# **RSC Advances**



### **PAPER**



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# Fast and complete in situ mineralization of contaminated soils using a novel method for superoxide generation†

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In situ chemical oxidation (ISCO) is a technique used to remediate contaminated soil and groundwater systems. In this study superoxide oxidations of chlorinated solvents, PAHs, PCHs, PCBs, diesel and petroleum products were investigated in soil slurry systems under a variety of experimental conditions. Superoxide, generated from hydrogen peroxide and sodium hydroxide, functions as a super nucleophile and strong oxidizing agent, which rapidly reacts with different organic pollutants and swiftly mineralizes them to sodium carbonate.

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## Introduction

The contamination of soils and groundwater by organic chemicals and petroleum leftovers remains a significant world-wide problem, even after decades of research and development work.1 Frequently land contamination is driven by human activities such as inadequate intensive agriculture, construction works, industrial and military activities, etc. It has been estimated that only in the European Union 3.5 million sites are potentially contaminated.2 The most common soil pollutants are: polychlorinated hydrocarbons (PCHs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated hydrocarbons (solvents), petroleum products and pharmaceutical leftovers.3 The contamination of soils and sediments by persistent organic pollutants (POPs) such as PAHs, PCHs and petroleum products are an environmental concern because of their high chronic toxicity to both flora and fauna, and their long-lasting sorption by soils and sediments.4 Diesel and oil derivatives are classified into the group of the most dangerous compounds for the environment. These contamination migrates to deeper layers through leaching, and release of aromatic (polychlorinated biphenyls, PAH and phenols) and aliphatic compounds. These contaminations are highly hydrophobic and, therefore, strongly adsorbed to soils and sludge's.

Soil type, pH, polarizability, cation exchange capacity, particle size and contaminants all affect at contamination removal efficiencies. During the past decades, several new and innovative solutions for efficient contaminant removal from soils have been proposed and investigated. These methods includes: thermal desorption, thermal destruction, incineration, soil washing, biological remediation, vacuum extraction, centrifuge technologies, chemical extraction (solvent and cyclodextrins), surfactant, chemical oxidation, photocatalysis, and EK-ISCO treatment. We can characterize these technologies in two main groups of remediation methods, *in situ* and *ex situ* (for excavated soils) either on site or in designated soil treatment facilities.

In situ chemical oxidation (ISCO) remediation is on site chemical oxidation of pollutants. This method allows treatment of contamination without removing the soil. Chemical oxidation is a promising process for degrading an extensive variety of hazardous compounds in remediation of soil. Hence, during the last decades, numerous studies were carried out to develop in situ technologies for treating contaminated soils. In situ chemical treatment offers several advantages over conventional treatment protocols. Those methods are attractive because of the potential lower cost, less disruption to the environment, and reduced worker exposure to the hazardous materials.16 Chemical oxidation is far more rapid than biological techniques and even thermal or vapor recovery technologies. This technology does not generate large volumes of waste that must be disposed of and treated. Moreover, bioremediation has limited application for biorefractory pollutants and slow response particularly under cold climate conditions. Mostly this method involves direct injection of strong oxidants such as hydrogen peroxide, potassium and sodium permanganate, sodium persulfate, and ozone into the soil. Nonetheless, each oxidizing agent used in this preferred in situ technology has its specific

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pros and cons. The most important disadvantages of these oxidation methods are long treatment time (from several days up to a few months) and selective effectiveness. For example, permanganate is not an effective oxidant for degradation of chlorinated alkanes, most aromatic derivatives and PCBs contaminants. Under alkaline conditions persulfate can decompose chlorinated methanes, ethanes and dechlorinating of PCBs. However, persulfate is kinetically slow in oxidation of organic contaminants.<sup>17</sup> Ozone technology is a very effective method for PCHs and PAHs treatment.18 Nevertheless, longer injection times may be required than for other oxidants. Hydrogen peroxide and Fenton reagent are the most commonly used chemicals for contaminated soil remediation.19 Hydroxyl radicals are strong, relatively non-specific oxidants that react with most organic compounds even highly halogenated alkenes and aromatics.20 Nonetheless, the limitations are pH control and difficulties in controlling the in situ heat and gas generation. Hydrogen peroxide treatment typically needs days or weeks to be effective.21 Another common drawback is that hydroxyl radicals generated by diluted Fenton reagents can oxidize only water soluble contaminants.22

In this research we propose a new method for chemical in situ remediation of contaminated soils by a unique superoxide reagent. We have recently described a novel method for the in situ generation of a remarkably stable superoxide anion in water by reacting sodium or potassium hydroxide with hydrogen peroxide under ambient conditions.23 Our unique reagent exhibits properties of a super oxidizing agent. This reagent was effectively utilized for the destruction of bulk of carbon tetrachloride and other polyhalogen compounds and mineralization of carbondioxide.24 In this work we demonstrate the effective and rapid reaction of superoxide with various hydrocarbons and other organic contaminants in soil. Beside the advanced oxidizing capacity of the material our reagent is extremely potent nucleophile and it swiftly reacts (within minutes-hours) at ambient conditions with PCHs, PAHs, PCBs compounds and petroleum products. Thus pollutants such as the industrial solvents (carbon tetrachloride, trichloroethylene and etc.), and petroleum products e.g. crude oil, diesel, xylene and the like (all typical ground and groundwater pollutants)25 are rapidly hydrolyzed and totally mineralized.

# **Experimental section**

#### Reagents and materials

30% aqueous hydrogen peroxide, sodium hydroxide, carbon tetrachloride, DBCE, PCE and TCE, phenol, toluene, m-xylene, bromobenzene and other materials and solvents were purchased from Sigma-Aldrich Ltd and were used without further purification. Diesel and oil was purchased from Paz Ltd. Soil A was taken from Judean desert area in one meter depth and preliminary dried at 400 °C two hours. Soil B was taken from coast area in one meter depth and preliminary dried at 400 °C two hours. Soil C (pure sand) was purchased from Sigma-Aldrich Ltd and preliminary dried at 400 °C two hours. Soil D was taken from upper Galilee area in one meter depth and preliminary dried at 400 °C two hours.

#### Physical measurements

Organic mixtures were analyzed by means of GC (FID detector), column 30 m, 0.32 mm ID, 0.25  $\mu$ m Resteck. Famewax<sup>TM</sup>. Peak areas were compared to a standard curve of each hydrocarbon prepared in dichloromethane. Solid end products were separated by filtration and analyzed by FTIR and XRD. FTIR studies were conducted using Peact IR 4000, manufactured by Metler Ltd. XRD studies were conducted using X-ray diffractometer, range: 1100 < 2 $\theta$  > 1680, D8 advance by Bruker AXS. TOC studies were conducted by using TOC analyzer N/C UV HS, Analytic-Jena, Germany Ltd.

#### Mineralization of hydrocarbons in soil slurry

Current study was carried out with artificially spiked samples at −13 °C−+37 °C in a laboratory scale. The experiment was conducted in an adiabatic glass reactor (500 ml). A glass reactor contains 60 gram of soil type A, B, C and D respectively, soil characterization shown in Table 1. The soils preliminary dried at 400 °C and was artificially spiked with contaminant by adding a contaminated solution. The initial concentrations of varied contaminations in soil matrix were 2000–300 000 mg kg<sup>-1</sup>. Two different syringes (50 ml) with reactants mixtures were injected in to the soil. The first one contains 0.05-1.6 mol of sodium hydroxide and the second one contains 0.05-0.75 mol of hydrogen peroxide. The reaction was continued for 20 minutes. Conceptual design for a soil remediation unit based on this technology proposed in Fig. 1. After the treatment, part of the sample was assayed by TOC analysis for solid samples. The remaining part (majority) of the sample (aqueous and solid phases) was separated and extracted with 20 ml of dichloromethane. The organic phases were combined and analyzed. The organic solution was assayed by GC-FID analysis. The solid phase was washed filtered and dried and analyzed by means of XRD and FTIR. The remaining water solution was assayed by TOC analysis for water samples.

The conversion amount calculated according to the equation below. Conversion =  $(C_i - C_o)/C_i \times 100$ . This definition is universal and matches variety of treatment process in variable conditions.  $C_i$  and  $C_o$  are the concentrations of hydrocarbon contamination in the inlet and outlet of the process respectively.

In the current study we selected CTC and *m*-xylene as two model compounds for polychlorinated hydrocarbon and aromatic hydrocarbon contamination. The remediation process is a moderate exothermic reaction with, reaction time is 20 minutes.

Table 1 Characteristic and classification of studied soils

Classification (%)	Soil A	Soil B	Soil C	Soil D
Sand	36.6	62.9	100	28.8
Clay	37.8	14.1	0	52.7
Silt	9	13.3	0	9.7
Carbonate minerals	16.6	9.7	0	8.8
Organic carbon	0.5	0.5	0	0.5
pH	8.4	7.9	5.5	7.4

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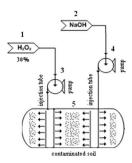


Fig. 1 Illustration of an apparatus for soil remediation system based on the proposed technology ((3 and 4) pump; (1)  $H_2O_2$  source; (2) NaOH source; (5) contaminated soil).

#### Results and discussion

In initial experiments the rate of removal of the different organic contaminants in soil with the *in situ* prepared superoxide reagent was found to be strongly dependent on several experimental parameters. These are  $\rm H_2O_2$ : NaOH mole rations, original concentration of contamination, soil type, treatment time and temperature and the pattern of hydrogen peroxide and sodium hydroxide addition.

#### Mineralization of hydrocarbons and polychlorinated hydrocarbons by sodium superoxide

In this study we demonstrate the efficacy of superoxide reagent as *in situ* chemical oxidation agent for effective soil remediation for wide range of organic contaminations. CTC and *m*-xylene were chosen as a model compounds. Both materials are toxic and biorefractory and typical waste of the chemical, fuel or military industries. The GC and TOC analysis of the reaction products clearly shows that there are almost no traces of CTC or xylene respectively. Moreover, the only solid products found were sodium carbonate and sodium chloride (in the case of CTC). Carbon tetrachloride and xylene swiftly mineralized in >98% efficacy, as shown in Table 2. Analysis has shown that these contaminants are almost totally and swiftly mineralized in minutes according the stoichiometry shown in eqn (1) and (2).

$$CCl_4 + 6NaOH + 9H_2O_2 \rightarrow Na_2CO_3 + 4NaCl + 4.5O_2 + 12H_2O$$
 (1)

Eqn (1): CTC mineralization

$$C_8H_{10} + 16NaOH + 24H_2O_2 \rightarrow 8Na_2CO_3 + 37H_2O + 1.5O_2$$
 (2)

Eqn (2): xylene mineralization.

# Effect of the base and hydrogen peroxide concentrations and of soil classification

The effect of NaOH/H<sub>2</sub>O<sub>2</sub> molar ratio on the efficacy of mineralization of CTC and xylene in the four different soils was tested. The results of CTC mineralization are shown in Fig. 2 and results of xylene mineralization are shown in Fig. 3.

It is apparent that in our reaction conditions and reaction time (20 min) hydrogen peroxide alone and sodium hydroxide alone have practically no effect on soil contaminated with CTC or with m-xylene. However, once a mixture of sodium hydroxide and hydrogen peroxide is applied rapid decomposition of CTC and of m-xylene is observed. Conversion higher than 98% is measured for both contaminants after less than 20 minutes. We found that optimal CTC removal is achieved when the initial molar ratio of the substrate and the reagents was CTC: NaOH:  $H_2O_2$  (1:6:9) for m-xylene destruction this ratio was xylene: NaOH:  $H_2O_2$  (1:16:24).

We then tested the role of the contaminants concentration in the soil (w%). This was tested for CTC and for xylene in soil of type A. Results are displayed in Fig. 4. It can be concluded that the concentration of both compounds in the soil had no effect on the efficacy of the treatment. The efficacy of treatment was more than 99% (conversion) in all these experiments. Nevertheless, the soil natural pH has a direct influence on the treatment efficacy as shown in Fig. 2 and 3. As higher initial soil pH less sodium hydroxide is required.

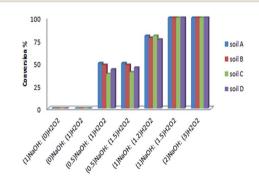


Fig. 2 Effect of sodium hydroxide and hydrogen peroxide molar ratio on reaction conversion of CTC remediation. Reaction conditions: 0-0.5 mol sodium hydroxide, 0-0.75 mol hydrogen peroxide 30%, 0.1 mol CTC and 50 gram of soils type A, B, C and D, reaction time 20 min.

Table 2 Mineralization of CTC and xylene by superoxide agent. Reaction conditions: 0.25 mol of sodium hydroxide, 0.37 mol of hydrogen peroxide 30% and 2000 mg kg $^{-1}$  (0.013 mol) of CTC in soil type A

	CTC (GC) (mg $kg^{-1}$ )	Xylene (GC) (mg kg <sup>-1</sup> )	CTC (TOC) (ppm)	Xylene (GC) (ppm)
Original concentration	2000	2000	2000	2000
Final concentration	0	20	<1 <sup>a</sup>	19

<sup>&</sup>lt;sup>a</sup> Sensitivity of the method.

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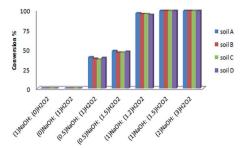


Fig. 3 Effect of sodium hydroxide and hydrogen peroxide molar ratio on reaction conversion of xylene remediation. Reaction conditions: 0-0.5 mol sodium hydroxide, 0-0.75 mol hydrogen peroxide 30%, 0.02 mol of xylene in 50 gram soils type A, B, C and D, reaction time 20 min.

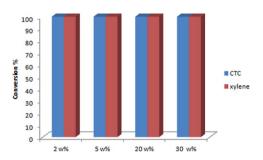


Fig. 4 Effect of CTC and xylene remediation as function of contamination: soil w/w ration. Reaction conditions: 0-0.5 mol sodium hydroxide, 0-0.75 mol hydrogen peroxide 30%,  $2000-30\,000$  mg kg<sup>-1</sup> of xylene in soil type A, reaction time 20 min.

#### Removal of halogenated solvents from soil matrix

Halogenated solvents are common and toxic biorefractory waste of the chemical, military and metal industries, we selected to test our reagent for the treatment of carbontetrachloride (CTC), trichlorobromomethane (TCBM), dichlorobromomethane (DCBM), dibromochloroethane (DBCE), trichlorobromoethane (TCBE), 1,2 dichloroethene (DCE), 1,1,1 trichloroethane/ methylchloroform (MCF), perchloroethylene (PCE), trichloroethylene (TCE). Samples of soil of type A separately containing these nine solvents in concentration of 200 g kg<sup>-1</sup> were treated with mixture of 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%, under ambient conditions of reaction for a period of 20 minutes. GC analyses of the samples clearly show that these contaminations are swiftly mineralized in <95% yield, as shown in Fig. 5. The end product of this remediation process is sodium carbonate and salt (NaCl or NaBr depending on the type of contamination). This was confirmed by XRD analysis shown in Fig. S1 in ESI.†

#### Aromatic hydrocarbons and aryl halides mineralization

Aromatic contaminants are generally more difficult to mineralize that the halogenated solvents tested above. We have examined the impact of our superoxide reagent on soil type A containing 70 g kg $^{-1}$  of phenol, toluene, m-xylene and bromobenzene under our standard conditions, (room temperature and atmospheric pressure) for a period of 20 minutes. Based on

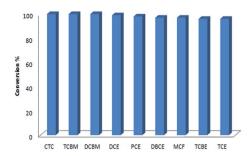


Fig. 5 Destruction of halogenated and poly halogenated solvents in soil by superoxide reagent. Reaction conditions: 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%,  $100\ 000-200\ 000$  mg kg<sup>-1</sup> of each halogenated solvents, soil type A, reaction time 20 min.

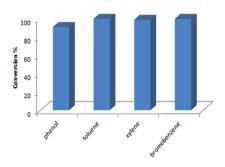
GC and TOC analyses these contaminations are swiftly mineralized in >99% yield, except phenol that mineralized in 91%. This is shown in Fig. 6. The end product of this remediation process is sodium carbonate or thermonatrite (hydrated sodium carbonate) and halide ions (in a case of bromobenzene), as shown by XRD analysis in Fig. S2 in ESI.†

#### Effect of the nature of the soil on the mineralization process

Soil type, characteristics, porosity and particle size are crucial parameters in efficiency of pollutants removal. We compared the rate of remediation of soils (types A–D, Table 1) contaminated with halogenated solvents, by aromatic hydrocarbons by aryl halides. Results of CTC, DBCE, PCE and TCE mineralization in soils A–D are shown in Fig. 7. Results of mineralization of phenol, toluene, *m*-xylene and bromobenzene in soils A–D are shown in Fig. 8. Soil type has scanty impact on the remediation process using the superoxide reagent. The 94–100% of mineralization was measured in 20 minutes with the four samples of soil contaminated with chlorinated solvents.

The corresponding result for soils contaminated with the aromatic compounds was 91–100% in all the four types of soils. Slightly more effective remediation was observed in soils type A and C.

We believe that the capacity of the soil to trickle initial reagents (effective mixing of sodium hydroxide and hydrogen



**Fig. 6** Efficacy of destruction of aromatic hydrocarbons and bromobenzene by superoxide reagent. Reaction conditions: 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%, 70 000 mg kg $^{-1}$  of aromatic hydrocarbons and chlorinated phenyls each, soil type A, reaction time 20 min.

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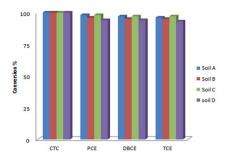
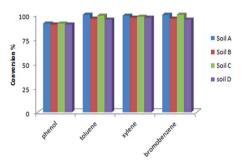


Fig. 7 Affectivity of destruction of halogenated solvents by superoxide reagent as function of type of soil. Reaction conditions: 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%, 120 000 mg kg $^{-1}$  of CTC, DBCE, PCE, TCE, soils types A, B, C and D reaction time 20 min



**Fig. 8** Affectivity of destruction of aromatic hydrocarbons and chlorinated phenyls by superoxide reagent. Reaction conditions: 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%, 100 000 mg kg $^{-1}$  of aromatic hydrocarbons and chlorinated phenyls, soil type A, B, C and D, reaction time 20 min.

peroxide in the soil) and initial soil pH are important factors in the soil treatment. At higher initial pH of the soil the superoxide radical is generated faster. If the initial pH of the soil is very high, the superoxide formation can start even before good mixing of NaOH and  $\rm H_2O_2$  is achieved. Reaction pH is a crucial parameter and initiation factor in superoxide generation as we already proved in our previous study.<sup>23</sup>

Soil type C (sand) allows fast and efficient mixing of the regents and soil type A has a highest initial pH with high concentration of sand. Therefore, these soils are more effective in the remediation process. Conversely, soil of type B has higher concentration of sand than soil type A, but the initial pH of this sample is lower than that of soil type A. Therefore, the remediation process in this soil is less effective than in soil type A but more effective than in soil type D. The initial pH of soil type D is the lowest. We may conclude that for our remediation process the initial acidity of the soil is more important parameter than soil porosity and particle size (percolating).

#### **Effect of temperature**

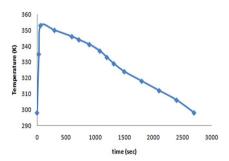
In a previous study we found that CTC mineralization is an exothermic process. In adiabatic batch reactor the reaction reached maximum temperature after 60 seconds than cooled down after 300 seconds. We examined the thermal behavior of

the soil remediation process using soil of type A containing 6 g  $\rm kg^{-1}$  of CTC. Results are shown in Fig. 9, where temperature of the sample as function of time is displayed. The reaction was started at 298 K and reached maximum temperature of 353 K after 60 seconds. However, in comparison with pure CTC mineralization, this reaction mixture cooling is significantly slower. This is due to the heat capacity and thermal insulation of the soil matrix. Moreover, in our previous study we proved that the initial temperature is a crucial parameter and that the reaction does not set off at all if the initial temperature is below 298 K. We tested this phenomenon in the current system and realized that the process takes off at any temperature provided the reagent mixture is not freezing. This is shown in Fig. 10.

We assert that the superoxide generation reaction is an exothermic process therefore, as long as the initial reagents did not freeze, the reaction will start and the temperature of soil will increase and the mineralization reaction will start.

At very low initial temperature of the soil (260 K) the overall conversion is somewhat lower (by 5%). We assume that at low temperature the superoxide agent is formed slower than at room temperature.<sup>26</sup>

On the other hand, if the initial temperature of the soil is high the rate of hydrogen peroxide natural evaporation increases. This evaporation lessens the initial amount of this major reagent in the soil and decreases the rate of the mineralization process. At initial soil temperature of 310 K where the mixture reaches a temperature of 60  $^{\circ}\mathrm{C}$  the reaction conversion



**Fig. 9** Temperature profile of CTC mineralization reaction. Reaction conditions: 0.25 mol of sodium hydroxide, 0.37 mol of hydrogen peroxide 30% and 6000 mg  $\rm kg^{-1}$  of CTC in soil type A.

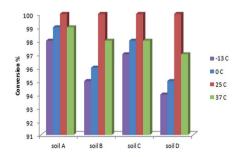


Fig. 10 Xylene remediation as function of temperature and soil type. Reaction conditions: 0.25 mol of sodium hydroxide, 0.37 mol of hydrogen peroxide 30% and 6150 mg kg $^{-1}$  of xylene in soils type A, B, C and D at temperatures gradient of soil between -13 °C and +37 °C, reaction time 20 min.

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is merely 3% lower depending on the type of the soil. Yet, the preferred initial temperature of the soil for the most effective soil remediation is at room temperature. Soil type and classification (heat insulation) has a negligible impact in remediation efficacy.

#### Diesel and crude oil mineralization

Oil spills are a major cause for soil contamination in various parts of the world. Crude oil and refinery products are composed of alkanes, cycloalkanes and aromatic hydrocarbons. The exact molecular composition varies widely from formation to formation.

Diesel and oil products are classified as one of the most harmful compounds for the environment. We confirmed that the proposed superoxide reagent under ambient conditions swiftly mineralize diesel and oil in soil in more than 90% yield, after one cycle of treatment, and completely mineralized after second treatment cycle. This is shown in Fig. 11. The end product of this remediation process is sodium carbonate, as shown in Fig. S3 in ESI,† where the XRD of the final reaction mixture is displayed.

# Benchmarking of the proposed system in comparison with the leading market technologies for *in situ* soil remediation

Hydrogen peroxide (Fenton agent) and sodium persulfate are the most extensively used chemical reagents for in situ treatment of contaminated soils. We advocate that our novel methodology described herewith has a clear kinetic and conversion edge over these methods. We have demonstrated this claim experimentally by comparison of the Fenton and persulfate protocols with our superoxide methodology in mineralization of m-xylene in soil (10 g kg $^{-1}$ ). Results are shown in Fig. 12. Our new superoxide system demonstrates more than 90% of soil remediation in the first cycle of treatment (20 minutes) and 100% of remediation after second cycle of treatment (additional 40 minutes) under ambient conditions. Conversely, the competing technologies exhibit low conversion, less than 20% for both reagents after first cycle of treatment (60 min). It should be noted that after treatment time of several days (weeks) and after scores of treatment cycles these technologies also reaches conversion higher than 90%. Nevertheless, our system has the same benefits as Fenton and ozone processes.

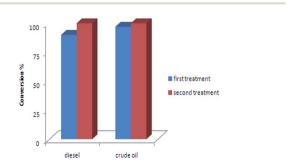


Fig. 11 Destruction of diesel and crude oil by superoxide reagent. Reaction conditions: 0.25 mol sodium hydroxide, 0.37 mol hydrogen peroxide 30%, 10 w% of diesel and crude oil in soil, soil type A, reaction time 20 min.

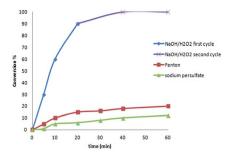


Fig. 12 Total affectivity of destruction of xylene in different soil remediation processes. Reaction conditions: superoxide system: 0.25 mol sodium hydroxide, 0.37 mol of hydrogen peroxide 30%, 10 000 mg kg $^{-1}$  of xylene in soils type A, first cycle reaction time 20 min and second cycle reaction time 20 min (total reaction time 40 min). Fenton reagent: 0.37 mol of hydrogen peroxide 30% and 10 w% (0.4gr) iron(III) oxide and 5 ml of HCl, 10 000 mg kg $^{-1}$  of xylene in soils type A, reaction time 1 hour. Sodium persulfate system: 0.37 mol of sodium persulfate and 5 ml of HCl, 10 000 mg kg $^{-1}$  of xylene in soils type A, reaction time 1 hour.

The contaminants are treated *in situ*, converted to innocuous and naturally occurring compounds ( $H_2O$ ,  $CO_2$ ,  $Na_2CO_3$ ,  $O_2$ , halide ions). We assume that by acting on the contaminant in place, there is no risk of vertical movement of the contaminant other than resulting from the act of vertical injection itself, which is often a concern in other remediation technologies. Additional advantage of the technology is the fact that natural iron oxide minerals (hematite, goethite, magnetite and ferrihydrite) present in soil not only do not hinder but catalyze decomposition of organic compounds (generation of Fenton reagent). Another advantage that should be cited is that aerobic biodegradation of contaminants can benefit from the presence of oxygen released during  $H_2O_2$  decomposition, if large quantities of reagent need to be applied.

#### Potential corrosiveness of the reagent

One of the main problems of *in situ* remediation technologies is that this technology implemented in many instances in grounds that contains underground infrastructure, for example water pipes and electrical wires. We examined the corrosion of metals in the presence of the superoxide reagent. The gravimetric measurements of pipe corrosion in presence of sodium hydroxide and hydrogen peroxide mixture are shown in Fig. S4 in ESI.† It is evident that even with very high concentration of the reagents (sodium hydroxide and hydrogen peroxide), up to four times more concentrated than the standard reaction conditions and with longer exposure time, five times more than standard reaction conditions the corrosion is negligible. The corrosion caused by our remediation reagent was 0.012% after 100 hours. We may claim that our remediation method is harmless to underground metal based infrastructure.

#### Conclusions

The exclusive mixture of hydrogen peroxide and sodium hydroxide allows effective application as ground treatment Paper RSC Advances

agent for wide range of soils contaminated with hydrocarbons, chlorocarbons and petroleum products. This application is novel and original. We show that soil type and initial soil temperature have minor impact on the efficacy of the proposed *in situ* remediation technology. This novel process is very effective and by far superior to any previous technologies for soil purification. This *in situ* treatment protocol was also confirmed to be harmless to underground infrastructure.

#### **Abbreviations**

**PCHs** Polychlorinated hydrocarbons **PAHs** Polycyclic aromatic hydrocarbons **PCBs** Polychlorinated biphenyls **POPs** Persistent organic pollutants **ISCO** In situ chemical oxidation  $\mathbf{E}\mathbf{K}$ Electro kinetic **EK-ISCO** Electro kinetic in situ chemical oxidation CTC Carbontetrachloride **TCBM** Trichlorobromomethane Dichlorobromomethane **DCBM** Dibromochloroethane DBCE **TCBE** Trichlorobromoethane DCE Dichloroethene MCF Methylchloroform PCE Perchloroethylene TCE Trichloroethylene

#### Notes and references

- 1 H. N. Quan, A. L. Teel and R. J. Watts, *Hazard. Mater.*, 2003, **102**, 277.
- 2 European Commission Environment Policies Soil A Strategy to Keep Europe's Soils Robust and Healthy, 2014, http://ec.europa.eu/environment/soil/index en.htm.
- 3 J. A. Lucas, L. J. Wibberley, E. M. Kennedy and B. Z. Dlugogorski, *ANZ Geo. Environ.*, 2001, 28.
- 4 W. Chu and C. Y. Kwan, Chemosphere, 2003, 53, 9.
- 5 M. Tejada, C. Garcia, J. L. Gonzalez and M. T. Hernandez, *Soil Biol. Biochem.*, 2006, **38**, 1413; C. N. Mulligan, R. N. Yong and B. F. Gibbs, *Eng. Geol.*, 2001, **60**, 371.
- 6 F. A. Caliman, B. M. Robu, C. Smaranda, V. L. Pavel and M. Gavrilescu, *Clean Technol. Environ. Policy*, 2011, **13**, 241.
- 7 P. Conte, A. Agretto, R. Spaccini and A. Piccolo, *Environ. Pollut.*, 2005, **135**, 515.
- 8 G. P. Warren, B. J. Allowaya, N. W. Leppb, B. Singhc and F. J. M. Bochereaua, *Sci. Total Environ.*, 2003, **311**, 19; C. Macci, S. Doni, E. Peruzzi, S. Bardella, G. Filippis, B. Ceccanti and G. Masciandaro, *Biodegradation*, 2013, 24, 521; K. Haahtela, *Environ. Pollut.*, 2000, **107**, 179.

- 9 S. Wang and C. N. Mulligan, Chemosphere, 2004, 57, 1079.
- 10 C. N. Mulligan, R. N. Yong and B. F. Gibbs, *Eng. Geol.*, 2001, **60**, 371.
- 11 M. Hamerski, J. Grzechulska and W. A. Morawski, *Sol. Energy*, 1999, **66**, 395.
- 12 S. Machado, W. Stawiński, P. Slonina, A. R. Pinto, J. P. Grosso, H. P. A. Nouws, J. T. Albergaria and C. Delerue-Matos, Sci. Total Environ., 2013, 461-462, 323.
- K. Hannaa, S. Chironb and M. A. Oturana, Water Res., 2005,
  39, 2763; L. M. Vane and G. M. Zang, Hazard. Mater., 1997,
  55, I; J. Virkutyte, M. Sillanpaa and P. Latostenma, Sci. Total Environ., 2002, 289, 97.
- 14 M. Z. Wu, D. A. Reynolds, A. Fourie and D. G. Thomas, *Groundwater Monit. Rem.*, 2013, 33, 62.
- 15 J. Scullion, *Naturwissenschaften*, 2006, 93, 51; H. I. Gomes,C. Dias-Ferreira and A. B. Ribeiro, *Sci. Total Environ.*, 2013, 445–446, 237.
- 16 S. Ho, P. Waynesheridan, C. J. Athmer, M. Heitkamp, J. Brackin, D. Weber and P. Brodsky, *Environ. Sci. Technol.*, 1995, 29, 2528.
- 17 C. Liang, C. J. Bruell, M. C. Marley and K. L. Sperry, Chemosphere, 2004, 55, 1225; C. Liang, C. J. Bruell, M. C. Marley and K. L. Sperry, Soil Sediment Contam., 2003, 12, 207.
- 18 I. Kima and M. Leeb, J. Hazard. Mater., 2012, 241, 173.
- D. L. Sedlak and A. W. Andren, Environ. Sci. Technol., 1991, 25(4), 777-782;
  S. Kong, R. J. Watts and J. Choi, Chemosphere, 1998, 37, 1473;
  L. L. Bisseya, J. L. Smithb and R. J. Wattsc, Water Res., 2006, 40, 2477;
  R. J. Watts, M. D. Udell and S. W. Leung, Hazard. Waste Hazard. Mater., 1990, 7, 335.
- 20 A. Teel, C. R. Warberg, D. A. Ankinson and R. J. Watts, *Water. Res.*, 2001, **35**, 977.
- 21 R. J. Watts, D. R. Haller, A. P. Jones and A. L. Teel, *J. Hazard. Mater.*, 2000, **76**, 73.
- 22 M. Starks, L. Liotta and M. Halpern, A review of "Phase-transfer catalysis fundamentals, applications, and industrial perspectives", Chapman and Hall, Inc., New York, 1994; M. Makosza and M. Fedoryński, Adv. Catal., 1987, 35, 375; R. J. Watts, P. C. Stanton, J. Howsawkeng and A. L. Teel, Water Res., 2002, 36, 4283.
- 23 U. Stoin, A. I. Shames, I. Malka, I. Bar and Y. Sasson, *ChemPhysChem*, 2013, **14**, 4158.
- 24 U. Stoin, A. I. Shames and Y. Sasson, RSC Adv., 2013, 3, 24440; U. Stoin, Z. Barnea and Y. Sasson, RSC Adv., 2014, 4, 36544.
- 25 P. E. Savage, Water. Chem. Rev., 1999, 99, 603; D. Bose, Sci. Tech., 1983, 35, 187.
- 26 A. W. Petrocelli and D. L. Kraus, J. Chem. Educ., 1963, 40, 3.