradation (Da Rocha et al., 2009; Deflaun and Condee, 1997; Shi et al., 2008; Suni and Romantschuk, 2004; Wick et al., 2004) and electro-osmotic drag, which has been applied for the drag of non-charged water soluble pollutants (e.g. PAHs) (Niqui-Arroyo et al., 2006; Niqui-Arroyo and Ortega-Calvo, 2007). Heating caused by the high ohmic drops when an electric field is applied have also been applied in order to increase the rate of the bio-remediation process in cold climate areas (Suni et al., 2007). Unfortunately, electro-bioremediation is also known to have a number of negative consequences for the biological process. Specifically, water electrolysis reactions that occur on the

surface of the active electrodes result in the formation of an extreme acid and basic pH in the sections of soil near to the anode or to the cathode, respectively. In these sections, viability of the microbial consortia is not possible and, consequently, biological degradation process will be inhibited.

In this work, it is proposed to use the electrokinetic soil flushing technology (EKSF) coupled with the biological degradation process in three different alternatives (direct application, periodic electric field inversion and biological permeable reactive barriers) and results obtained in each of them are going to be compared with those of single bioremediation in the same operation conditions. Therefore, the goal of this manuscript is to evaluate the most efficient electro-bioremediation alternative for the treatment of a diesel polluted low-permeability soil.

2. Materials and methods

Bench-scale set-up used in the experiments is schematized in Figure 1. It was made in transparent methacrylate and divided into five compartments: in the central one, the diesel polluted soil was loaded. In the single and reversal EBR experiments, previously to the tests the soil was uniformly bioaugmented with a population of acclimated diesel degrading microorganisms. On a similar way, inorganic nutrients necessary for the biological degradation process were added to the soil with the electrolyte solution. In the experiment using the diesel degrading microorganisms supported on the biobarrier, this biobarrier was located in the fifth central part of the total polluted soil section. In this case, biobarrier was permanently immersed in inorganic nutrient solution. Graphite electrodes were both used as anodic and as cathodic materials. Both electrodes and soil had the same sections in order to have a homogeneous distribution of current lines throughout the soil. Kaolinite as a model of synthetic low permeability soil was used in all the experiments. All the experiments were performed in a potentiostatic way, setting a constant voltage gradient value of 1 V / cm. Duration of the experiments was two weeks, during which different parameters directly related with the biological degradation process were daily monitored (e.g. electrical current, temperature, pH and inorganic nutrient concentrations). In the same way, at the end of the experiments an in-depth sectioned analysis of the complete soil section was done.

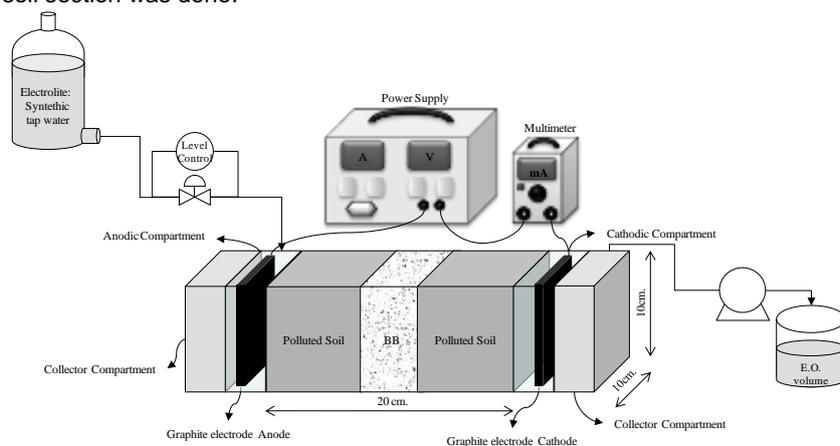


Figure 1: Bench-scale setup.

3. Results and Discussion

Figure 2 shows the changes in the resulting electrical current during the different bio-electroremediation test carried out. All the experiments shown in this work were done applying a constant voltage gradient of 1 V / cm, and the value of the intensity current depend on the characteristics of the system. As can be noted, the highest values were obtained when the electric field was directly applied to the polluted bioaugmented soil. In this case, the alternative used to buffer the pH in the sections near to the electrodic wells was to add carbonate-bicarbonate buffer in the electrolyte. This procedure made that every day conductivity in the system increased and, because this, also the value of electrical current. In the other tests, salinity of the medium was lower than in the single EBR process, and because this, electrical current values obtained were also lower.

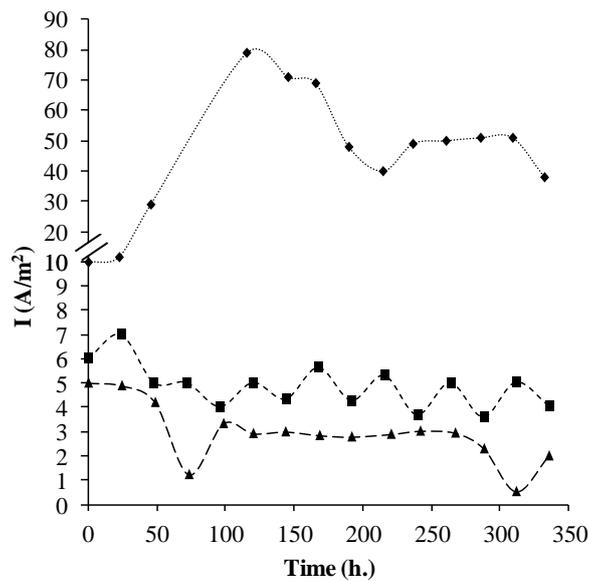


Figure 2: Electrical current variation. Single EBR test (◆), Reversal EBR test (■), EKSF BioPRB test (▲).

Figure 3 shows the variation in the temperature during the remediation tests. The highest increase in the temperature values was obtained in the single EBR experiment, for which also highest values of electrical current were achieved. Opposite, lowest temperatures were obtained in the single bioremediation experiment, when no current was applied and therefore there was no soil heating due to ohmic resistances. It is important to take into account that changes in temperatures can influence on the biological processes promoting or inhibiting the performance of microorganisms.

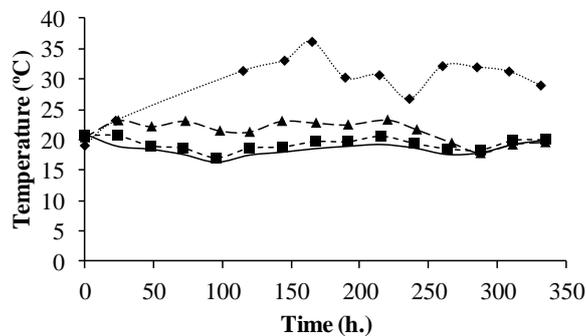


Figure 3: Temperature variation. Single Bioremediation test (—), Single EBR test (◆), Reversal EBR test (■), EKSF BioPRB test (▲).

Figure 4 shows the values of the electro-osmotic flows obtained in the three electro-bioremediation tests carried out in this work. Values obtained for this parameter are related to the value of the applied electric field. Thus, as it was expected, electrokinetic processes take part in greater extension working at higher electrical current. Therefore, electromigration and electrophoresis of charged species and electro-osmotic drag of water soluble compounds should have greater influence on the biological degradation process at higher current. This effect can be interesting for providing nutrients to microorganisms but it can be also harmful when the electrokinetic transport rates are too high and depletion of inorganic nutrients can inhibit the biodegradation removal.

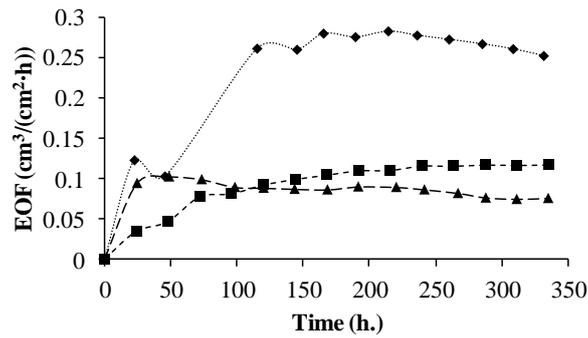


Figure 4: Electro-osmotic flow values variation. Single EBR test (◆), Reversal EBR test (■), EKSF BioPRB test (▲).

Figure 5 shows the pH gradient obtained along the soil section at the end of the remediation tests. As it was expected, there was not variation in the pH values in the bioremediation test (experiment in which no electric field was applied). However, because of the water electrolysis reactions significant variations are observed when an electric field is applied. In the nearest section to the anode, pH changes to acid values, and in the nearest sections to the cathode, pH becomes alkaline. To try to avoid the negative effects of the pH change, in the single EBR test carbonate buffer was used to control pH variations. However, this was not an adequate strategy because, as can be noted in the Figure 5, except in the nearest section to the anode, pH has values incompatible with the microbial life. Opposite, using the periodic electric field inversion, pH values are maintained near to the neutrality without marked changes in the anodic or in the cathodic sections and it seems to be an optimum alternative to control the influence of the acid and basic fronts in the soil media. Finally, in the experiments with the biobarrier it is also observed acidification and basification in the areas near to the electrodes. However, in the section where the biobarrier was located, pH was around the neutrality and therefore its value was adequate for the microbial life.

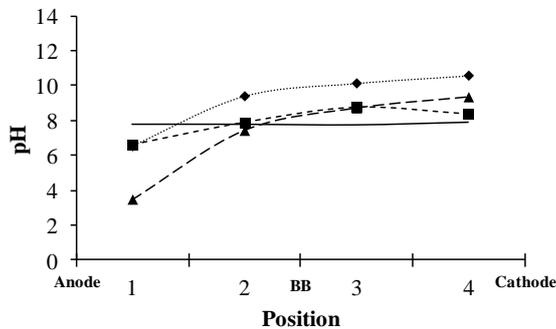


Figure 5: pH gradients at the end of the tests. Single Bioremediation test (—), Single EBR test (◆), Reversal EBR test (■), EKSF BioPRB test (▲).

Table 1 summarizes the main results obtained for the diesel degradation, N and P removal at the end of the remediation tests which lasted 14 days. Power consumption in the tests was also calculated in order to evaluate the most efficient alternative. As can be observed, the most efficient technology was obtained when EKSF and BioPRB were combined, with the removal of 25420 mg of COD (which correspond with the 26.78% of the initial COD present in the system) with an energy cost of 90.3 kW·h/Tm. This value is much higher than that obtained using single bioremediation (11.8%) in the same treatment period and also higher than that obtained by single EBR (11.4%) and reversal EBR (18.1%), in spite of being less energy demanding.

Table 1: COD and inorganic nutrients degraded and power consumption

	Single Bio	Single EBR	Reversal EBR	EKSF BioPRB
mg COD Removed	10215	10827	14677	25420
mg N Removed	251	337	186	733
mg P Removed	107	26	208	285
% COD Removed	11.79	11.36	18.12	26.78
Power Consumption (kW·h/T _{Soil})	--	1238.5	145.3	90.3

4. Conclusions

From the results presented in this work, the following conclusions can be drawn:

- Direct combination of biological and electrokinetic treatment is not a good alternative for the treatment of soils. Undesirable consequences of applying an electric field to a soil (strong pH and temperature changes) make not possible to carry out efficiently the biological diesel degradation process.
- Polarity reversal strategy makes softer the pH gradients produced in the soil and help microorganisms to degrade more efficiently the diesel contained in the soil. An enhancement of 54% in the removal of diesel is obtained in a 14-days long treatment with respect to single bioremediation
- The best results were obtained using biobarriers through the combined EKSF BioPRB process. An improvement of 127% is obtained in the removal of diesel in a 14-days long treatment with respect to bioremediation, with energy consumption 38% lower than that required for the polarity reversal strategy

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References

- Cunningham J.A., Rahme H., Hopkins G.D., Lebron C., Reinhard M., 2001, Enhanced in situ bioremediation of BTEX-contaminated groundwater by combined injection of nitrate and sulfate, *Environmental Science and Technology*, 35, 1663-1670.
- Da Rocha U.N., Tótoia M.R., Pessoa D.M.M., Júnior J.T.A., Neves J.C.L., Borges A.C., 2009, Mobilisation of bacteria in a fine-grained residual soil by electrophoresis, *Journal of Hazardous Materials*, 161, 485-491.
- Deflaun M.F., Condee C.W., 1997, Electrokinetic transport of bacteria, *Journal of Hazardous Materials*, 55, 263-277.
- Gan S., Lau E.V., Ng H.K., 2009, Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs), *Journal of Hazardous Materials*, 172, 532-549.
- Mulligan C.N., Yong R.N., Gibbs B.F., 2001, Remediation technologies for metal-contaminated soils and groundwater: An evaluation, *Engineering Geology*, 60, 193-207.
- Niqui-Arroyo J.L., Bueno-Montes M., Posada-Baquero R., Ortega-Calvo J.J., 2006, Electrokinetic enhancement of phenanthrene biodegradation in creosote-polluted clay soil, *Environmental Pollution*, 142, 326-332.
- Niqui-Arroyo J.L., Ortega-Calvo J.J., 2007, Integrating biodegradation and electroosmosis for the enhanced removal of polycyclic aromatic hydrocarbons from creosote-polluted soils, *Journal of Environmental Quality*, 36, 1444-1451.
- Peyton B.M., 1996, Improved biomass distribution using pulsed injections of electron donor and acceptor, *Water Research*, 30, 756-758.
- Schmidt C.A.B., Barbosa M.C., de Almeida M.d.S.S., 2007, A laboratory feasibility study on electrokinetic injection of nutrients on an organic, tropical, clayey soil, *Journal of Hazardous Materials*, 143, 655-661.
- Shi L., Müller S., Harms H., Wick L.Y., 2008, Factors influencing the electrokinetic dispersion of PAH-degrading bacteria in a laboratory model aquifer, *Applied Microbiology and Biotechnology*, 80, 507-515.
- Suni S., Malinen E., Kosonen J., Silvennoinen H., Romantschuk, M., 2007, Electrokinetically enhanced bioremediation of creosote-contaminated soil: Laboratory and field studies, *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 42, 277-287.
- Suni S., Romantschuk M., 2004, Mobilisation of bacteria in soils by electro-osmosis. *FEMS Microbiology Ecology*, 49, 51-57.
- Wick L.Y., Mattle P.A., Wattiau P., Harms, H., 2004, Electrokinetic transport of PAH-degrading bacteria in model aquifers and soil. *Environmental Science and Technology*, 38, 4596-4602.

- Xu W., Wang C., Liu H., Zhang Z., Sun H., 2010, A laboratory feasibility study on a new electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil, *Journal of Hazardous Materials*, 184, 798-804.
- Yeung A.T., Gu Y.Y., 2011, A review on techniques to enhance electrochemical remediation of contaminated soils, *Journal of Hazardous Materials*, 195, 11-29.