Coupled Chemical and Biological Treatment of Oil Contaminated Soils

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The aim of this study was to assess the feasibility of coupling chemical oxidation (active phase) with natural attenuation (passive phase) for diesel contaminated soils remediation and also, to evaluate the impact of natural organic matter in the soil matrix on the remediation efficiency. For that, two soil types with different organic matter content (TOC) were used - one sandy soil (18g/kg d.w.) and one clayey soil (39 g/kg d.w.) spiked with 6g/kg d.w. diesel fuel. As oxidants, sodium persulfate and sodium percarbonate were evaluated as active treatment step in soil remediation. Thus, four experimental and two control variants were conducted in batch tests - laboratory conditions, and monitored regularly for 11 months. The results indicated that using sodium persulfate as oxidant, for both sandy and clayey soil, lead to C8-C40 removal efficiencies of up to 53% and respectively 68% during active treatment and global removal efficiencies of 95 and 93% respectively. It must be noted that sodium persulfate affected (reversibly) the soil microbial populations; a lag period of approximately two months characterized by small removal efficiencies (1-3%) was observed. Using percarbonate as an active treatment phase lead to C8-C40 removal efficiencies of 62% for sandy soil and 34 % for clayey soil and global removal efficiencies of 85 and 96 % respectively. However, in case of percarbonate, no clear boundary can be set between chemical and biological treatment as it can act both as oxidant and as an oxygen source for aerobic biological processes. In case of control samples, representing natural attenuation, slow removal rates were observed during the first 4 months, removal efficiencies of only 7 and 23% being recorded. To conclude, combining chemical oxidation and bioremediation is a viable option for dealing with diesel contaminated soils, where bioremediation alone would not be time-effective and chemical oxidation alone would not be cost-efficient.

Keywords: soil remediation, diesel, chemical oxidation, natural attenuation

Today soil and groundwater contamination is a widespread and challenging problem threatening groundwater resources throughout the world. The contamination originates from introduction of xenobiotic chemicals to the environment or from naturally occurring sources, one of the most common chemical contaminants found in the environment is petroleum hydrocarbons [1]. Contaminated soils often present challenges that complicate the remediation process and result in very high remediation costs, if stringent clean-up goals need to be met [2]. Chemical oxidation has been used successfully to remove significant contaminant mass from soils at numerous sites [3-5]. Other studies indicates bioremediation as a cost effective technology for degradation of less contaminated sites [6-8] Combining different technologies in an integrated strategy can help overcome the limitations of individual technologies and lead to cost-efficient remediation. This strategy can include a fast and aggressive remediation technology based on chemical oxidation designed to remove the main volume of the contamination, whereafter a low maintenance, cheaper and long term technology deals with the remaining pollution in the same contaminated zone [9].

Persulfate is the second strongest oxidant used in soil remediation practice [5]. Persulfate (peroxodisulfate) salts dissociate in water to persulfate anions ($S_2O_8^{2-}$), which are strong oxidizing agents with an oxidation potential of 2.01 V [4], reaction 1.

$$S_2O_8^{2-} + 2H_2O + H^+ \rightarrow 2HSO_4^- + H_2O_2 \qquad (1)$$

One of the main advantages of persulfate is that, with a half-life of approximately 50 days, it can be present for relatively long time in the subsurface, but its fundamental chemistry in the subsurface is still being researched [10].

Sodium percarbonate (PC) is a cheap, mass-produced solid peroxygen compound that can be easily stored with minimal handling hazards, having no shock sensitivity, and is non-toxic, presenting no environmental hazard [11]. The name “sodium percarbonate” does not represent the true structure and nature of the material, which is also called sodium carbonate sesquiperhydrate, $2Na_2CO_3 x 3H_2O_2$. The alkaline compound shows H_2O_2 to be loosely bound and is readily displaced by moisture, disrupting the crystal structure [12]. PC chemistry in aqueous solution is similar to alkaline H_2O_2 chemistry, and SPC reactivity may be enhanced by true percarbonate formation. In solution, H_2O_2 is liberated and the perhydroxyl ion is formed,

$$H_2O_2 \rightarrow H^+ + HO_2^- \qquad (2)$$

Percarbonate, CHO_4^-, formation may be attributed to CO_2 action [13]

$$HO_2^- + CO_2 \rightarrow HCO_4^- \qquad (3)$$

or it is formed in equilibrium [12],

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Table 1
DESCRIPTION OF EXPERIMENTAL SETUP

Soil sample	Diesel fuel	Experimental variant		
		Natural attenuation (NA)	Sodium peroxidisulfate (SPS)	Sodium percarbonate (PC)
Clayey soil (A) 500 g	6 g/kg d.w.	-	20 g/kg d.w.	30 g/kg d.w.
Sandy soil (N) 500 g		-	20 g/kg d.w.	30 g/kg d.w.

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O \qquad (4)$$

Due to its relative lack of handling hazards, non-toxicity to the environment, low cost and availability, PC is potentially a viable oxidant for remediating petroleum contaminated soils.

The aim of this study was to assess the feasibility of coupling chemical oxidation (active phase) with natural attenuation (passive phase) for diesel contaminated soils remediation and also, to evaluate the impact of natural organic matter in the soil matrix on the remediation efficiency.

Experimental part

Two soil samples with different organic carbon content were collected from unpolluted areas, as follows: one sandy soil with 18g/kg d.w. TOC and one clayey soil with 39 g/kg d.w. TOC.

All reagents used for sample processing and analysis have been of reagent grade (Merck) quality; Chemical oxidants used: sodium peroxidisulfate and sodium percarbonate were reagent grade (Sigma Aldrich).

Experimental setup. Three experimental variants were conducted for each soil sample, according to table 1. corresponding to three experimental aproaches: sodium persulfate oxidation +natural attenuation, sodium percarbonate oxidation + natural attenuation and natural attenuation only.

500 g (d.w.) of each soil was sieved through a 2mm mesh and weighed in 2.5L test bottles (brown) and were spiked with 6g/kgd.w. diesel fuel. Chemical oxidants were weighed (analytical balance Sartorius Adventurer Pro) and added to the test bottles. Distilled water was added to all samples to correct humidity to 50%.

All samples were incubated at room temperature (20-24^0C), on an orbital shaker -160rpm (GFL 3017). The remediation process was monitored regularly for a total experimental period of 11 months. Monitored parameters: petroleum products as C8-C40 fractions (GC-FID, *Agilent 890N)*, sodium peroxidi-sulfate (spectrophotometric, λ = 400 nm, Hach Lange DR5000), sodium percarbonate (as active oxigen – iodometric), *p*H (WTW multi350i with gel electrolite SenTix electrode).

Removal efficiencies were calculated using equation (1), where : $C_{c8\text{-}c40i}$ represents initial C_8-C_{40} concentration and $C_{Cb\text{-}C40f}$ represent the concentration of C_8-C_{40} at time x.

$$\eta_{C8-C40} = \frac{(C_{C8-C40i} - C_{C8-C40f})}{C_{C8-C40i}} * 100 \qquad (2)$$

Results and discussions

Coupling sodium persulfate oxidation with natural attenuation

The results obtained for the remediation strategy based on coupling sodium persulfate with natural attenuation are presented graphically in figure1 for sandy soil and figure 2 for clayey soil.

In case of sandy soil high removal rates were observed during active treatment, 53% removal efficiency being registered after first two months. The following two months, pollutant removal rate was insignificant (only 1%) due to oxidant consumption and inhibitory effect of the active treatment upon the soil microorganism populations. After other two months, when biological functions of soil were recovered, removal rates increased leading to overall removal efficiency of 95% and a residual C8-C40 concentration of only 311 mg/kg d.w. (value below the intervention level - 500 mg/kg d.w. - according to Order 756/1997).

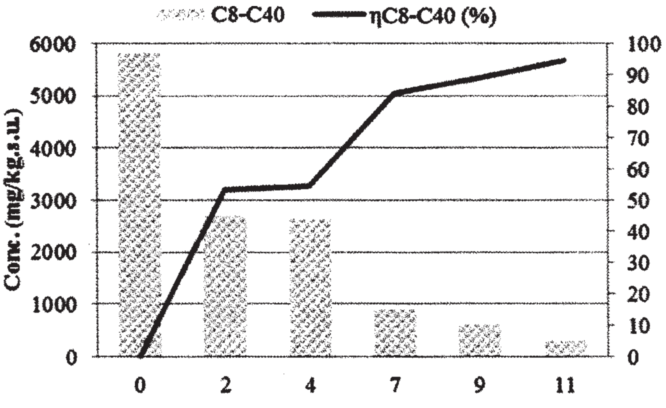

Fig. 1. Coupling sodium peroxidisulfate oxidation and natural attenuation - sandy soil

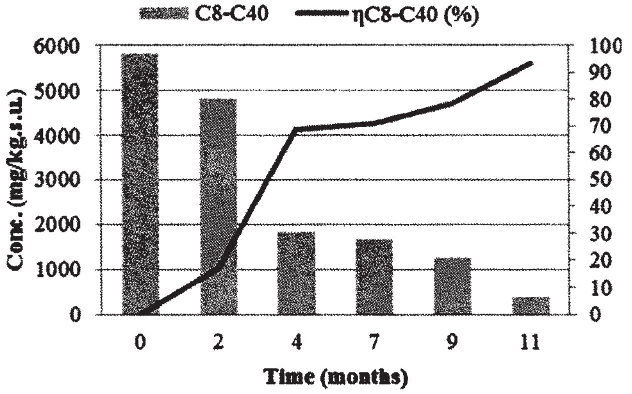

Fig. 2. Coupling sodium peroxidisulfate oxidation and natural attenuation -clayey soil

In case of the clayey soil, slower removal rates were observed during the first two months, removal efficiency of only 17% being registered in that period. After 4 months of incubation, the removal efficiency reached 68% (slightly higher than in case of sandy soil). This active period of 4 months was followed by a 3 months lag period, similar to the sandy soil case, due to microbial activity temporary inactivation. However, the biological functions of soil were recovered and global efficiency of 93% was achieved at the end of experiment, a residual concentration of 380 mg/kg d.w. being registered.

Comparing the results obtained for both types of soils (fig.3), the evolution of residual concentrations and removal efficiencies had a similar patterns for both types of soils: active treatment is followed by a lag period necessary for

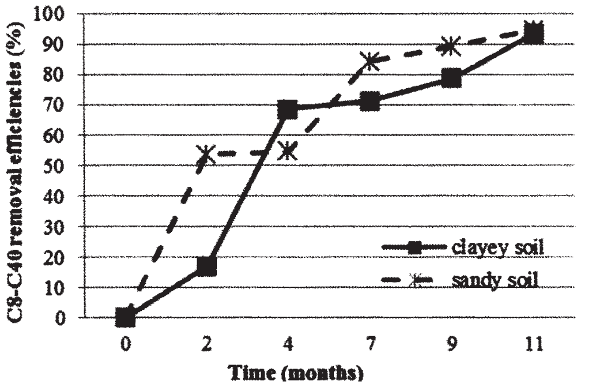

Fig. 3. Influence of soil matrix on the coupled SPS+NA remediation efficiencies

soil function recovery. The difference in timeframe of active treatment between the two types of soils could be explained by the fact that in clayey soils which tend to compact (even in shaking conditions) the contact between oxidizing agent and pollutant was hindered by lower diffusion. The lag period registered after oxidant consumption was registered in both soils due to the aggressivity of the oxidant towards native microbial populations. It must be noted that, most probably, in real conditions - in situ, the lag period will be much shorter due to transport phenomenon and microorganisms migration from and towards the injection point of the oxidant. The overall removal efficiencies were similar in both cases (95% and 93% respectively which leads to the conclusion that natural organic matter of the soil matrix has limited influence on remediation efficiency.

Coupling sodium percarbonate oxidation with natural attenuation

For the second remediation approach of coupling percarbonate oxidation with natural attenuation, the results of time evolution of residual concentration and removal efficiency are presented in figure 4 and figure 5 for the sandy and clayey soil respectively.

In case of sandy soil polluted with diesel, high removal rates were registered during first 4 months reaching a removal efficiency of 62% (8% higher than in persulfate case for same soil). The following 7 months, slow decreasing removal rates were recorded reaching at the end of experiment at a global removal efficiency of 86%.

In case of clayey soil, a slower removal rate was observed during first two months, a removal efficiency of only 10% being registered probably due to substrate competition with natural organic matter of the soil matrix. The next 9 months, we can observe an almost linear decrease of pollutant concentration reaching at the end of the experiment a global removal efficiency of 96%. Comparing the results obtained for both types of soil (fig. 6.) we can observe a slightly different trend in removal efficiency evolution in time. Lower removal efficiencies in case of clayey soil during the first four months are caused by the high total organic carbon (39g/kg d.w.) in the soil matrix which is competing for oxidation with the pollutant. No lag period was observed in either types of soil, thus we can say that when using percarbonate, no clear boundary can be set between chemical oxidation and biological oxidation as it does not have a negative impact on soil microbial population as persulfate, on the contrary, it may act as an oxygen source boosting aerobic biological activity.

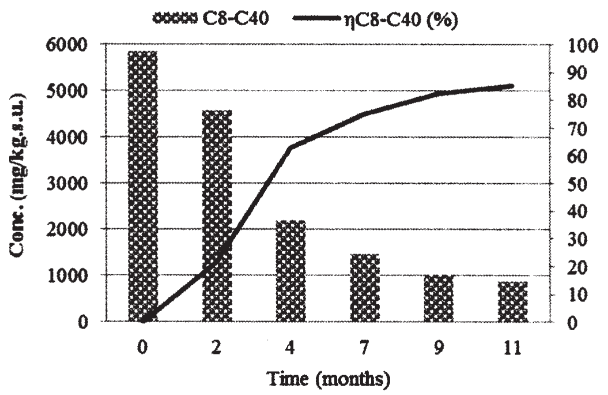

Fig. 4. Coupling sodium percarbonate oxidation and natural attenuation - sandy soil

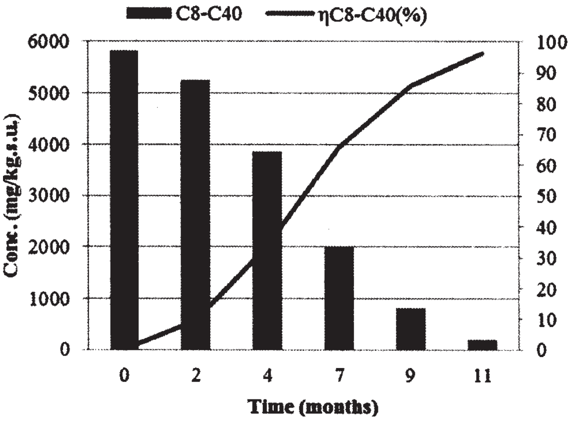

Fig. 5. Coupling sodium percarbonate oxidation and natural attenuation -clayey soil

Natural attenuation

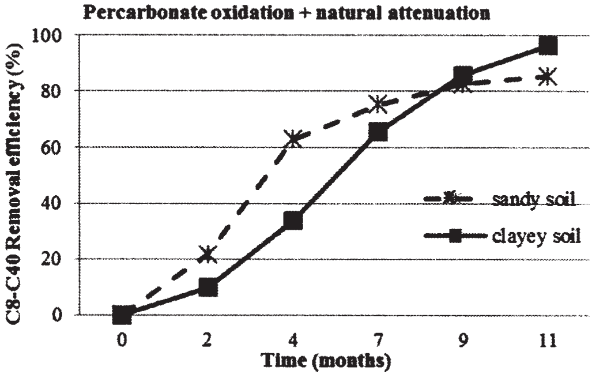

Fig. 6. Influence of soil matrix on the coupled PC+NA remediation efficiencies

In case of control samples representing natural attenuation, the evolution of residual C8-C40 concentrations in time and corresponding removal efficiencies are presented in figures 7 and 8. For sandy soil, no removal efficiency was recorded during the first 2 months, very slow removal rates were observed after 4 months, removal efficiencies of only 7% being registered. This long lag period was caused by the toxic impact of the added pollutant and represents the time needed for microorganisms to multiply and adapt for diesel metabolization. Once the bacteria adapted, relative high removal efficiencies were registered, reaching by the end of experiment 70%.

For clayey soil, the lag period was shorter (only two months) followed by an increase in pollutant removal rates, reaching at the end of experiment almost 50% removal efficiency.

Comparing the results obtained for sandy and clayey soil we can say that high concentrations of natural organic

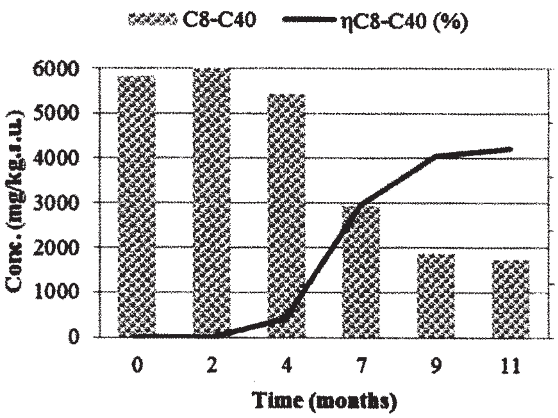

Fig. 7. Sandy soil remediation through natural attenuation

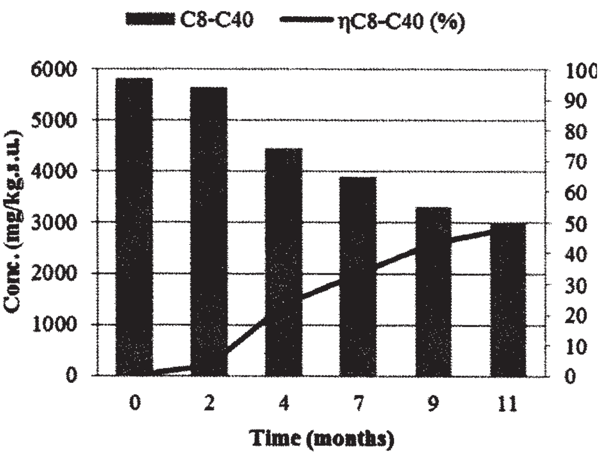

Fig. 8. Sandy soil remediation through natural attenuation

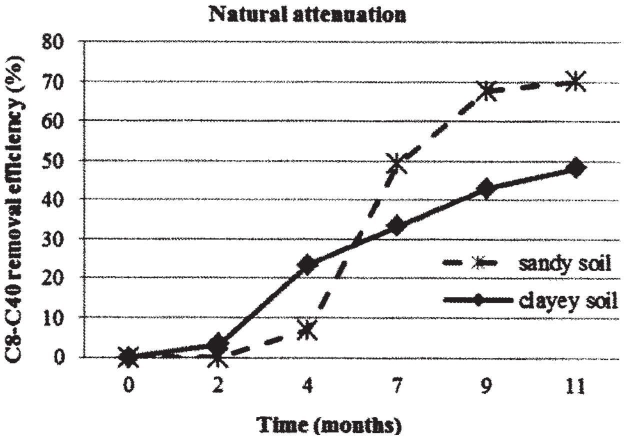

Fig. 9. Influence of soil matrix on natural attenuation remediation efficiencies

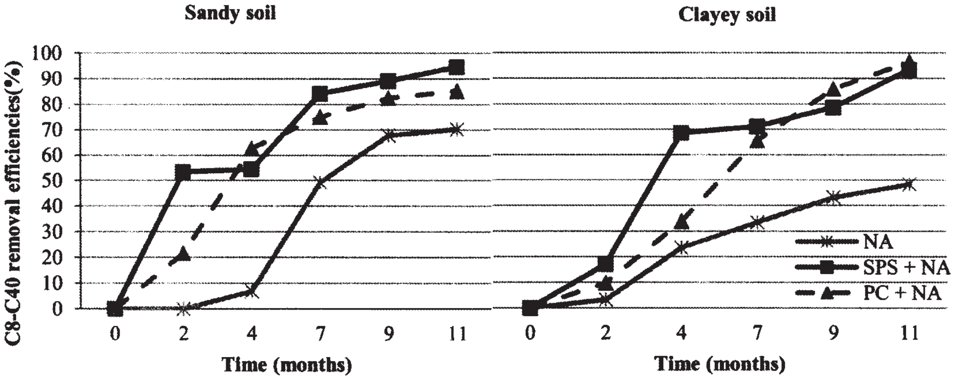

Fig. 10. Comparative analysis of remediation efficiencies

matter (as TOC) in clayey soil is initially favorable, acting as a protective buffer for existing microbial populations, minimizing the toxic effect on contact with the pollutant and shortening the lag phase of microbial degradation. However, after 4 the removal rates of the pollutant decreases because of substrate competition leading to global removal efficiency with 20% lower than in case of sandy soil.

Comparing the results obtained for all experimental variant (fig.10) we can conclude that chosing the remediation strategy depends on the available timeframe, available funds and intended use. Chemical treatments fill a niche in soil remediation, specifically for an active phase of source removal. Current applications can be improved considering the dimensions of cost, time, and sustainability by coupling an active phase of chemical oxidation with a passive phase of natural attenuation.

Conclusions

Both remediation strategies based on coupling chemical and biological remediation proved better than the natural attenuation approach. Sodium peroxydisulfate is a stronger oxidizing agent which leads to higher removal efficiencies on short term but also has a (reversible) inhibiting effect on soil microorganisms – a relative high period of time is required for soil biological function recovery. In case of sodium percarbonate no clear boundary could be set between chemical oxidation and bioremediation as it can act both as an oxidant. Using sodium percarbonate as an active phase lead to constant removal rates during the entire experimental period and high removal efficiencies comparable with the ones obtained in the peroxydisulfate approach. Considering these results we can conclude that if a short term remediation approach is required to lower the mass contaminant, the use of sodium peroxydisulfate coupled with bioremediation is advised, if a mid-term remediation strategy is needed than a less aggressive active treatment with percarbonate is appropriate and last, if remediation time is not a stringent constraint than bioremediation is advised.

Coupling of chemical oxidation and natural attenuation is a viable option for dealing with diesel contaminated soils, where bioremediation alone would not be time-effective and chemical oxidation alone would not be cost-efficient.

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