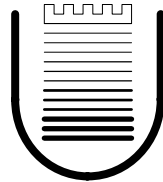


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"ADVANCED OXIDATION PROCESSES (AOPs) AS INNOVATIVE TECHNOLOGY FOR THE REMEDIATION OF CONTAMINATED SITES"

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Il problema della contaminazione dei terreni e delle acque di falda da composti organici biorecalcitranti sta diventando sempre più preoccupante agli occhi della comunità scientifica e dell'opinione pubblica. L'aumento del numero di siti contaminati da tali sostanze sta spingendo alla graduale sostituzione delle tradizionali operazioni di smaltimento in discarica con tecnologie che consentano la bonifica attraverso la riduzione del carico inquinante fino al raggiungimento di concentrazioni residue non pericolose per la salute umana.

I comprovati limiti operativi dei processi convenzionali per il trattamento di siti contaminati quali l'Air Sparging (AS), il Pump and Treat (P&T), il Bioventing (BV) ed il Soil Vapour Extraction (SVE), richiedono di sviluppare processi alternativi e di valutarne le prestazioni in relazione a casi di contaminazione rappresentativi della situazione nazionale. Tali limiti operativi sono legati alla resistenza al trasporto di materia che rende tali tecnologie molto efficaci nella fase iniziale di trattamento e gradualmente meno efficaci man mano che ci si avvicina agli obiettivi di bonifica, con andamento spesso asintotico della concentrazione raggiunta (fenomeno del tailing), oltre ai fenomeni di rebound legati all'aumento della concentrazione del contaminante subito dopo la sospensione del trattamento. Tra i possibili processi alternativi, i processi avanzati di ossidazione chimica (AOP) possono costituire una potenziale soluzione a molti casi di contaminazione da composti organici. Se opportunamente progettati, tali sistemi possono condurre alla completa mineralizzazione degli inquinanti o, eventualmente, alla loro trasformazione in molecole più facilmente biodegradabili. Il loro principio operativo è basato sull'idea di generare un pool di specie ossidanti altamente reattive, radicaliche e non. I diversi AOP si differenziano solo nel modo in cui tale pool di sostanze viene generato. Una volta prodotte, tali specie sono in grado di reagire efficacemente con i principali inquinanti di interesse ambientale come idrocarburi, solventi clorurati, idrocarburi policiclici aromatici e policlorobifenili. Inoltre, alcuni AOP sono in grado di trattare efficacemente anche composti adsorbiti sulla superficie del suolo, in quanto le specie radicaliche ne favoriscono il desorbimento rendendole disponibili all'ossidazione in fase acquosa. Alla luce di queste considerazioni i processi di ossidazione chimica stanno attraversando fasi di sempre maggiore sviluppo, perfezionamento ed applicazione. Le caratteristiche degli AOP li rendono perfettamente idonei come tecnologia di bonifica in-situ. In questa configurazione, si prevede l'iniezione nel sottosuolo (suolo insaturo o saturo) della soluzione ossidante senza la necessità di rimuovere il terreno e di estrarre le acque di falda. I principi base dei trattamenti di ossidazione chimica derivano dalle esperienze accumulate nel campo dei processi di trattamento delle acque reflue e della chimica organica industriale. La possibilità di utilizzare tali processi

per il trattamento in-situ di acquiferi contaminati ha innescato, pertanto, un crescente interesse scientifico e tecnologico, a partire dai primi anni '90.

Il presente studio è stato sviluppato con l'intento di perseguire un duplice obiettivo: da un lato approfondire le conoscenze di base sui meccanismi di azione degli AOP, al fine di sviluppare criteri di progettazione innovativi; dall'altro valutare l'applicabilità di diversi processi AOP a situazioni rappresentative dei siti contaminati tipicamente riscontrati in Italia. Il primo obiettivo è stato perseguito mediante uno studio di base finalizzato ad identificare la relazione tra condizioni operative del processo e formazione di specie radicaliche e non, nei sistemi di ossidazione basati sul reattivo di Fenton, sul processo a persolfato attivato e sul processo di ossidazione basato sugli acidi perossi-organici (perossiacidi). In questa ottica, per il sistema Fenton è stato sviluppato ed utilizzato un metodo indiretto per la stima quantitativa delle specie radicaliche ossidanti, che ha permesso di evidenziare e discutere il ruolo di alcuni parametri operativi chiave del processo Fenton quali la concentrazione di perossido d'idrogeno (H_2O_2), il rapporto molare $Fe(II):H_2O_2$, il ruolo e la concentrazione delle specie organiche presenti e l'influenza, sulle prestazioni del processo, della presenza di matrice solida nell'ambiente di reazione. Per quanto riguarda invece il sistema a persolfato attivato è stato sviluppato un approccio multi-parametrico basato sui parametri fondamentali che intervengono nella formazione delle specie radicaliche. Tale approccio ha consentito di evidenziare la relazione esistente tra le diverse condizioni operative come la concentrazione di persolfato di sodio ($Na_2S_2O_8$), il rapporto $Fe(II):Na_2S_2O_8$ e $Na_2S_2O_8$:inquinante e le prestazioni del processo espresse in termini di efficienza di rimozione del contaminante in esame (MtBE). Infine, l'approccio utilizzato nel caso del processo basato sui perossiacidi è stato quello di confrontare i risultati di uno studio multi-parametrico applicato a due diverse matrici: un sedimento di origine lacustre ed uno di origine marina. In questo modo è stato possibile studiare non solo l'influenza di diversi parametri operativi, quali la concentrazione di perossido d'idrogeno (H_2O_2), di acido acetico (CH_3COOH) ed il rapporto molare $CH_3COOH:H_2O_2$ sull'efficienza di rimozione del contaminante e sul tempo di vita dell'ossidante, ma anche quello di evidenziare le difformità legate alla diversa composizione chimico-fisica dei due sedimenti in esame.

Il secondo obiettivo è stato invece perseguito sviluppando, sulla base delle evidenze emerse dai diversi studi di base, un approccio progettuale incentrato sulla redazione di studi di fattibilità. Tale approccio ha consentito di arrivare, nel caso del processo Fenton, fino alla realizzazione di un intervento di ossidazione chimica in-situ (ISCO) in scala pilota per la bonifica di un sito contaminato da MtBE, mentre nel caso del sistema a persolfato attivato e dei perossiacidi si è

limitato alla fase di studio di fattibilità in scala di laboratorio. La progettazione delle diverse fasi sperimentali é stata, ove possibile, effettuata utilizzando il metodo Rotatable Central Composite (RCC), mentre i risultati ottenuti sono stati interpolati mediante opportuni strumenti statistici, come il Metodo delle Superfici di Risposta (RSM) al fine di individuare le relazioni quantitative tra le prestazioni dei processi investigati e le condizioni operative impiegate.

La presente tesi è stata scritta dedicando ad ogni tecnologia presa in esame una prima parte bibliografica, nella quale la tecnologia viene introdotta e ne vengono messe in evidenza le caratteristiche, seguita da una seconda parte in Appendice, dove i risultati sperimentali ottenuti vengono mostrati e discussi attraverso una selezione delle pubblicazioni prodotte durante il triennio di svolgimento del dottorato di ricerca, compreso tra il 2004 ed il 2007, e sottomesse a riviste specializzate del settore o presentate nell'ambito di convegni internazionali.

INTRODUCTION

The contamination of soil and groundwater by means of bio-recalcitrant organic compounds, is becoming a matter of concern for scientific community and public opinion. The increase of the number of contaminated sites, is forcing to gradually switch from traditional dump disposal, towards innovative technologies which are capable of reaching the remediation goals, thus reducing the pollutant load to concentrations which are considered harmless for human health.

The performance of traditional processes for the treatment of contaminated sites such as Air Sparging (AS), Pump-and-Treat (P&T), Bioventing (BV) and Soil Vapour Extraction (SVE), are limited by resistance to mass transport, which makes them effective only during the first phase of the treatment, and gradually less effective when the remediation goals are approached (tailing phenomena). Besides, rebound phenomena may occur after the site closure, requiring further remediation efforts. For this reason, it looks necessary to develop alternative processes and to assess their performance on those contamination cases of national concern.

Among these, Advanced Oxidation Processes (AOPs) could represent a potential solution to be applied for remediating contamination by bio-recalcitrant organic compounds. Their operative principle is based upon the idea of generating a pool of highly-oxidative species (radicals and non-). The AOPs differ only by the way in which this pool is generated. Once formed, these species are capable to effectively react with most of common pollutants such as hydrocarbons, chlorinated solvents, polycyclic aromatic hydrocarbons and polychlorobiphenyls until their complete oxidation to carbon dioxide and water, or at worst their transformation to more bio-degradable products.

Moreover, some AOPs are able to effectively tackle sorbed compounds, since oxidative radicals can desorb these compounds from the soil surface, thus allowing their oxidation in aqueous phase. In view of these considerations, AOPs are acquiring more and more attention and their development, optimization and application is currently growing up. Besides, it is worth pointing out that the AOPs characteristics make them suitable to be applied as in-situ remediation technologies. In this configuration, the oxidant is injected directly into the subsurface (vadose or saturated zone) without the need of soil excavation or groundwater extraction.

The basic principles of chemical oxidation derive from the experience gained in the field of wastewater treatment and industrial organic chemistry. The possibility of applying traditional

wastewater treatment to in-situ groundwater remediation allowed to create a growing interest within scientific community towards chemical oxidation since the 90's.

The present study has been developed with the intention of achieving a two-fold objective: on the one hand, to better understand the fundamental mechanisms of AOPs, in order to develop innovative criteria for their design; on the other hand, to assess the feasibility of different AOPs to those situations which are somehow representative of the Italian contaminated sites.

The first objective was pursued by developing a fundamental study aimed to identify the relationship between the process operating conditions and the formation of radical and non-radical species. As far as Fenton's process is concerned, an indirect method for the quantification of the oxidative radicals was developed and applied in order to assess the role of the main operating parameters on the process performance. Among these, hydrogen peroxide concentration, Fe(II):H₂O₂ molar ratio, the role played by the organic matter and the influence of the presence of the solid matrix in the reaction environment were considered. Concerning the activated persulfate technology, a multi-parametric approach was developed, based upon the main parameters responsible of the radicals formation. This approach allowed to show the relationship between the main operating conditions such as sodium persulfate concentration (Na₂S₂O₈), Fe(II):Na₂S₂O₈ and Na₂S₂O₈:contaminant molar ratios, and the process performances expressed in terms of target compound removal efficiency (MtBE). Finally, in the case of peroxy-acid oxidation technology, the approach was based upon a comparison between the experimental result of a multi-parametric study, which was performed on marine and river sediments. This way of performing the experimental study allowed to assess not only the influence of different operating parameters such as hydrogen peroxide (H₂O₂), acetic acid (CH₃COOH) concentrations and their molar ratio (CH₃COOH:H₂O₂) on removal efficiency and oxidant lifetime, but also to show the differences among the experimental results obtained on sediments characterized by different chemical-physical parameters.

The second objective was instead pursued by developing, based on the experimental results of the fundamental study, a design approach based on the execution of feasibility studies. In case of Fenton's process, a pilot-scale In-Situ Chemical Oxidation (ISCO) treatment for the remediation of an MtBE-contaminated site was developed, whereas in the case of activated persulfate and peroxy-acid oxidation technologies a lab-scale feasibility test was carried out.

The design of the different experimental phases was performed, as much as possible, by applying the Rotatable Central Composite method (RCC), whereas the relationships between process

performance and applied operating conditions was found by handling and interpolating the experimental results by proper statistical tools based on the Response Surface Method (RSM).

In this Ph.D. thesis, each tested AOP is first discussed in a bibliographic part, where the process is introduced and its main features are explained, based on the available and updated literature. The main findings obtained in this part and the innovation introduced with respect to the state of the art is also described in this section of the Ph.D. thesis. The details of these results are shown in the second section of the thesis, which consists of four Appendices, where a selection of papers submitted either to international conferences and peer-reviewed journals during my Ph.D. research are included.

FENTON'S OXIDATION TECHNOLOGY

Introduction

Fenton's reagent has been used to oxidize organic pollutants in many applications, from treatment of wastewaters to remediation of contaminated aquifers ([38]). In the so-called classic Fenton process, hydrogen peroxide (H_2O_2) reacts with Fe(II), yielding hydroxyl radicals and Fe(III) as reported in Eq.(1) and then Fe(III) is reduced back to Fe(II) via reaction with hydrogen peroxide (Eq.(2)) or superoxide radical (Eq.(3)) ([30]).



In environmental applications, hydrogen peroxide and hydroxyl radical can participate in a variety of reactions, making it difficult to anticipate hydroxyl radical activities and rates of OH^\bullet -dependent reactions. The contaminant oxidation is due to the high reactivity of OH^\bullet radicals generated when hydrogen peroxide oxidizes Fe(II) to Fe(III). The main disadvantage of the application of classic Fenton's reagent is that Fe(III) produced is only sparingly soluble, especially at circumneutral pH, so that high concentrations of ferric oxyhydroxides precipitates are generated when stoichiometric quantities of Fe(II) are used. A possible option to overcome this drawback is to acidify the soil to the optimal pH value between 2 and 3 or to use proper quantities of iron and try to regenerate the Fe(II) needed for the Fenton reaction by continuously reducing Fe(III) ([38]). In situations where hydrogen peroxide is added to destroy organic contaminants, non-target chemical species such as chloride, carbonates, other inorganic constituents and organic matter can react and "scavenge" those hydroxyl radicals that would otherwise oxidize the target contaminants. Moreover, since hydrogen peroxide is generally used at high concentrations in remediation systems (1–3 M) and has a moderate reaction rate constant with hydroxyl radicals, hydrogen peroxide scavenging may consume a considerable fraction of the hydroxyl radicals produced. Hydrogen peroxide also participates in non-productive reactions (i.e. those that don't lead to hydroxyl radicals formation) involving some metals such as manganese and copper, and enzymatic catalysts such as catalase or peroxidase. In environmental systems with sufficient concentrations of these reactants, the previous mechanisms could lead to the decreasing in Fenton's process efficiency ([30]).

Fenton's chemistry

During the catalytic oxidation involving ferrous ion and hydrogen peroxide, the former acts as a homogeneous catalyst, while the latter serves the role of the oxidant. In an attempt to describe the interaction between hydrogen peroxide and ferrous ions, in aqueous phase, Haber and Weiss proposed that, in the absence of other reactants, the generated hydroxyl free radical (OH^\bullet) (Eq.(1)) can react with ferrous ions (4) or with hydrogen peroxide (Eq.(5a)-(5b)):



Once formed, OH^\bullet may readily non-selectively interact with a broad range of organics. The rate of reaction of hydroxyl radical with an organic compound (C) is described by the second-order rate expression (Eq.(6)):

$$-\frac{dC}{dt} = k[\text{C}][\text{OH}^\bullet] \quad (6)$$

The reaction rates of highly reactive compounds are limited by the rate of diffusion of hydroxyl radical in water, which is $\cong 10^{10} \text{ M}^{-1}\text{s}^{-1}$. Therefore, the rate at which hydroxyl radical attacks highly reactive contaminants in aqueous systems is referred to as diffusion controlled. Some general rules have been established for the reactivity of hydroxyl radical with organic and inorganic species. Rate constants $> 10^9 \text{ M}^{-1}\text{s}^{-1}$ are considered high enough to be effective for AOP and ISCO treatments, while rate constants $< 10^8 \text{ M}^{-1}\text{s}^{-1}$ are considered too low. Almost all aromatic compounds, even those with a high degree of halogenation, react rapidly with hydroxyl radical. In contrast, alkanes exhibit relatively low reactivity with hydroxyl radical; in particular, chlorinated and fluorinated alkanes are basically nonreactive with hydroxyl radical ([83]).

Hydroxyl radical is characterized by a deficit of one electron in its valence orbitals, and is therefore an electrophile species. The most common reactions of hydroxyl radical are H-atom abstraction from C-H or O-H bonds and addition to aromatic ring in aromatic compounds and addition to alkenes. In the addition reactions, the hydroxyl radical attacks a ring carbon with its unpaired electron and upon contact forms a C-O bond, while a π -bond of the aromatic system is broken and a hydroxycyclohexadienyl type radical is formed. Whereas, in the H-abstraction paths, an oxygen-centered phenoxyl type radical and a water molecule are formed. The process of H-abstraction by the hydroxyl radical is a simple atom-transfer reaction in which the bond to

the hydrogen atom in the functional –OH group is broken and a new bond to the oxygen atom of the hydroxyl radical is formed ([34],[86]).

Another class of hydroxyl radical reactions is hydrogen abstraction from saturated compounds such as alkanes: this pathway is known to proceed at a slower rate relative to electrophilic substitution and addition. In the abstraction of a hydrogen atom from an alkane, an alkyl radical is produced and the hydroxyl radical is converted to water. Alkyl radicals can then participate in a number of propagation reactions, including a one-electron transfer to hydrogen peroxide that also generates hydroxyl radical ([83]). In general it has been shown ([13]) that in the presence of various organic substances, OH• radicals, which are the principal and primary oxidant in the classic Fenton's system ([39]), abstract hydrogen atoms from organic compounds (RH) and produce organic radicals (R•): in some cases, the organic radicals can further react with hydrogen peroxide as shown in the last two reactions below (Eqs.(7)-(8)):



The simultaneous generation of hydroxyl and organic radicals initiates chain reactions leading to oxidation of the organic substrates in the aqueous phase. The catalytic oxidation of organics leads to the formation of total or partial oxidation products such as alcohol or acids which are generally less toxic and more biodegradable compared to the original parent substrates ([13]).

There is evidence that hydroxyl radicals preferentially attack aromatic compounds: the aliphatic structures of natural organic matter react slower than aromatic moieties. Moreover, a higher chemical resistance of low-molecular weight aliphatic hydrocarbons (C₅-C₈) compared with aromatic compounds was reported ([53]). These results are consistent with the general order of reactivity shown in Eq.(9) and may account for the enrichment of aliphatic compounds in H₂O₂-treated soils:

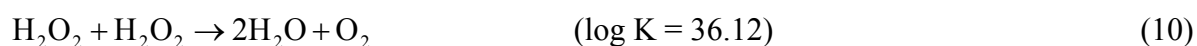


Accordingly, the aromatic hydrocarbons, would be more reactive with the radicals than chlorinated ethylenes, which contain only one double bond ([86]).

Routes of H₂O₂ and OH[•] unproductive consumption

In general, the consumption rate of H₂O₂ does not imply the same generation rate of OH[•] because H₂O₂ can decompose via non-radical-producing pathways: examples of these include reactions involving the organic matter content and the constituents naturally present in the soils such as biological enzymes and inorganic chemical species such as manganese ([39]).

Hydrogen peroxide is thermodynamically unstable and decomposes into oxygen and water according to Eq.(10). Decomposition of hydrogen peroxide increases with pH, being maximal close to the reagent's pK_a at 11.6 ([53]):



The possible decomposition pathways of hydrogen peroxide in soils imply that several reactive hydrogen peroxide species can interact with organic matter. In the simplest case hydrogen peroxide directly oxidizes organic compounds in a peroxidic-type reaction by a two-electron process without oxygen formation, being itself reduced to water ([53],[64]). This type of reaction is catalyzed by the peroxidase enzymes; whether this reaction can be catalyzed by abiotic metal species within the soils is so far unknown. Disproportionation can also take place through an even two-electron process induced by the enzyme catalase, which is found ubiquitously within aerobic organisms. In this case, hydroxyl radical is not produced during the decomposition of hydrogen peroxide to oxygen and water, and soil constituents are not subject to oxidation by hydrogen peroxide. Manganese oxides and some manganese complexes may be capable of performing this type of disproportionation as well ([64]). In contrast, the products of the metal-catalyzed Fenton's reaction will fall between these limiting cases, potentially producing both oxygen and hydroxyl radicals depending on the relative concentrations of hydrogen peroxide and hydroxyl radical-reactive soil constituents ([64]).

In surface soils, with higher organic matter or manganese content, hydrogen peroxide usually decays rapidly, with disproportionation to water and oxygen dominating the decomposition whereas formation of hydroxyl radicals represents less than 10% of the total hydrogen peroxide decomposed. In contrast, for soils with lower organic matter content, hydrogen peroxide usually decays much more slowly, but hydroxyl radical is the main product of the hydrogen peroxide decomposed ([64]).

The presence of scavengers decreases the contaminant oxidation rate, which is a function of these concentrations and reaction rates with hydroxyl radical, as well as a function of the contaminant concentration.

Scavenging of hydroxyl radical can be the result of:

1. the chemicals added as part of Fenton's reagent;
2. naturally occurring species in the system (e.g. anions and organic matter).

At sufficiently high concentrations, inorganic and organic soil constituents will react with hydroxyl radicals in place of hydrogen peroxide, thus decreasing the rate of hydrogen peroxide decomposition and lowering the yield of evolved oxygen. Under these conditions, iron catalyzes oxidation of reduced inorganic and organic compounds by hydrogen peroxide via hydroxyl radicals ([64]).

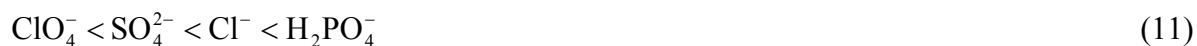
Many inorganic species found in natural and treatment systems, or added as salts of the iron catalysts, play the role of hydroxyl radical scavengers. Carbonates are most likely to scavenge hydroxyl radical and lower the effectiveness of modified Fenton's treatment. Most soils, groundwater, and treatment systems contain high concentrations of carbonates, so their scavenging of hydroxyl radicals becomes an important consideration in applying Fenton's reagent to the treatment of industrial wastes, soils and the subsurface ([83]).

Scavenging of hydroxyl radical by Natural Organic Matter (NOM) is more complex than scavenging by inorganic anions. The traditional concept of hydroxyl radical scavenging by NOM in aqueous systems is that NOM proceeds through oxidation by hydroxyl radical and, therefore, directly competes with the oxidative treatment of contaminants of concern. The effect of organic matter on Fenton's reaction may be a function of the state of the organic material (e.g. soluble or sorbed), the hydrophobicity and reactivity of the probe compound or contaminants, the nature of the Fenton's catalyst and perhaps many other factors ([83]).

Influence of inorganic ions

The Fenton reaction is extremely sensitive to the inorganic anions present in the solution. In the presence of inorganic ions the rate for the reaction of H_2O_2 with ferrous ions is different: the rate of decomposition of H_2O_2 in the presence of sulfate ions was observed to be more rapid than in the presence of perchlorate anion. In contrast, the presence of chloride in the reaction environment does not affect the rate of H_2O_2 decomposition ([71]). If chloride and phosphates ions are present in the reaction environment, oxidation of the target organic compound can be inhibited, whereas the presence of sulfates influences the oxidation rate to a much smaller extent.

Some authors ([71]) reported that some anions are able to suppress the MtBE decomposition in the following Eq.(11) sequence:



There are at least two reasons why ClO_4^- has a less important effect on decomposition than the other ions:

1. perchlorate ions do not form complexes with Fe(II) and Fe(III);
2. they do not react with hydroxyl radicals.

Probably there are several mechanisms affecting the oxidation process: the presence of SO_4^{2-} , Cl^- , H_2PO_4^- , ions leads to competition between the organics and the hydroxyl radicals, which retards MtBE oxidation. The inorganic ions react with hydroxyl radicals to generate inorganic radicals which are generally less reactive than hydroxyl radicals. Possible complexation reactions with iron are postulated as the main mechanisms, but scavenging of hydroxyl radicals and formation of inorganic radicals may also play a role ([71]).

Finally, in the presence of calcareous aquifer solids, carbonate and bi-carbonate ions can scavenge hydroxyl radicals which will enhance H_2O_2 decomposition rates ([85]).

The role of organic matter in Fenton's oxidation

Despite its potential importance, the role of Natural Organic Matter (NOM) in Fenton-driven oxidation has not been systematically investigated and remains uncertain ([30]). Organics can react with hydroxyl radical to produce a variety of organic radicals that may further react with target compounds ([30]).

Soil organic matter can reduce the efficacy of Fenton-type reaction by competing with contaminants for hydroxyl radicals or by catalyzing hydrogen peroxide decomposition. This suggests that results from lab-scale systems, which are built *ad-hoc* by using known amounts of selected organic matter, may not be directly useful for predicting the degradation of contaminants present in matrices that also contain NOM ([61]).

Organic substances can affect both the rate and the products of Fenton's reaction. Carboxylate ligands are known to accelerate the effective rate of the reaction by forming complexes with Fe(II) that react faster than the aqueous complexes. Although it is often assumed that OH^\bullet radicals produced by Fenton's reaction may oxidize Fe(II), OH^\bullet is also rapidly scavenged by organic matter ([79]). The organic intermediate product formed by the latter reaction can reduce oxygen to $\text{HO}_2^\bullet/\text{O}_2^\bullet$, whose reaction with Fe(II) results in regeneration of hydrogen peroxide and oxidation of Fe(II). Finally, if organic reducing agents are present, Fe(II) may be regenerated from Fe(III) ([79]).

Sorption of hydrophobic compounds to NOM plays a major role in inhibiting their degradation ([50]). Both physical and chemical changes upon sorption can alter the reactivity of a pollutant. For example, a pollutant in the interior of a particle may be physically isolated from reactants in bulk solution. In addition, changes in chemical reaction rate constants or mechanisms may occur upon partitioning to a chemically distinct micro environment ([50]).

Decreased degradation efficiency often occurs through reaction of hydroxyl radical with non-pollutant matrix compounds. Furthermore, binding of iron by NOM can alter the rate constant for Fenton's reaction or can change the formation rate of hydroxyl radical by affecting the redox cycling of iron ([50]).

The sequestration process of the organic compounds

One of the most important factors affecting the reactivity of organic compounds in environmental media is their tendency to associate with particulate matter. Organic contaminant partitioning is a function of particle composition (especially organic carbon content), particle concentrations and organic compound hydrophobicity, and can vary over a wide range. Particle-associated organic compounds may be incapable of reacting with aqueous phase OH^\bullet , because OH^\bullet react with dissolved species much faster than they can cross the solid-liquid interface and react with sorbed compounds. Thus, sorption of these compounds to particles may result in decreased removal rates. The magnitude of this effect will likely depend upon the relationship between the rates of adsorption-desorption and OH^\bullet reactions ([69]).

The soil contains two types of domain, both of which interact with contaminant molecules. The first of these consists of Humic Acid (HA) and Fulvic Acid (FA) bound or complexed to the surface of soil particles. This domain which is highly porous, flexible and lipophilic has been described as "rubbery" or "soft" by some authors ([11],[74]). In fact, the HA/FA overlayer may provide, due to its gel-like, colloidal nature and "indistinct" surface to regions of soil organic matter in which it is dominant. This is in contrast to the rigid, inflexible, "hard" or "glassy" nature of humin, the organic matter which predominates within the cores of soil particles.

Recent models of sequestration of contaminants recognize that the overall sequestration process most likely encompasses two individual mechanisms; namely, partitioning into or onto humic matter and diffusion into three-dimensional micropores of soil particles themselves.

Sequestration begins with partitioning of contaminant molecules into or onto HA and FA polymer layers at the surface of soil particles, followed by diffusion into micropores. The latter

structures most likely occur in the humin core of the particles and are rendered partially inaccessible to the bulk solution phase by the overlayer of polymeric HA and FA.

Some authors ([11],[74]) have demonstrated that sorbed molecules have significantly different reaction rates with OH^\bullet , and that soil-bound contaminants are more resistant to oxidative attack during chemical treatments than contaminants in solution. The effects of sorption on contaminant degradability can be minimized with high oxidant loads, which apparently result in generation of other species than hydroxyl radical, that are capable of oxidizing sorbed contaminants even in the absence of significant desorption.

The role of Humic material

Humic substances have been shown to reduce Fe(III) to Fe(II) in the absence of light ([79]). Similar redox coupling can be provided by constituents of humic materials (quinones, hydroquinones) in Fenton systems ([30]). If hydrogen peroxide is present at sufficient concentrations it will oxidize Fe(II) faster than oxygen does. Such reactions may provide an additional mechanism for Fe(III) reduction to Fe(II) resulting in more efficient radicals production. Hydrogen peroxide is likely to be a dominant oxidant of Fe(II) not only in acidic natural waters, where the rate of oxidation of Fe(II) by oxygen is very slow, but also at higher pH values (e.g. in marine waters at pH 8). Conversely, Fe(II) can be a dominant reductant of hydrogen peroxide in some surface waters ([79]).

Humic substances contain a high density of carboxylate functional groups that complex iron and are therefore likely to affect the rate of Fenton's reaction. They are also known to react rapidly with OH^\bullet radicals and to reduce Fe(III). Each of the latter two processes results in the oxidation of humic acid. In an aquatic system containing humic substances then, the reaction of Fe(II) with hydrogen peroxide can play a significant part in both the redox cycling of iron and in the oxidation of otherwise refractory organic matter ([79]).

The role of Fulvic Acid (FA)

Degradation of aqueous aromatic compounds with hydroxyl radical produced by Fenton chemistry is inhibited by dissolved fulvic acid ([50]).

A number of competing processes were observed in model systems containing dissolved iron, hydrogen peroxide and FA ([79]). First, the effective rate constant of Fenton's reaction increased with increasing FA concentration, indicating the formation of Fe(II)-fulvate complexes that react more rapidly with hydrogen peroxide than Fe(II)-aqueous complexes.

A second effect was the scavenging of the OH^\bullet radical produced in Fenton's reaction by FA and consequently the formation of an organic radical. The organic radical reduced oxygen to $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, which then regenerated hydrogen peroxide by reacting with Fe(II). Formation of $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ from OH^\bullet in the presence of fulvic acid and oxygen could occur either via OH^\bullet addition or via hydrogen atom abstraction ([79]). Finally, Fe(III) is reduced by a dark reaction with FA, characterized by an initially fast reduction followed by slower processes. The observed net result is an iron redox cycle in which hydrogen peroxide as well as oxygen are consumed (even though direct oxidation of Fe(II) by oxygen was not significant) and the oxidation of FA is accelerated ([79]). In conclusion, FA may play simultaneously the role of a carboxylate ligand, a radical scavenger and a reductant of Fe(III).

Stabilization of Fe(II) by the formation of complexes reacting with hydrogen peroxide more slowly than the Fe(II)-aqueous complexes is also a possibility. While even minor species can have an accelerating effect on Fe(II) oxidation, stabilization of Fe(II) through complexation can occur only if an Fe(II)-organic complex is a major species.

Under neutral pH conditions, hydrogen peroxide decomposes more slowly in soil with higher organic carbon rather than those with lower one: this fact may be due to soil organic matter coating the iron and manganese minerals and inhibiting their catalytic decomposition of hydrogen peroxide. At neutral pH regimes, soil organic matter may occlude iron and manganese oxides, which are the primary catalysts for hydrogen peroxide decomposition and soil organic matter destruction ([9]).

Separation of the hydroxyl radical formation sites from the location of the aromatic compound is believed to be the reason for the observed reduction in rate constants, indicating that these systems are heterogeneous on a micro environmental scale. The larger than expected inhibition of Fenton degradation by FA indicates that natural organic matter presents a significant impediment to remediation of pollutants in natural waters and soils ([50]).

FA molecules have physically separate hydrophobic and hydrophilic regions, and metal binding sites are spatially isolated from hydrophobic sites. Binding of iron to NOM would localize hydroxyl radical formation to these sites. Hydrophobic compounds, even those with considerable water solubility, would tend to avoid such strongly polar sites. Furthermore, compounds of greater hydrophobicity would have a lower likelihood of being in proximity to these polar sites ([50],[74]).

The access of hydroxyl radical to each of the organic compounds is somehow altered by the presence of FA. It is likely that binding of iron to hydrophilic sites of the FA also participates in sequestering the radical away from the aromatic compounds. In other words, hydroxyl radical formed in a hydrophilic site that is distant from the hydrophobic pollutant is not likely to diffuse to the pollutant before reacting with another scavenger (most likely Cl⁻) ([50]).

Modified Fenton Reagent (MFR)

Fenton process produces both hydroxyl and non-hydroxyl radicals (i.e. HO₂[•]). However, the dominant radical species and reactions occurring in a Fenton system depend on many factors, including compound reactivity with radicals, hydrogen peroxide doses, catalysts, pH, etc. Moreover, in contrast with oxidation under controlled laboratory conditions, the rate of contaminant oxidation in complex matrices such as treatment systems, soils and groundwater, is often affected by scavengers that deactivate hydroxyl radical ([83]). The reactivity of non-hydroxyl radicals with contaminants is relatively weak. Therefore, the reaction curve of substrates with highly reactive hydroxyl radicals usually exhibits a significant and quick drop of concentrations within minutes. On the contrary, the less reactive non-hydroxyl radicals tend to last longer and substrate concentrations usually decrease slowly but continuously for hours. Furthermore, the non-hydroxyl radicals are favourably formed at high hydrogen peroxide dose (e.g. > 1%) or high pH values (e.g. > 11) ([86]). When high concentrations of hydrogen peroxide are used for the Fenton's process, the so-called Modified Fenton's Reagent (MFR) occurs, as is commonly the case for treatment of industrial wastes and injection into the subsurface. During the MFR process, the hydroxyl radicals generated in the Fenton's initiation reaction (Eq.(1)) react with hydrogen peroxide and begin a series of propagation reactions that result in non-hydroxyl radical transient oxygen species, including perhydroxyl radical (HO₂[•]), superoxide radical anion (O₂^{•-}) and hydroperoxide anion (HO₂⁻) ([66],[83]):



Although the rate constant for Eq.(5a) is relatively low, these reactions become important when the concentration of hydrogen peroxide is high enough (e.g. > 0.3 M). Therefore, the rates of generation of perhydroxyl radical (HO₂[•]), superoxide radical anion (O₂^{•-}) and hydroperoxide

anion (HO_2^-) become significantly greater at higher hydrogen peroxide concentrations. Perhydroxyl radical is a relatively weak oxidant; superoxide is a weak reductant and nucleophile in aqueous systems. Hydroperoxide anion is a strong nucleophile. Processes that use high hydrogen peroxide concentrations are fundamentally different from the classic Fenton's reagent because they include propagation reactions that generate non-hydroxyl radical reactive species, resulting in a wide range of reactivity and lead to enhanced desorption of contaminants from the soil during modified Fenton reactions. The updated state-of-the-art is based on a model in which enhanced contaminant desorption is mediated by reductants and is followed by oxidation and reduction of the contaminants in the aqueous phase ([66],[83]).

Other modifications of Fenton's reagent are based on the use of alternate catalysts, including solid forms of iron (leading to the so-called Fenton-like process) and soluble iron chelates. Naturally occurring iron minerals have been studied extensively for catalyzing the decomposition of hydrogen peroxide. In many cases, Fenton's reactions are more stoichiometrically efficient when iron minerals are used as the catalyst, suggesting that injection of soluble forms of iron may not be needed for in situ treatment ([82]).

The existence of some iron ligands allow modified Fenton's reactions to proceed at neutral pH by minimizing the precipitation of iron and may eliminate the need to acidify the subsurface during in situ remediation ([82]).

Fe(III)-catalyzed oxidation process

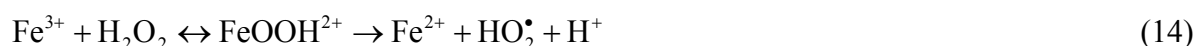
Iron in its divalent form (Fe(II)) is the most effective catalyst when dilute hydrogen peroxide concentrations are used; however, Fe(III) is a more effective catalyst at higher hydrogen peroxide concentrations (e.g. > 1000 mg/L (30 mM)). Fe(III) catalysis proceeds through a superoxide/perhydroxyl-driven reaction ([83]):



In Eq.(2), Fe(III) is reduced to Fe(II), which then serves to initiate the standard Fenton's reaction (Eq.(1)). MFR reactions with high concentrations of hydrogen peroxide are stoichiometrically more efficient when Fe(III) is used because they don't require the extra demand of hydrogen peroxide. In fact, during reactions conducted with Fe(II), the catalyst is rapidly oxidized to Fe(III), resulting in an immediate demand of hydrogen peroxide.

Thus, OH^\bullet is formed from hydrogen peroxide when either Fe(II) or Fe(III) is present, although generation rates are much slower in the latter case, even when the chain reaction is significant ([39]).

Two mechanisms have been proposed to account for the powerful oxidizing ability of Fe(III)/ H_2O_2 systems. The classical “radical” mechanism, abbreviated in Eqs.(1) and (14) generates OH^\bullet , which is one of the strongest oxidants known and reacts non-selectively with organic compounds:



Eq.(1) is also known as Fenton reaction. Recently, however, there has been strong evidence for formation of high-valent iron-oxo species originating from either Fe(II) or Fe(III), especially when the iron is complexed ([73]). These species may include the ferryl ion Fe(IV)=O and the one-electron ligand oxidized ferryl ion $[\text{L}^{\bullet+}]\text{Fe(IV)=O}$.

Three distinct disadvantages are found with the use of soluble iron as catalyst ([83]). First, an acidic pH regime is necessary to keep the iron in solution, which usually requires the addition of sulfuric acid. Second, the soluble iron usually precipitates as an amorphous iron oxide floc over the first few hours of contact with hydrogen peroxide. The floc formed is an inefficient catalyst, resulting in increased evolution of molecular oxygen and decreased hydroxyl radical production. Finally, Fe(II) and Fe(III) are strongly exchanged on subsurface solids, resulting in the potential loss of the catalyst with a lower catalytic activity downgradient ([83]).

Iron-chelated oxidation process

The low pH requirement (pH 2-3) for optimum Fenton reaction would make the process incompatible with biological treatment and poses potential hazards to the soil ecosystem where the reagent is used. Low pH itself can result in significant environmental perturbation and can enhance the solubility of heavy metal ions that may be presents as co-contaminants. The efficiency of the Fenton reaction greatly decreases with increasing pH because the solubility of ferric ions declines at pH values above 3. The decline in reactivity is due to precipitation of ferric ions as oxyhydroxide complex ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). In order to overcome such limitation, a modified Fenton-type reaction should be performed at near neutral pH by stabilizing the solubility of ferric ions with chelating agents ([61],[73]). To be useful, an iron chelate must also:

1. have catalytic activity toward oxidation of the target compound, i.e. be capable of generating hydroxyl radical or other reactive oxidant from H_2O_2 ;
2. be resistant to oxidation in the medium;
3. be environmentally safe.

It is likely that chelates are attacked by the oxidant even though in many cases the resulting complex containing the oxidized ligand remains soluble and active. As already stated, hydroxyl radical reacts rapidly with aromatic rings, double bonds and aliphatic C-H bonds, with rate constants as high as the diffusion-controlled limit ([73]).

From a practical standpoint, oxidation of the chelating ligand should be viewed also as advantageous, provided the iron remains soluble and catalytically active long enough to carry out degradation. Destruction of the ligand may alleviate concerns about the introduction of another component into the environment ([73]).

Manganese-catalyzed Fenton's reaction: formation of reductants

Other transition elements such as manganese, also catalyze Fenton's reactions but have not been studied to the extent of iron catalysis. Soluble manganese promotes hydroxyl radical production at acidic pH regimes; however, significant concentrations of catalyst are required compared to iron-catalyzed reactions ([82]).

Soluble Mn(II) is a stoichiometrically efficient catalyst for the generation of hydroxyl radicals at acidic pH, but not at the near-neutral pH regimes: in fact, as the pH of the manganese-catalyzed systems approached 6.8, an amorphous precipitate formed.

Some authors ([82]) studied the formation of reductants during the Fenton's process in the presence of Mn(II). The results indicated that in this conditions, generation of reductants may occur. The reductants formed in manganese-oxide catalyzed reactions may include superoxide radical anion, hydroperoxide anion and hydrogen atoms.

Thus, one or more reductants may be generated in the manganese oxide-catalyzed decomposition of hydrogen peroxide. Although amorphous manganese oxide-catalyzed Fenton's reactions generate reductants, they do not generate hydroxyl radicals ([82]).

The effect of inorganic and organic stabilizers

The use of stabilizers has the potential to improve hydrogen peroxide transport and its contact with contaminants, resulting in more effective remediation of contaminated groundwater ([84]).

A major advantage of the use of stabilizers is the potential ease of delivery; under current practice, acid, soluble iron or iron chelates are first injected into the subsurface followed by a second delivery of hydrogen peroxide. Use of the stabilizers may provide the potential for treatment using a single injection; hydrogen peroxide and the stabilizer could be mixed in a supply tank and injected into the subsurface together.

Several formulations have been developed to stabilize hydrogen peroxide decomposition because of its rapid decomposition in the presence of transition elements, metal oxyhydroxides and soil surfaces. Phosphate is most commonly used in bioremediation formulations because it is not only an inorganic stabilizer, but also a bacterial nutrient. Phosphate inhibits hydrogen peroxide decomposition by lowering the dissolved metal concentrations through either precipitation reactions or, in the presence of excess phosphate, conversion to relatively stable complexes. It can also act by affecting the surface charge or redox potential at the mineral surface. Once the iron is complexed, it is considered nonreactive with hydrogen peroxide. Phosphate also functions as a radical scavenger because it quenches hydroxyl radicals and terminates chain decomposition reactions. However, phosphate does not inhibit biological decomposition of hydrogen peroxide by the bacterial enzyme catalase. The rates of hydrogen peroxide decomposition for both the stabilized and unstabilized formulations increased as the pH increased ([51],[81]).

Stabilization has usually minimal negative effect on the generation of hydroxyl radical. Relative hydroxyl radical generation rates increased in some stabilized systems and decreased in other stabilized systems relative to the corresponding rates in unstabilized systems; however, most of the differences between the relative rates of generation were minimal and should not negatively impact the efficacy of Fenton's treatment ([84]).

Some organic stabilizers such as phytate, citrate and malonate can significantly increase the half-life of hydrogen peroxide in the presence of subsurface solids during Fenton's reactions while maintaining a significant portion of the reactive oxygen species activity ([84]).

Organic acids that chelate transition metals have been used to initiate Fenton's reactions. The low activity of some of the iron ligands is likely related to their high stability constants; these ligands that strongly bind iron may also stabilize hydrogen peroxide in the presence of subsurface solids. The conceptual model for such stabilization is to add the sodium salt of the organic acid to the hydrogen peroxide. When the hydrogen peroxide-organic acid mixture is injected into the subsurface, the labile transition metals in the subsurface would bind to the organic acid, reducing their catalytic activity and lowering the rate of hydrogen peroxide decomposition ([84]).

State of the art and research overview

As clearly reported previously, the chemistry of Fenton's process is quite complex and includes several pathways which may lead to the unproductive consumption of both hydrogen peroxide and the oxidative radicals, such as hydroxyl radicals. The undesired reaction of the latter with organic fraction and metals present in reduced form cannot be avoided, whereas that of hydrogen peroxide can be somehow modified, by properly adjusting the operating conditions of the Fenton's process. Instability of H_2O_2 , results from its reaction with inorganic compounds, such as iron oxyhydroxides and manganese oxyhydroxides catalysts or with organic compounds such as catalase or peroxidase enzymes, that are widespread in surface soils. In typical in-situ applications, this instability may dramatically reduce the concentration of H_2O_2 at increasing distance from the injection point and consequently the total amount of oxidative radicals available for oxidation of pollutants. In conclusion, the Radius Of Influence (ROI) of a Fenton-based ISCO application is a function of hydrogen peroxide lifetime and is susceptible to the groundwater and soil intrinsic properties. Moreover, all the case studies available in literature, where the Fenton's process was successfully applied as ISCO technology refer to typical US hydro-geological environments. Therefore specific studies are required if we would like to evaluate the applicability of this technology to the typical Italian scenarios.

Based on these remarks, I started my research with the aim of performing a Fenton's process feasibility study, looking if the experimental results could be transferred to the design and implementation of a pilot-scale treatment of an MtBE-contaminated site in Italy (the obtained results are reported in [Appendix A](#)).

The lab-scale experiments were performed in view of minimizing the amount of applied oxidant and amendments and to maximize the contaminant removal efficiency. A Rotatable Central Composite method (RCC) was applied to evaluate the minimum number of experiments required for the optimization procedure. Then, a Response Surface Method (RSM) was applied to provide a graphical representation of the influence of the operating parameters on the process performance. The obtained results showed that Fenton-like process is feasible for the treatment of contaminated sites, whose hydro-geological properties are representative of those often encountered in Italian subsurface, with low hydraulic conductivity values ($K = 10^{-6} \div 10^{-4}$ m/sec), high total oxidant demand ($\text{TOD} > 5$ g/kg) and high metals content ($[\text{Fe}] > 2$ g/kg, $[\text{Mn}] > 500$ mg/kg). The removal efficiencies of a single-injection process, tested in lab-scale, showed that the goal of reducing MtBE concentration to the limit of $10 \mu\text{g/L}$ suggested by Italian

Health Institute (ISS) cannot be met; nevertheless, the ten-fold MtBE removal achieved suggests that a multiple-injection technique could reach this goal.

Concerning the pilot-scale application, the positive results obtained under hydraulic confinement, by activating a P&T system, suggested that the drawbacks linked to the addition of hydrogen peroxide, iron catalyst and chelating agent (i.e. the observed moderate increase of groundwater temperature and metals content), are of small entity as far as the injected volumes are small. The applied low-dosage condition (i.e. hydrogen peroxide concentration equal to 1.47 M (5% wt/wt), iron and chelate concentration equal to 10 mM) led at most to temporary and localized variations of the water quality parameters, which very soon came back to their baseline values. It was also noticed that low-dosage conditions coupled with low hydraulic gradients and high NOM contents, are responsible of low hydrogen peroxide lifetime and then low ROI (during this application ROI was approximately equal to 50 cm).

The results of the feasibility study and pilot-scale application were useful to focus that the enhancement of Fenton-based contaminant removal efficiency has to be pursued by enhancing the hydrogen peroxide lifetime, thus maximizing the oxidative radicals amount and concentration within the reaction environment. In fact, during Fenton process, the species that are directly involved in the oxidation are hydroxyl radicals and other oxygen transient species like perhydroxyl radical (HO_2^\bullet), superoxide radical anion ($\text{O}_2^{\bullet-}$), hydroperoxide anion (HO_2^-) and not H_2O_2 .

Recently, my research group proposed the possibility of using the hydrogen peroxide lifetime as an indicator of the oxidation efficiency of Fenton's and Fenton-like processes ([5],[6]). That means a more simple preliminary screening phase of operating conditions, allowing to reduce the number of cases to be tested completely. Although the procedure was successful for comparing the different Fenton's process operating conditions for the same soil, it failed when applied to make a comparison between different soils so that, even though the presence of hydrogen peroxide in the reaction environment is a pre-requisite for the formation of oxidative radicals, the obtained results demonstrate that its concentration is not necessarily related to the radicals one.

A direct measurement of these radicals would allow to assess the influence of the operating conditions on the effectiveness of the Fenton's reaction. Unfortunately, the methods applied so far (i.e. Electron Spin Resonance spectroscopy (ESR)) result unsuitable for being applied as routine procedures, due to their high-cost and time-consuming features.

In view of these considerations, my research dealt with the application of an indirect method, based upon the quantification of the products generated from the reaction between reactive radicals and a probe compound, in order to get a two-fold objective: on the one hand, for evaluating the influence of the operating conditions on the oxidative radicals produced during the Fenton's reaction; on the other hand, for assessing the feasibility of the method on both aqueous and slurry Fenton's systems (for the complete results and discussion see [Appendix B](#)).

To this purpose, experiments in aqueous phase (with and without humic acid) and in soil slurry phase were performed. The selection of the operating conditions was based upon Rotatable Central Composite approach, in order to minimize the number of meaningful experiments to be performed and to obtain a correct evaluation of the influence of the operating conditions on the process performances. These were evaluated by measuring the total amount of generated radicals, their concentration, and their production efficiency (i.e. the fraction of H₂O₂ converted to radicals).

Within the tested operating conditions ($[H_2O_2] = 0.2 \div 1 \text{ mM}$, $[Fe^{2+}] = 0.2 \div 0.5 \text{ mM}$), the results indicated the feasibility of the applied procedure in terms of sensitivity and data repeatability. The Fe(II):H₂O₂ ratio was observed to affect the oxidative radicals production efficiency, which achieved a maximum 70% value for the highest tested Fe(II):H₂O₂ ratio. At low Fe(II):H₂O₂ molar ratios, the production efficiency was particularly low, suggesting that the Fe(II) was unable to complete the redox cycle generally supposed to occur during a Fenton's reaction. Moreover, the organic matter content was observed to negatively affect the radicals production efficiency, especially for the higher Fe(II):H₂O₂ molar ratios. Concerning the oxidative radicals concentration, it was observed to decrease sharply after few minutes of reaction time.

Despite some weak effects were noticed and discussed, the influence of dissolved organic matter on the radicals production was considered of minor importance. On the contrary, a one order of magnitude reduction in both radicals amount generated and concentration was observed when soil was added to the reaction environment.

It is worth mentioning that the obtained results were obtained on a simplified system, characterized by low H₂O₂ concentrations and using a model soil, consisting on a silica matrix. Therefore, the validity of the proposed method should be further demonstrated on real soil systems, also by using reagents concentrations typical of ISCO applications. Once generalized, such a method could become a useful tool for the effective design of in-situ Fenton's treatment.

PERSULFATE OXIDATION TECHNOLOGY

Introduction

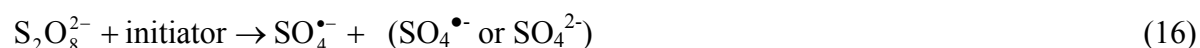
The technology based on persulfate oxidation chemistry is an emerging and promising tool for the In Situ Chemical Oxidation (ISCO) of chlorinated and non-chlorinated organic compounds. Activation of persulfate to form sulphate radicals ($\text{SO}_4^{\bullet-}$) would enhance the remediation of a wide variety of contaminants, including chlorinated solvents (ethanes, ethenes and methanes), BTEX, MtBE, 1,4-dioxane, PCBs and PAHs. Several activation technologies are available to catalyze the formation of sulphate radicals, including persulfate combined with chelated-metal complexes, persulfate combined with hydrogen peroxide and alkaline persulfate. The choice of the proper activation system should take into account the type of contaminant and the site characteristics.

Persulfate chemistry and its activation routes

Persulfates are strong oxidants that have been widely used in many industries for initiating emulsion polymerization reactions, clarifying swimming pools, hair bleaching, micro-etching of copper printed circuit boards and TOC analysis ([10]). In the last few years there has been increasing interest in sodium persulfate as an oxidant for the destruction of a variety of soil and groundwater contaminants. Persulfates are typically manufactured as the sodium, potassium and ammonium salts. The sodium form is most commonly used for environmental applications. Persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants among those usually employed. The standard oxidation-reduction potential for the main reaction reported below (Eq.(15)) is 2.1 V, as compared to 1.8 V for hydrogen peroxide (H_2O_2).



This potential is higher than the redox potential for the permanganate anion (MnO_4^-) at 1.7 V, but slightly lower than that of ozone at 2.2 V. In addition to direct oxidation, sodium persulfate may form sulfate radicals ($\text{SO}_4^{\bullet-}$) (see Eq.(16)), thus providing a free radical reaction mechanism similar to the hydroxyl radical pathways generated by Fenton's chemistry.



The sulfate radical is one of the strongest aqueous oxidizing species with a redox potential of 2.6 V, similar to that of the hydroxyl radical, 2.7 V. Sulfate radical initiation can be achieved through the application of heat ([29]), transition metal catalysts ([43],[44]) or UV radiation.

In addition to its oxidizing strength, persulfate and sulfate radical oxidation has the following several advantages over other oxidant systems:

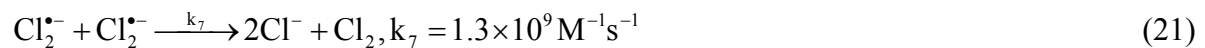
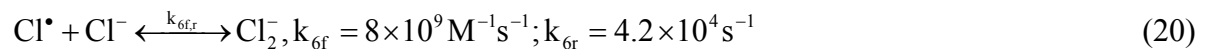
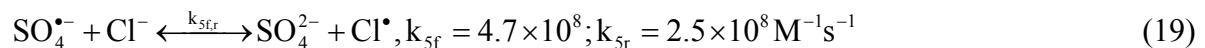
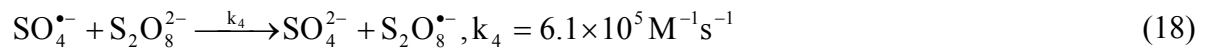
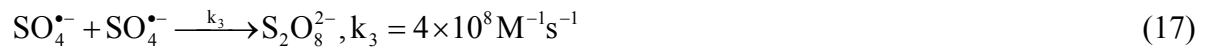
1. the sulfate radical is more stable than the hydroxyl radical and thus able to transport greater distances in the sub-surface;
2. persulfate has less affinity for natural soil organics than does the permanganate ion and is thus more efficient in high organic soils.

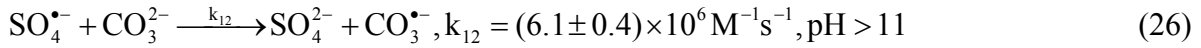
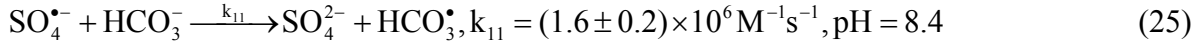
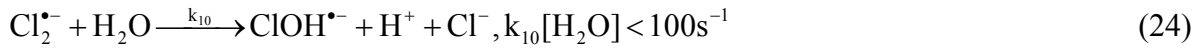
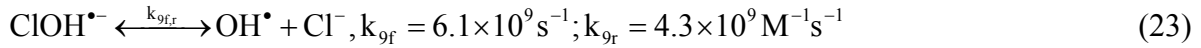
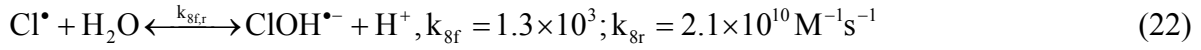
These attributes allow to make the persulfate-based oxidation a viable option for the chemical treatment of a broad range of contaminants.

Influence of anionic species on persulfate oxidation

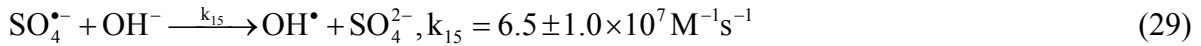
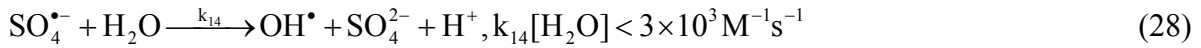
When persulfate is used for ISCO applications at relatively low temperatures, the oxidation reactions are usually less aggressive due to a slow generation rate of sulfate radicals. As already stated, the oxidation rate of target compound may be accelerated by activation of persulfate, which increases the rate of persulfate decomposition and thereby increases the rate of sulfate radical formation. However, competing side reactions with various species in groundwater systems other than the target contaminant can result in scavenging of sulfate radical and could possibly limit its oxidation efficiency.

Competition for sulfate free radicals could be from reactions with groundwater constituents such as chloride ions and carbonate species. The chemical mechanism and rate constants of persulfate with carbonates or chlorides in the aqueous phase includes, among others, the following reactions (Eqs.(17)-(27)):





Moreover, in aqueous solution, water and hydroxyl ion (OH^-) could also consume the sulfate radical formed. The reaction with sulfate radical could result in the formation of hydroxyl radical according to the following equations (Eqs.(28)-(29)):



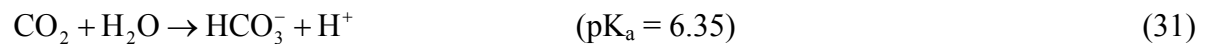
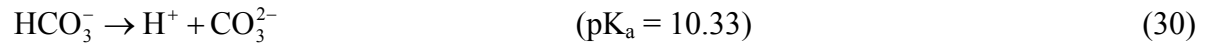
It can also be noticed that in aqueous solution, sulfate radical reaction leads to a decreasing of the pH value (see Eq.(28)). The above equations represent some of the simultaneous chemical reactions that occur immediately after sulfate radical is formed and show the possible coexistence of sulfate and hydroxyl radicals. Such coexistence has been demonstrated by electron spin resonance (ESR) ([45]). However, some authors reported that as pH increases above 7, the conversion of sulfate radical into hydroxyl radical becomes increasingly important ([46]). Additionally, a study using ESR to investigate the reactions of the sulfate radical with organic compounds revealed that as the pH is increased above 8.5, sulfate radical decays rapidly in aqueous solution by reacting with OH^- to generate hydroxyl radicals. Hence, it can be concluded that under acidic to neutral conditions, sulfate radical would be the predominant radical oxidant species.

The reactivity of sulfate radical in groundwater system may be affected by the presence of background ions. For ISCO applications, transition metal activators are usually added to induce the formation of sulfate free radicals. However, a quick release of sulfate free radicals may not necessarily increase the rate of oxidation of the target contaminant, since once formed it may be scavenged according to the equations above reported.

Comparing the rate constants of the equations above, it may be noted that the reaction involving sulfate radical and persulfate ion is a minor sink for the radical compared with its self-reaction (see in particular Eqs.(17)-(18)).

Influence of alkalinity species ($\text{HCO}_3^-/\text{CO}_3^{2-}$)

Speciation of alkaline anions (i.e. carbonate and bicarbonate species) depends upon pH which attacks the following equilibrium reactions (Eqs.(30) and (31)):



In a solution buffered at pH 7, HCO_3^- would be the dominant species at equilibrium. The bicarbonate radical generated by the reaction of sulfate radical with bicarbonate ion at a constant ionic strength was reported to yield redox potential ~ 1.65 V at pH 7. Bicarbonate radicals, which can possibly destroy some target compounds are formed although at a significantly lower rate compared to other reactions. It is likely that, based on the “slow” reaction rate of Eq.(25), the contribution of bicarbonate radical might be negligible. It should be noted that the pK_a for the process of deprotonation reaction (Eq.(27)) is 9.5; therefore in neutral solutions the dominant species is expected to be the bicarbonate radical. This has been verified in ESR spectra ([45]).

Scavenging reactions (Eq.(28)) may also occur. At higher pH values, the (bi)carbonate ions shift to carbonate ions (Eq.(30)) and the form of the (bi)carbonate radicals shifts to carbonate radical (Eq.(27)). The rate constant for the reaction of sulfate radical with carbonate ion is about 4 times higher than that of sulfate radical with bicarbonate ion and the redox potential of carbonate radical is lower than the bicarbonate radical. Hence, at elevated pH, due to the relatively low redox potential of carbonate radical and a preferential reaction between sulfate radical and carbonate ion, the inhibition on persulfate oxidation by carbonate ion results more important than the one by bicarbonate ion. As a result, addition of carbonate ions concurrently with persulfate to prevent pH drop in an ISCO application with persulfate at a site should be evaluated as an element of feasibility analysis.

Influence of chloride ion (Cl⁻)

Some authors reported that the presence of low concentrations (in the order of 0.2 mM) of chloride ions seems to have no effect on the oxidation of the target compounds. However, when the concentration of chloride increases, the degradation was inhibited ([45]). Eq.(19) shows a possible sink for sulfate free radical due to the highest rate constant among the reactions with

sulfate free radical. However, a rate constant for a reversed Eq.(19) similar to the forward rate may push the reaction backward, hence little or no loss of sulfate free radical oxidation efficiency could occur. On the other hand, if chloride ions are present at elevated concentrations ($> 0.3 \text{ M}$), the forward reaction of Eq.(19) would be important compared to the reverse reaction and would result in a greater degree of scavenging of the sulfate free radicals. Eqs.(19)-(24) show the chain reactions that occur when excess chloride ions are present. According to Eq.(21), chloride ions are regenerated and chlorine is formed. At elevated background chloride concentration (i.e. $> 0.2 \text{ M}$) chloride could cause inhibitions on the reactivity of sulfate ion.

Influence of pH on persulfate oxidation

Some studies based on radical scavenging tests coupled with application of Electron Spin Resonance technique (ESR) were performed to identify predominant radical species involved in persulfate-based oxidation ([46]). It has been shown that sulfate radical predominates under acidic conditions and hydroxyl radical predominates under basic conditions. The presence of sulfate free radical in aqueous solution can result in radical interconversion reactions to produce the hydroxyl radical in accordance with the following reactions:



Both radical species are responsible for the destruction of organic contaminants and either radical may predominate over the other depending on pH conditions. Sulfate radicals exhibit a higher standard potential than hydroxyl radicals at neutral pH and both radicals exhibit similar standard potentials under acidic conditions. In general sulfate radical is more selective for electron transfer reaction than hydroxyl radical and is likely to participate in hydrogen abstraction or addition reactions.

At acidic pH values, sulfate radical presents a minor redox potential value with respect to hydroxyl radical and reaction rate constant of Eq.(28) is small in comparison with those for sulfate radical reactions with organic compounds (e.g. aromatic compounds), thus leading to more inhibition of the persulfate oxidation. At higher pH relatively more hydroxyl radical could be generated. Under neutral or basic pH conditions, sulfate radical formed may undergo reactions with H_2O or OH^- in agreement with Eqs.(28)-(29) respectively, to generate hydroxyl radicals. Even though sulfate radical can be converted to hydroxyl radical, which exhibits a slightly higher redox potential, the presence of various ions in solution may result in inhibition of

the reactivity of hydroxyl radical or sulfate radical. Moreover, the higher sulfate radical generation rate cause higher radical concentrations, which could favour some unproductive radicals reactions over the others (e.g. radical-radical or radical-scavenger reactions). Possible chemical scavenging mechanisms in addition to Eqs.(28)-(29) that compete with the sulfate radical attack are:



By comparing reactions of sulfate free radical with H_2O , OH^- , $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{2-}$, the rate constant of Eq.(17) is the greatest. Therefore, when additional $\text{SO}_4^{\bullet-}$ is produced, scavenging of $\text{SO}_4^{\bullet-}$ by itself would be more significant than scavenging by OH^- . The reaction between $\text{SO}_4^{\bullet-}$ and H_2O does not appear to be significant under all pH conditions.

Persulfate activation by transition metals

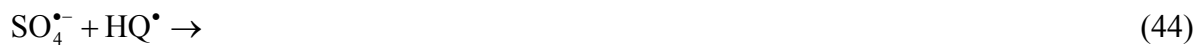
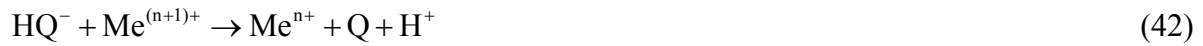
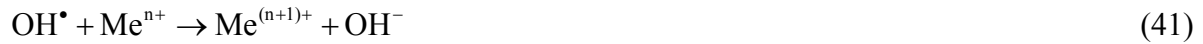
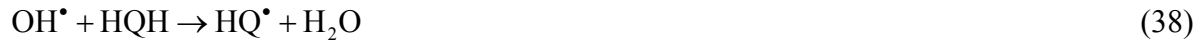
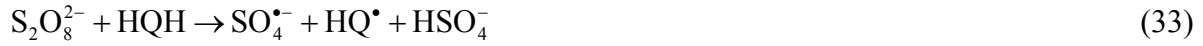
Variable-valence metal ions accelerate the dissociation of the persulfate ion. Therefore, these redox systems are widely used and also explain the capability of the metal ions to intensify the oxidation of organic substances by persulfate. The interest in this matter is confirmed by a large number of publications ([2],[16],[43],[44],[47],[60]). These papers reported that the variable-valence metal ions catalyze the oxidation of organic substances by persulfate and thereby accelerate its consumption. In this case, the reaction exhibits:

1. the fractional orders with respect to persulfate, the substrate and/or the metal ion;
2. the reduced effective activation energy of the process;
3. the dependence of the rate order on the reagent concentrations.

The participation of a metal ion in reactions with the components of the persulfate-substrate redox system and/or their radicals substantially hampers the kinetic scheme of the reaction, especially when metal ions form complexes with an organic substance [36].

The redox processes in the organic substrate-persulfate ion-metal ion system are governed by the $\text{Me}^{(n+1)+}/\text{Me}^{n+}$ redox potential; two different behaviours are possible, related to the value of the $\text{Me}^{(n+1)+}/\text{Me}^{n+}$ redox potential: if this is rather high, the system will contain mainly the metal ions with a low oxidation degree because of the rapid reduction of the $\text{Me}^{(n+1)+}$ ions to Me^{n+} by an organic substance and/or its radicals; if the $\text{Me}^{(n+1)+}/\text{Me}^{n+}$ metal redox potential is low, the system contains mainly the metal ions with a high oxidation degree because of the rapid

oxidation of the Me^{n+} ions to $\text{Me}^{(n+1)+}$ by the persulfate ion. In the first case, analysis of the kinetic data on the interaction of persulfate with organic substances with and without metal ions suggests that generally the radical-chain process in an inert atmosphere may be represented by kinetic scheme including the chain initiation by the Eqs.(32)-(34), propagation by Eqs.(35)-(41) and termination by Eqs.(42)-(45):



Where respectively HQH, HQ^{\bullet} and Q are the organic substrate, its radical and the oxidation product. In the second case, if the pseudo-steady-state approximation is applicable to Me^{n+} metal ions, the generalized kinetic scheme of a radical-chain process is similar to that presented above. The initiation may occur by Eqs.(32),(33) and (35); Eqs.(34),(36)-(39) and (42) are the chain propagation steps and chain termination occurs by Eqs.(40),(41) and Eqs.(43)-(45) [36].

While the overall mechanism is dependent on catalyst type, organic substrate and oxidant concentration, the rate equation of persulfate decomposition can be generally stated as reported in Eq.(46)

$$\frac{d[S_2O_8^{2-}]}{dt} = -k[S_2O_8^{2-}]^x [\text{catalyst}]^y \quad (46)$$

where $1/2 < x < 3/2$ and $0 < y < 3/2$ ([10]). This suggests that the reaction rate is independent of the contaminant loading. For activation by transition metal catalysis, ferrous iron (Fe^{2+}) is the most common and readily available activator, usually added as ferrous sulfate ($FeSO_4$) and ferrous chloride ($FeCl_2$). Additions of ferrous iron in excess can unfortunately lead to the rapid decomposition of persulfate and a loss in remediation performance.

The overall stoichiometric reaction between persulfate and ferrous ion is shown in the following equations (Eqs.(47)-(49)):



Through the steps:



The general activators found in literature include also the ions of copper, silver, manganese, cerium and cobalt. The persulfate-ferrous ion reaction results in the rapid production of sulfate free radicals. A free radical half-life of 4 seconds was reported at a persulfate and ferrous ion concentration of 10^{-3} M and a temperature of 40 °C. Sulfate free radical converts ferrous ion to ferric ion through Eq.(49). The reaction rate constant at a diffusion-controlled rate for Eq.(49) has been reported to be $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ([10]).

The rate of reaction between persulfate and ferrous ion is dependent on the concentration of each reactant. According to Eq.(47), reaction stoichiometry requires a $Fe^{2+}:S_2O_8^{2-}$ molar ratio of 2; however, the rate-determining step is the reaction between one $S_2O_8^{2-}$ and one Fe^{2+} to form $SO_4^{\bullet-}$ (Eq.(48)), which then rapidly reacts with a second Fe^{2+} (Eq.(49)). When the reactions are completed, no sulfate free radical is available for further attack of target organic contaminants. Therefore, increasing the concentration of Fe^{2+} would speed up the reactions shown in Eqs.(48)-(49) and thus lead to completion of the reaction shown in Eq.(47). Conversion of Fe^{2+} to Fe^{3+} results in the production of $SO_4^{\bullet-}$, which immediately reacts with the target compound. However, the fast reaction between $SO_4^{\bullet-}$ and excess Fe^{2+} could possibly result in the destruction

of $\text{SO}_4^{\bullet-}$ resulting in a lowering of the degradation efficiency of the target organic contaminant. This behaviour can be characterized as competition for the $\text{SO}_4^{\bullet-}$ between the target organic contaminant and excess Fe^{2+} . In order to optimize ferrous ion activated persulfate oxidation of the target organic contaminant, it is necessary to slow down or control the reaction shown in Eq.(49). This process could possibly be accomplished by gradually providing small quantities of Fe^{2+} activator, thereby preventing the rapid conversion of Fe^{2+} to Fe^{3+} by the $\text{SO}_4^{\bullet-}$ as shown in Eq.(49) ([43]).

The problem with the use of Fe^{2+} as an activator is its transportability. Fe^{2+} is eventually oxidized by the persulfate to Fe^{3+} , which, at pH above 4, is insoluble. The net reaction is reported here below (Eqs.(47) and (50)):



Some authors discussed the effect of iron precipitation on the loss of persulfate activation in field applications. Greater reduction of contamination was achieved when additional Fe^{2+} was added, as compared to when only additional persulfate was added, suggesting a lack of available catalyst, and not oxidant, in the subsurface at the down-gradient monitoring point. If significant amounts of reduced metals are available in the subsurface, addition of metal catalysts may not be necessary to catalyze the persulfate ([10]).

In order to limit the addition of chemicals to allow the production of sulfate free radicals, several new persulfate activation systems have recently been developed. A few of these technologies use non-metal routes to generate sulfate radicals.

New persulfate activation methods

Chelated metal catalyst

The solubility and availability of the transition metal catalysts are critical factors in the activation of persulfate. The maintenance of metal ions in either oxidized or reduced forms can be controlled, to a certain extent, by the use of appropriate complexing agents. Therefore, the obstacle of maintaining available ferrous ion in solution can be overcome by employing complexing agents in conjunction with sufficient Fe^{2+} content. Chelation is an effective mean of maintaining metal activity at neutral or alkaline groundwater conditions. Chelated metal catalysts are complexes of transition metals bound to strong chelating agents. Examples of chelating

agents include: ethyldiaminetetracetic acid (EDTA), citrate, polyphosphate, glycolic acid, catechol, nitroacetic acid (NTA), tetrahydroquinine (THQ) and others in the class of materials. Previous work ([73]) demonstrated the benefit of chelated iron complexes to activate hydrogen peroxide for the destruction of complex pesticides. Chelated trivalent iron (Fe^{3+}) in addition to Fe^{2+} , was found to have excellent oxidation performance. Laboratory tests were conducted to test the efficacy of chelated iron catalysts for persulfate activation utilizing several different iron-chelant complexes ([16],[44],[60]).

The availability of Fe^{2+} resulted to be controlled by the chelate: Fe^{2+} molar ratio. In general, if the initial ferrous ion contents are relatively low, sufficient quantities of chelate must be provided to ensure the chelation of a greater percentage of the limited ferrous ion present ([44]). Higher chelated ferrous ion concentrations resulted in faster target compound degradation and higher extent of persulfate decomposition. However, high levels of unchelated ferrous ion resulting from insufficient chelating agent or excessive initial ferrous ion, will compete for sulfate free radicals formed and result in a decrease of organic contaminant treatment effectiveness and a decrease in persulfate use efficiency. Chelating agents such as citric acid has been proven to be effective in mobilizing and removing metals from soils and sediments. In this situation, the citric acid serves to first extract native metals from soils that are then available to activate the production of sulfate free radicals and promote subsequent target compound destruction. It was also reported that some chelating agents are also able to enhance the release of soil organic matter, which might alter the association between soil organic matter and the inorganic matrix. Iron is likely to absorb onto soil organics, so the addition of the chelating agent would desorb the organic matter and also improve the chelating availability of ferrous ion in the soil slurry system. In a soil matrix, consumption and/or decomposition of oxidant by soil components, especially soil organic matter, is an important factor influencing in-situ chemical degradation of contaminants. The use of chelated ferrous ion is far superior to the use of unchelated ferrous ion as an activator. Therefore, it appears that in-situ chemical oxidation using chelated ferrous ion activated persulfate could be a viable method for aquifer remediation ([44]).

Dual oxidant system: sodium persulfate and hydrogen peroxide

Hydrogen peroxide technology, known as Fenton's reagent, has been widely applied in treating groundwater contaminants with varying results. In general, it is highly reactive and is able to oxidize a wide range of contaminants. However, hydrogen peroxide is unstable in some soil matrices, and it rapidly decomposes, thus limiting its transport and effectiveness. A dual oxidant system utilizing hydrogen peroxide and sodium persulfate has been developed that combines the

reactivity of peroxide in the reduction of compounds of concern with the enhanced stability of persulfate.

Hydrogen peroxide and persulfate react together to form oxygen according to Eq.(51) ([28]):



The kinetics were first studied by Friend, who found the rate to be independent of the hydrogen peroxide concentration and first order with respect to persulfate concentration. A study over a wider range of reactant concentrations has been made by Tsao and Wilmarth, who give the empirical rate law for the reaction at 30 °C as (Eq.(52)):

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = [\text{S}_2\text{O}_8^{2-}] \left\{ \frac{9.5 \times 10^6}{[\text{H}_2\text{O}_2]} + \frac{7.6 \times 10^7 [\text{S}_2\text{O}_8^{2-}]}{[\text{H}_2\text{O}_2]} + 2.9 \times 10^{10} [\text{S}_2\text{O}_8^{2-}] + 7.9 \times 10^8 \right\}^{\frac{1}{2}} \quad (52)$$

With varying hydrogen peroxide and persulfate ion concentrations this rate expression approaches the limiting forms (Eqs.(53)-(55)):

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_{(i)} [\text{S}_2\text{O}_8^{2-}] [\text{H}_2\text{O}_2]^{\frac{1}{2}} \quad (53)$$

(i) 0.001 – 0.005 M H₂O₂ and 0.001 – 0.025 M K₂S₂O₈

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_{(ii)} [\text{S}_2\text{O}_8^{2-}] \quad (54)$$

(ii) 0.025 M H₂O₂ and 0.002 – 0.01 M K₂S₂O₈

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_{(iii)} [\text{S}_2\text{O}_8^{2-}]^{\frac{1}{2}} \quad (55)$$

(iii) 1.0 M H₂O₂ and 0.1 – 0.25 K₂S₂O₈

The overall mechanism ascribed to the reaction is reported below (Eqs.(56)-(61))





It is assumed that hydrogen peroxide and persulfate may have several synergistic attributes:

1. hydroxyl radicals can initiate persulfate radical formation. Similarly, sulfate radicals can stimulate formation of hydroxyl radicals;
2. hydrogen peroxide may react with a significant portion of the more reactive contaminants, allowing the sulfate radicals to destroy the more recalcitrant compounds of concern;
3. a combination of peroxide and sulfate radicals may provide a multi-radical attack mechanism, yielding either a higher efficiency in destroying contaminants, or allowing for recalcitrant compounds to be more readily degraded.

The combined peroxide-persulfate system has been tested with good encouraging results on several contaminants of concern. The combined peroxide-persulfate reaction system appears to have a broad range of applicability. It not only oxidizes compounds generally amenable to persulfate oxidation, but also oxidizes compounds not readily oxidized by conventional persulfate technology.

Conclusions

In general, based on the experimental evidences it can be concluded that there are three levels of persulfate activators that can be used. These include “Mild Oxidation” in which persulfate alone is used and it should be appropriate for BTEX sites. If oxygenates such as MtBE have to be targeted, the “Strong Oxidation” system, i.e. persulfate activated with Fe-EDTA, would be appropriate. This “Strong Oxidation” system is also appropriate for those sites contaminated by only chlorinated ethenes (PCE, TCE, DCE) or chlorobenzenes. If there are chlorinated ethanes or methanes present that need treatment, an “Aggressive Oxidation” system should be evaluated, based on combined peroxide and persulfate, or heated persulfate. These aggressive activation may be applied also for BTEX and chlorinated ethene sites if faster remediation is desired, or in the case of high contaminant load. Therefore, persulfate technology is not a “one-size-fits-all” technology. There is a rich and varied chemistry that can be applied to tackle a wide variety of contaminant problems.

State of the art and research overview

The features of activated persulfate oxidation technology, make its application feasible in those situations where the high NOM content, the presence of high metals amount, the presence of high content of fine fractions, make the application of Fenton's technology unfeasible. In fact, due to its high stability (in view of its slow degradation kinetic) and high standard redox potential, activated persulfate technology, can overcome the typical drawbacks of Fenton-based application. Once generated, sulfate radicals are able to attack and remove the organic compounds, as good as hydroxyl radicals ($E^\circ = 2.6 \text{ V}$). The possibility of applying this technology to a typical Italian soil has to be considered since our soils are characterized by the presence of high metals content (e.g. iron and manganese), high NOM, a widespread presence of fine fraction over the others and high (bi)carbonates content. The application of Fenton's technology requires, in these cases to provide an extra-load of oxidant and a series of amendments to stabilize the oxidant and to allow the hydrogen peroxide catalytic decomposition. On the contrary, the typical persulfate application requires only to provide the right oxidant dosage and eventually a small iron amount to let the activation get started.

In view of these considerations, I performed a lab-scale feasibility study, whose complete description is reported in [Appendix C](#) of this manuscript, which was focused on the applicability of the persulfate oxidation process as method to remediate source areas of MtBE. The experiments were carried out either in aqueous and in soil slurry system, with a soil amount of 10 g and a slurry volume of 50 mL. The experimental approach was based upon the Rotatable Central Composite method in order to define the minimum number of meaningful experiments to be performed and to optimize the independent parameters involved in the oxidation process. The RCC method was built by taking in account three independent parameters: sodium persulfate ($\text{S}_2\text{O}_8^{2-}$) concentration, which varied between 5 and 10 g/kg, Fe(II) concentration, set between 0 and 0.21 mM and sodium citrate monohydrate concentration (chelating agent), which was between 0 and 0.42 mM. Then, a Response Surface Method was applied to provide a graphical representation of the effect of the operating parameters on the process efficiency.

The obtained results for aqueous and soil slurry systems revealed that also in the case of a typical Italian groundwater environment, iron activated persulfate process is feasible as remediation technology, even though the obtained results suggest that a maximum MtBE removal efficiency of approximately 50% could be achieved; this is due substantially to the unproductive pathways generated by the excess either of ferrous ions and persulfate ions which substantially hinder the activity of the sulfate radicals. It's clear that further research is needed to overcome this

inconvenience and optimize the operating conditions involved in the activated persulfate chemistry; a very important parameter should be, with respect to this, the Fe(II):S₂O₈²⁻ molar ratio rather than the Fe(II):MtBE or the S₂O₈²⁻:MtBE molar ratios. The optimization of this parameter should, by consequence, lead to a better understanding also of the mechanisms involved during the Fe(II)-chelate activated persulfate oxidation process.

PEROXY-ACIDS OXIDATION TECHNOLOGY

Introduction

The peroxy-acids technology is based on the production of a class of soluble oxidants which is able to remediate high-organic matter soils, such as sediments. This technology has an innovative feature combining both solvent extraction and an advanced oxidation process (AOP). This AOP is relatively selective and may hold several advantages over other AOP currently in use. In this AOP, peroxy-acids are formed when hydrogen peroxide and an organic acid (e.g. acetic acid) interact with certain types of organic compounds, due to significant activity of the peroxy-acid itself or its breakdown product, hydroxyl cation or even hydroxyl radicals in an aqueous solution. The sediment is first contacted with organic acid at a relatively high concentration. This step creates a desorption gradient for hydrophobic contaminants to dissolve and/or desorb from any separate organic or particle associated phases. In the second step, hydrogen peroxide is added at a determined dose to the organic acid solution under defined conditions of time, temperature and pH. The use of this technology for the treatment of sorbed, hydrophobic and particle associated organics offers the potential of significantly increasing solubility of compounds in the organic acid solution thus increasing their susceptibility for subsequent chemical or biological attack. Although complete destruction of organics is possible in theory, even partial transformation of these recalcitrant compounds will have a significant effect on biodegradability.

Historical background and chemistry of peroxy-acids

The use of peroxy-organic acid oxidation to alter chemical structure has been practiced since the 1940s in the pulping industry where delignification of wood pulp without degradation of cellulose and hemicellulose fibers has been a longstanding goal. Peroxy-acids are formed by the reaction between organic acids (e.g. acetic, propionic, etc.) and hydrogen peroxide. Peroxy-organic acids are relatively selective oxidizing agents with activity that can be targeted towards the electron dense structures such as aromatic rings, double and triple bonds and ether bonds with no further unwanted side-reactions with structures like sugars ([42]). The effectiveness of peroxyacetic acid as a delignification reagent is due to the low reactivity with carbohydrates and the high reactivity with the electron-rich sites such as olefinic, carbonyl and aromatic ring structures that are found in lignin. The reactions of peroxy-acid with these compounds involve a stepwise addition of OH^+ to the aromatic ring structure. Other studies

indicated that oxygen-containing substituents direct initial ortho- and para-hydroxylation to give o- and p-quinone. Whereas p-quinones are relatively stable to excess peroxyacetic acid, the o-quinones are readily oxidized to muconic acids. The same studies also showed that the rate of peroxyacetic acid reaction is considerably increased by the introduction of a second oxygen-containing substituents in the aromatic ring and that free-phenolic compounds react faster than their corresponding methyl ethers ([40]).

Peroxy-acids have been also used for epoxidation of alkenes. Some authors ([1]) proposed a mechanism for the peroxy-acid process, which involves the transfer of an oxygen atom from a peroxy-acid to an alkene. This is facilitated by electron-donating substituents on the carbon-carbon double bond (C=C) on the alkene and the electron withdrawing groups on the peroxy-acid molecule. Another hypothetical mechanism for the peroxy-acid process would involve the reaction of an organic acid (e.g. acetic acid) with hydrogen peroxide through hydrogen abstraction and hydrogen peroxide cleavage to form a peroxy-acid molecule. Once formed, the peroxy-acid molecule can directly react with the organic compound as reported above, thus generating an acetic acid molecule as reaction product or it can also dissociate and release a hydroxyl cation or radical and an acetate anion molecule. This phenomenon is partially due to the fact that certain chemical, such as acetic acid, are resistant to oxidation by hydroxyl radicals. The hydroxyl cation (or radical) would in turn oxidize the contaminant, while the resulting reaction products such as acetic acid or acetate anion are recycled to participate in more reactions. It is also noticed that both mechanisms described above could occur simultaneously and/or sequentially. If this suggested combined mechanism actually takes place in a peroxy-acid process it could explain why this technique has proven to be so effective.

Hydroxylation appears to be an important result of reactions between peroxy-acids and many aromatic compounds. Few well-defined examples of ring cleavage induced by peroxyacid oxidation of phenyl ethers exist. Peroxyacetic acid is known to react with and solubilise lignin (which contains phenolic and phenyl ether moieties) of certain wood species. It is known that peroxy-acid oxidation can be quite selective since very little carbohydrate material is oxidized. Moreover, it has been found that ring cleavage and demethylation do occur in peroxyacetic acid delignification ([22]).

Even though the peroxy-acid process could be an AOP of choice for the treatment or pre-treatment of contaminated sediments and soils, its mechanism is not well understood and is still under investigation. A proposed mechanism for the peroxyacid process involves the formation of a peroxy-acid ring initiated by the addition of acetic acid and hydrogen peroxide.

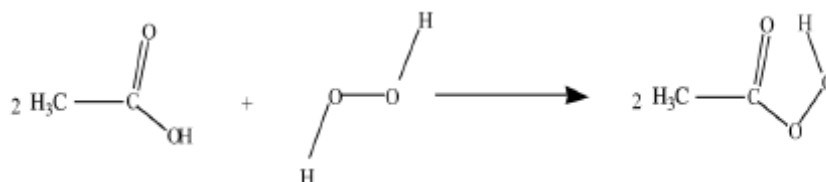


Figure 1: Formation of the peroxyacetic acid ring.

The break-up of the peroxyacid ring leads to the release of hydroxyl radicals.

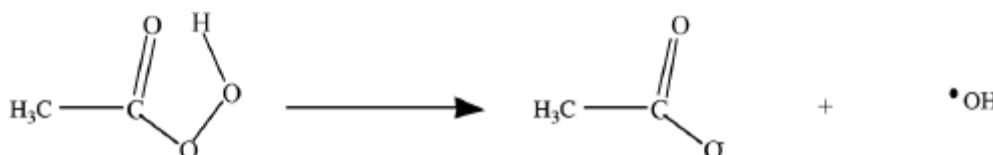


Figure 2: Break-up of the peroxyacetic acid ring.

These reactive radicals then oxidize the target compound (pyrene, in this case).

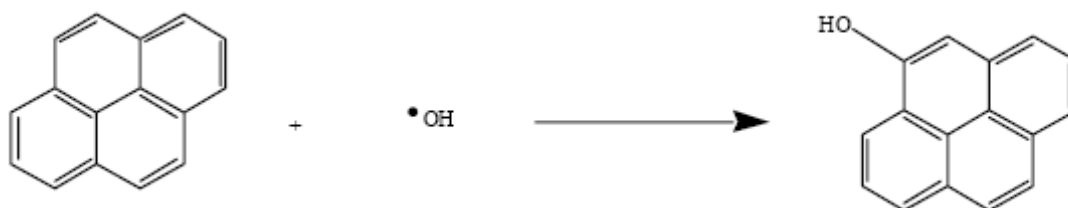


Figure 3: Hydroxyl radical (OH^\bullet) attack of the target compound molecule.

Acetic acid act as a catalyst in this process and is therefore recycled ([59]).

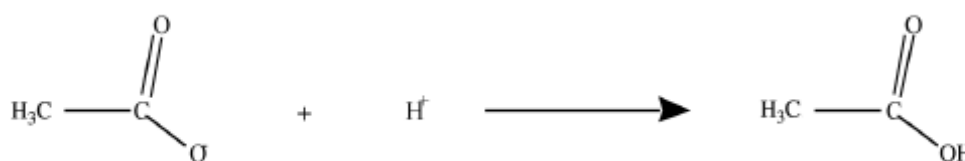


Figure 4: Acetic acid (CH_3COOH) re-generation process.

Thus, the formation of the oxidizing agents in peroxy-acid treatment can be viewed as a cyclical catalytic process in which hydrogen peroxide decomposition, with the formation of peroxy-acid is somehow activated by the presence of an organic acid (e.g. acetic acid) ([42]). Once formed, the peroxy-organic acid may in turn directly react with organics or in the case of aqueous solutions, re-generate the acetic acid and forming an hydroxyl cation (Figure 5). In general, abiotic degradation of the target compound using peroxy-acids is a rapid process, where the rate

of reaction seems to be dependent on the type of peroxy-acid, the organic carbon content and the surface area of the sediment.

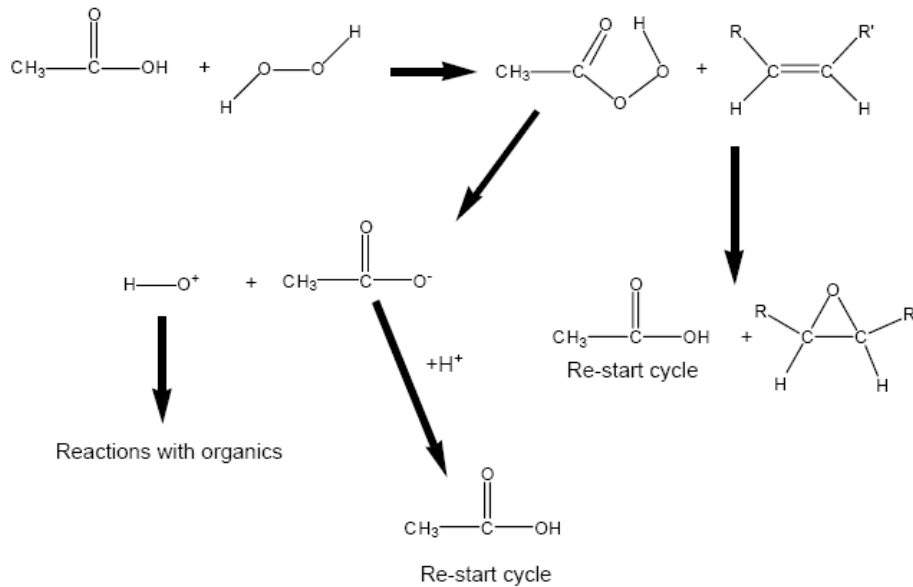


Figure 5: Peroxyacetic acid formation, cleavage and re-generation reactions.

In particular, the presence of a soil matrix seems to be important for the efficiency of this process, while hydrogen peroxide concentration doesn't affect the target compound rate of disappearance ([57],[59]).

The peroxy-acid reaction seems to cause also small changes in the amount of the dissolved metals, due to the presence of acetic acid which is capable to dissolve either the pollutants sorbed onto the solid particles and the metals present into the soil matrix as oxyhydroxides ([58]).

In conclusion, the disappearance of the target compound using peroxy-acid requires the presence of sediment as reaction surface, acetic acid as solubilizing agent and hydrogen peroxide as source of hydroxyl species.

Kinetics of peroxyacetic acid formation

As reported above, an aqueous solution of peroxy-acetic acid can be obtained by reaction of hydrogen peroxide with acetic acid in water. The process is described by the following scheme (Eq.(62)).



The reaction is reversible and the concentrations of all four components at the equilibrium state are comparable. Both forward and reverse reactions are fairly slow at room temperature, and a

long time is necessary for equilibrium to establish. Moreover, it has been shown in literature ([21]), that the equilibrium constant decreases as the temperature rises.

The process accounting for the reactions of carboxylic acids with hydrogen peroxide was reported to be of first order with respect to carboxylic acid and hydrogen peroxide. Using an ^{18}O isotope label it was found that the reaction does not involve dissociation of the O-O bond in initial hydrogen peroxide. Either in the formation and in the hydrolysis of peroxy-acids, the bond between the acyl group and oxygen atom is cleaved: the two processes may be described by the following scheme (Eq.(63)):



The reaction could be catalyzed by mineral acids, according to the following theorized mechanism:

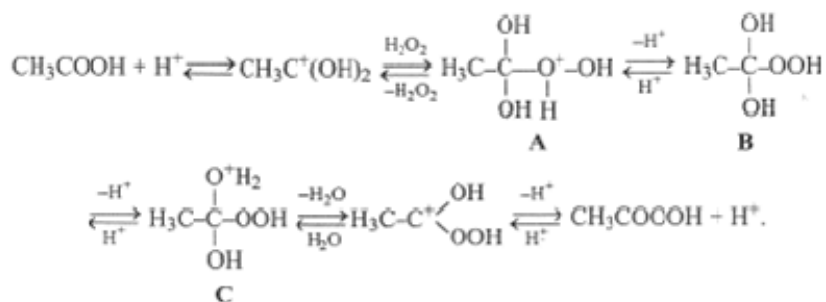


Figure 6: Mechanism of reaction of peroxyacetic acid catalyzed by mineral acids.

It is also known that the reaction of acetic acid with hydrogen peroxide in water is accompanied by weak evolution of heat and that peroxyacetic acid is an unstable compound, whose decomposition is known to follow two paths, catalytic and non-catalytic. Trace amounts of transition metals or dust are capable of acting as catalysts of its decomposition. Among the typical peroxyacetic acid decomposition products, CO_2 , CO and CH_3OH were detected. Addition of stabilizers to the reaction environment such as phosphates or stannates, suppress the catalytic decomposition. In the absence of catalysts, spontaneous decomposition of peroxyacetic acid occurs according to the following equation (Eq.(64)):



By performing kinetic experiments it has been found that the concentration of peroxyacetic acid reached its maximal value in approximately 36 hrs after mixing the reactants and that it then remained almost unchanged. The results allowed also to determine the optimal initial molar ratio

of acetic acid and hydrogen peroxide which ensured the maximal equilibrium concentration of peroxyacetic acid: at a temperature of 20°C this ratio was 1:2.5 ([21]).

State of the art and research overview

The ubiquitous presence of so-called persistent organic compounds in the environment is a concern due to their toxicity and in some cases carcinogenicity. Their capacity to be adsorbed onto carbon particles and others solid matrices allowed these compounds to be found in both soils and sediments. In literature, complete treatment of this recalcitrant organic compounds has been so far demonstrated in a number of advanced oxidation processes (AOPs) such as Fenton's reaction or permanganates, persulfates and ozone-driven reactions. The main drawbacks of these applications are significant cost due to competition of formed radicals and/or reacting species with respect to natural organic matter, which cause an increase of chemicals (oxidizing agents, acids, metals, stabilizers, chelating agents etc.) to be applied, production of toxic or undesired intermediates and by-products and system fouling due to instability of radical species. The use of peroxy-acid, which is selective towards dense electron structures such as double, triple and aromatic bonds as an innovative AOP, could overcome the previous drawbacks.

My research in this field aimed to assess the feasibility of this process as suitable and innovative in-situ and/or on-site technology to remediate contaminated sediments. Two different sediments were spiked with a PAH total concentration of 100 mg/kg (respectively with 50 mg/kg of anthracene and pyrene). Namely, sediment A was collected from a river, while sediment B was a marine one. In order to evaluate the effect of different operating conditions such as hydrogen peroxide (H_2O_2) concentration, acetic acid (CH_3COOH) concentration, H_2O_2 : CH_3COOH molar ratio on the PAHs removal efficiency, 7 g of each sediment were treated for 24 hours in a 50 mL amber glass bottle (batch reactor) by applying a mixture of different amounts of water, hydrogen peroxide and acetic acid (soil:water weight ratio \cong 1:4). First, a series of hydrogen peroxide decomposition experiments was carried out by varying the CH_3COOH : H_2O_2 molar ratio; the hydrogen peroxide lifetime was equal respectively to 26 hours (sediment A) and 45.5 hours (sediment B); the obtained results showed a strong decreasing of H_2O_2 concentration in the first 24 hours for sediment A (1.8 % Organic Carbon, Total Oxidant Demand (TOD) = 9.6 g/kg), while sediment B (0.46 % Organic Carbon, TOD = 2.9 g/kg) exhibited a quasi-constant value in H_2O_2 concentration during the first 24 hours; the H_2O_2 decomposition appeared weakly affected by acetic acid content, leading to exclude any interaction between hydrogen peroxide and acetic acid. A Rotatable Central Composite design (RCC) was used for the design of the operating conditions to be tested, allowing to carry out the minimum number of meaningful experiments:

namely, H₂O₂ concentration was in the 0.66÷3.30 M range, whereas acetic acid was between 1.16÷9.34 M. The obtained results confirmed the feasibility of the peroxy-acid towards the PAH removal (up to 99%), even though the treatment performance varied with the number of PAH-aromatic rings. Moreover, the experiments also showed that the presence of an organic acid (such as acetic acid), could enhance PAHs desorption from sediment into aqueous phase, thus easing its degradation.

The presentation and discussion of the obtained experimental results is reported in [Appendix D](#) of this thesis.

CONCLUSIONS

My Ph.D. research has been developed and carried out in order to reach a two-fold objective: on the one hand, to improve the basic knowledge about the AOPs operating mechanism, in order to develop innovative criteria for designing the different applications; on the other hand, to assess the feasibility of different AOPs to those scenarios which account for the typical Italian contaminated sites. In view of this double goal, three different technologies were studied and applied: namely, Fenton's process, activated persulfate and peroxy-acid oxidation technologies were used respectively for the remediation of contaminated soil and sediments from bio-recalcitrant compounds such as MtBE and PAHs. Namely, while the first two oxidation technologies (Fenton's and activated persulfate) were applied to remediate an MtBE contaminated aquifer, the peroxy-acid was applied to treat two different PAH-contaminated sediments.

The first objective was achieved by investigating case studies with the aim of identifying the relationship between the operating conditions and the efficiency of the process (formation of oxidative species). For Fenton's system, an indirect method for the quantification of oxidative radicals was developed and tested. This method allowed to assess the role of several operating parameters on the production of oxidative radicals and hence on the process efficiency. Among the operating parameters investigated, hydrogen peroxide concentration, Fe(II):H₂O₂ molar ratio, the role and the concentration of the organic matter and the influence on the process performance of the presence of a solid matrix in the reaction environment were evaluated. The obtained results showed that Fe(II):H₂O₂ ratio affected the oxidative radicals production efficiency, which achieved a maximum 70% value for the highest tested Fe(II):H₂O₂ ratio of 2:1. At low Fe(II):H₂O₂ molar ratios (between 0.28:1 and 1:1), the production efficiency was particularly low, suggesting that the Fe(II) was probably unable to complete the redox cycle generally supposed to occur during a Fenton's reaction. The organic matter content negatively affected the radicals production efficiency, especially for the higher Fe(II):H₂O₂ molar ratios. Concerning the radicals concentration, it was observed to decrease sharply after few minutes of reaction time. On the contrary, a one order of magnitude reduction in both radicals amount generated and concentration was observed when soil was added to the reaction environment.

As far as the activated persulfate system is concerned, a multi-parametric approach based on main parameters which are involved during the radicals formation was developed and applied. This approach allowed to show the relationship between different operating conditions such as

persulfate concentration, Fe(II):Na₂S₂O₈ molar ratio and Na₂S₂O₈:contaminant molar ratio, and the process performance expressed in terms of contaminant (MtBE) removal efficiency. The obtained results for aqueous phase experiments showed that an MtBE removal efficiency of 55% was obtained when Fe(II):Na₂S₂O₈ and Na₂S₂O₈:MtBE molar ratios were equal respectively to 1:1 and 450:1, while in case of slurry phase experiments, Fe(II):Na₂S₂O₈ equal to 1:1 and Na₂S₂O₈:MtBE equal to 600:1 allowed to obtain an MtBE removal efficiency of 66%.

Finally, the approach which was applied in the case of peroxy-acid oxidation technology was based upon a comparison between the results of a multi-parametric study which was performed respectively on marine and river sediments. This approach was aimed to assess not only the influence of selected key-parameters such as hydrogen peroxide (H₂O₂) concentration, acetic acid (CH₃COOH) concentration, CH₃COOH:H₂O₂ molar ratio on the contaminant removal efficiency and hydrogen peroxide lifetime, but also to show the differences due to the different chemical-physical properties of the sediments. The obtained results showed that for both sediments, it is possible to obtain high PAHs removal efficiencies (up to 99%) when a CH₃COOH:H₂O₂ molar ratio of at least 3:1 and hydrogen peroxide concentrations of at least 2.9 M (10% wt/wt) are applied.

The second objective of the Ph.D. work was achieved by developing, taking in account the experimental results obtained for the case studies, an approach which was based on performing feasibility studies.

This approach allowed to design, in the case of Fenton's process, a pilot-scale test for an in-situ Fenton application for the treatment of an MtBE-contaminated site, while in the case of activated persulfate and peroxy-acid oxidation technologies, to perform lab-scale applications.

The design of different experimental phases was performed, eventually, by applying Rotatable Central Composite (RCC) method, whereas the obtained results are handled and presented by means of proper statistical tool such as Response Surface Method (RSM), in order to find quantitative relationships between process performance and applied operating conditions.

As far as the pilot-scale Fenton's application is concerned, the positive results obtained under hydraulic confinement, by activating a P&T system, suggested that the observed moderate increase of groundwater temperature and metals content, due to injection of hydrogen peroxide and amendments into the subsurface, are of small entity as far as the injected volumes are small. The applied concentrations of hydrogen peroxide ([H₂O₂] = 1.47 M (5% wt/wt)) and amendments ([Fe²⁺] = [Chelate] = 10 mM) may lead at most to temporary and localized

variations among the water quality parameters, which came back to their normal values after few weeks. It was also noticed that low-dosage conditions coupled with low hydraulic gradients and high NOM contents, are responsible of low hydrogen peroxide lifetime and then low ROI (during this application ROI was approximately equal to 50 cm).

With respect to this, it is worth pointing out that the typical hydro-geologic features of Italian environment could represent a limitation for the AOP performances. Such limitations are basically due to low hydraulic conductivities ($K = 10^{-6} \div 10^{-4}$ m/sec), the presence of oxidant and/or radical scavengers (e.g. (bi)carbonates and chlorides), high total oxidant demand ($TOD > 5$ g/kg) or high metals content ($[Fe] > 2$ g/kg, $[Mn] > 500$ mg/kg) and can influence the oxidant delivery in the subsurface or its lifetime in the environment, thus generally reducing the Radius Of Influence (ROI) of each AOP application. These problems could be overcome by optimizing the oxidant and/or amendments load, taking into account the side-effects due to unproductive consumption. To this perspective, the obtained results demonstrated that chemical oxidation is a process of interest for its application to Italian contaminated sites, where the presence of bio-recalcitrant organic compounds is widespread and hard to tackle. This is an important result which should be useful especially during the scale-up phase of these technologies, from the lab-scale to pilot- and full-scale applications.

APPENDIX A

FEASIBILITY STUDY AND PILOT SCALE APPLICATION OF THE FENTON-LIKE TREATMENT OF A MtBE-CONTAMINATED SITE

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Abstract: This work presents the results of a feasibility study of a Fenton-like process, aimed to the design and implementation of a full-scale treatment of an MtBE-contaminated site. The feasibility study consisted in a series of lab-scale experiments, carried out in order to assess the effect on the process performance of the operating parameters involved in the Fenton-like process such as hydrogen peroxide concentration, Fe(II) concentration and Fe(II):chelate molar ratio. All the experiments were carried out in agreement with recent guidelines issued by the Italian Environmental Agency (APAT). A Rotatable Central Composite method was applied to evaluate the minimum number of experiments required for the optimization procedure. Then, a Response Surface Method was applied to provide a graphical representation of the influence of the operating parameters on the process performance. The results of the lab-scale tests were used for the design of a field pilot test, which confirmed the feasibility of Fenton-like treatment for MtBE removal. The full-scale remediation project is also described.

Keywords: Advanced Oxidation Processes (AOPs), Fenton-like treatment, MtBE, Optimization Procedure, Pilot Test

Introduction

MtBE is the oxygenate compound most commonly used as octane-enhancing replacement for lead tetraethyl. From an industrial view point, MtBE has many positive features such as low production costs, ease of production, high octane number and favorable blending characteristics. From an environmental view point, despite a positive effect on air pollution, MtBE has a negative effect on groundwater resources. It is a poorly biodegradable compound, with a degradation half-time life of 27 years, and is characterized by high solubility in water ($S = 48000$ mg/L) and low Henry constant (0.022 at 25°C) ([67]). This means that, once spilled from UST (Underground Storage Tank), it will readily migrate in both vadose zone and groundwater systems with essentially no retardation with respect to underground water flow. Besides, it is

worth pointing out that MtBE is characterized by a distinct odor at as low as 10 µg/L concentration.

Moreover, recent researches lead by U.S. EPA have tentatively classified MtBE as a possible human carcinogen. Despite MtBE is not included in the Italian list of priority pollutants as per D.Lgs. 152/06 ([17]), a recent document issued by the Italian Health Institute (ISS) has suggested a maximum concentration of 10 µg/L ([56]). The physical-chemical properties of MtBE also limit the remediation technologies that can be applied. Namely, Pump & Treat with adsorption by GAC is not efficient due to the poor adsorption properties of MtBE on this adsorbent; biological treatment is also not effective due to the low MtBE biodegradability; finally, air stripping treatment is also hard to apply, in view of the MtBE Henry constant. Recently, the possibility of applying In Situ Chemical Oxidation (ISCO) for treatment of MtBE contaminated groundwater has been proposed and, among these, the advanced oxidation processes (AOPs) based on the use of hydrogen peroxide rely on the well known Fenton's reaction (Eq.(1)):



This reaction generate hydroxyl radicals (OH^\bullet) from hydrogen peroxide and ferrous ion. Hydroxyl radicals are then capable to oxidize, not selectively, the organic compounds present in the polluted matrix. The contaminant degradation kinetic may be described by a second-order law (Eq.(2)):

$$\frac{dC}{dt} = k_{\text{OH}^\bullet} [C] [\text{OH}^\bullet] \quad (2)$$

Kinetic constant value k_{OH^\bullet} depends on the chemical characteristics of the contaminant; nevertheless it presents an upper bound value ($10^{10} \text{ M}^{-1}\text{s}^{-1}$), limited by the diffusion rate of hydroxyl radicals. It has been noted that hydroxyl radicals are capable of oxidizing compounds that are refractory to biological treatments with high values of kinetic constant ([80]). There are many factors that may affect the efficiency of treatments based on Fenton's reaction; most of them are chemical-physical characteristics of soils. First of all, Fenton reaction is influenced by pH value. In particular it is well-known that optimal reaction environment is at pH values between 2 and 4. If pH is out of this range, Fe(III) produced by Eq.(1) may precipitate as iron hydroxide, thus interrupting the radical propagation reaction. Besides, the presence of inorganic catalysts (iron and manganese oxy-hydroxides) ([54]) and enzymatic substances (hydrogenase

and catalase) produced by microorganisms ([32]), may reduce the hydrogen peroxide stability, thus decreasing the Fenton's process effectiveness. Therefore, the application of Fenton's process for in-situ treatment of contaminated sites requires acidification of the aquifer, which is often not an easy task to be achieved. A possible alternative is represented by the so-called Fenton-like process. This process is based on the idea of avoiding Fe(III) precipitation by adding chelating agent as suggested by Sun and Pignatello ([73]), who also made a screening of chemical properties and activities during chemical oxidation of different chelating agents. All the case studies reported so far on Fenton's application to MtBE ([33],[41]), refer to typical US hydro-geological environments. Therefore specific data are required in order to evaluate the applicability of these technologies to other hydro-geological conditions. This work presents the results of a feasibility study of a Fenton-like process, aimed to the design and implementation of a full-scale treatment of an MtBE-contaminated site located in Italy. The feasibility study consisted in a series of lab-scale experiments, carried out in order to assess the effect on the process performance of the operating parameters involved in the Fenton-like process such as hydrogen peroxide concentration, Fe(II) concentration and Fe(II):chelate molar ratio. All the experiments were carried out in agreement with recent guidelines issued by the Italian Environmental Agency (APAT) ([65]). A Rotatable Central Composite method was used to define the minimum number of experiments required for the optimization procedure ([3]). Then, a Response Surface Method was applied to provide a graphical representation of the effect of the operating parameters on the process influence. The results of the lab-scale tests were used for the design of the field pilot tests, that were successfully performed, allowing to obtain the parameters required for the design of the full-scale remediation.

Site characterization

Contamination of groundwater was originated from a leaking underground storage tank of a gasoline service station. As emergency security action, the tank was removed and replaced with a new one. The contaminated soil was also removed by the area. Following these actions, a further characterization plan was carried out in order to quantify the residual contamination. As shown in [Figure 1](#) a series of monitoring wells inside the contamination area (PZ3-BIS, PZ4-BIS, PZ8, PZ9, W1, W2) and a series of control wells immediately out of the contaminated area (PZ1, PZ2, PZ5, PZ6, PZ7) were built. A maximum concentration of 1464 µg/L of MtBE and 19 µg/L of Total Hydrocarbons was detected in the well PZ9 (hot-spot).

General subsurface lithology at the site consist of:

3. 0 – 0.3 m mixed asphalt with granular;
4. 0.3 – 5 m sandy clay silt;
5. 5 – 8 m fine clay sand;
6. 8 – 10 m clay;
7. 10 – 15 m alternations of sands, silts and clays.

Interpretation of field data was carried out in order to define the site hydrogeology. The aquifer, which extends from a depth of 4 m to 10 m is lightly pressurized with NE – SW orientation, an hydraulic gradient of 0.025 and a permeability of $1.1 \times 10^{-5} \text{ ms}^{-1}$.

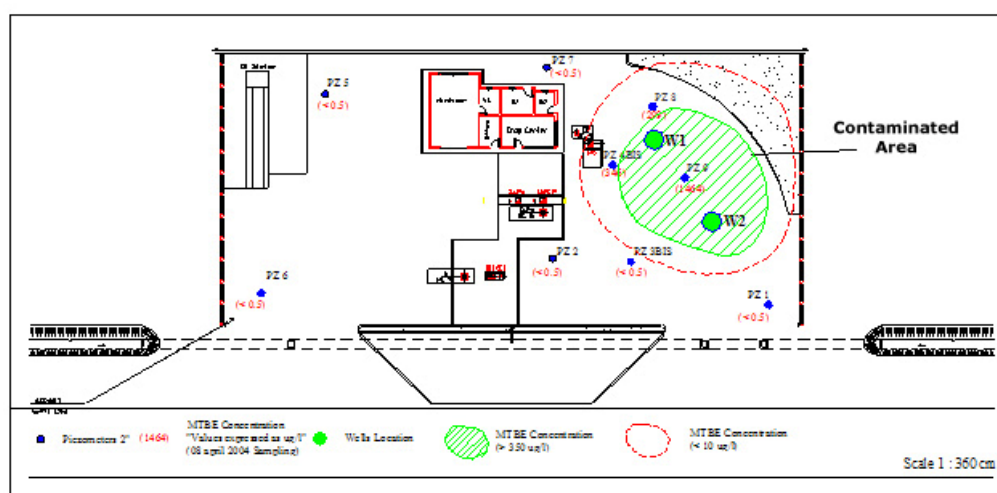


Figure 1: Site planimetry.

Field sampling

A further characterization activity was performed in order to collect samples for the lab-scale feasibility study. Water samples were collected in the hot-spot by pumping the water from the PZ9 well, whose characteristics are summarized in Table 1; uncontaminated soil samples were collected near the hot-spot point in order to obtain a representative sample of the site.

Parameter	Value
Depth	8.5 m
Water Table Level	3.5 m
Pumped Volume	100 L
Pumping Rate	1.5 L/min
Sampling Depth	7.0 m

Table 1: PZ9 characteristics.

All water samples were collected into special amber glass bottles and were cooled in order to avoid any volatilization during transport. All soil samples were collected into jar hermetically closed. During water sampling a series of field-measurements were carried out, whose results are summarized in [Table 2](#).

Parameter	Value	Instrument
Temperature	28.5 °C	HANNA HI 9025
pH	6.87	HANNA HI 9025
Dissolved Oxygen	2.2 ppm	HANNA HI 9143
Redox Potential	-57.0 mV	HANNA HI 9025
Electric Conductivity	887.0 μ S	HANNA HI 9033

Table 2: Field data collected from groundwater pumped from PZ9 well.

Lab-scale feasibility study

Materials

Hydrogen peroxide (30% wt/wt), Fe(II) sulfate heptahydrate, sodium citrate monohydrate (chelating agent), sulphuric acid (96%) were purchased by Fluka – Riedel-de Haën (ACS or HPLC grade).

MtBE determination

MtBE determination in water was performed by Headspace Solid Phase Micro Extraction (HS-SPME) coupled with analysis by GC-FID ([\[18\]](#)).

A 65- μ m poly(dimethylsiloxane)-divinylbenzene SPME fiber was used. Significant variables for extraction step were temperature (20 °C) and sodium chloride concentration (300 g/L). Sodium chloride was used in order to enhance the MtBE concentration in vapour phase. With these conditions, an extraction time of 5 min was sufficient to extract MtBE. The calibration linear range for MtBE was 31 – 2500 μ g/L. [Table 3](#) shows all parameters involved in MtBE determination.

Parameter	Value	Notes
Extraction Setting		
Sample Volume	8 mL	15 mL glass vial
Sampling Time	5 min	
Stirring Velocity	300 rpm	
GC Setting		
Temp Program 1	From 37 °C to 100 °C at 10 °C/min	
Temp Program 2	From 100 °C to 250 °C at 45 °C/min	Kept for 19 min
Injector	250 °C	
Detector	250 °C	
Split Valve	Closed	
Carrier	Nitrogen	
GC Column	Supelco Equity-5	30 m×0.25 mm×0.25 mm film thickness

Table 3: Extraction setting and GC setting for MtBE determination.

Experimental setup

All lab-scale experiments were carried out in agreement with the guidelines for application of ISCO technologies recently issued by the Italian Environmental Agency (APAT) ([65]). Namely, these tests were performed in a 50 mL vial with 20 g soil in each vial and 7 mL of contaminated water. This water amount was determined during preliminary tests as the amount required to fully saturate the soil until a thin layer of water above the soil was observed. The water, used in these tests collected as above described from the PZ9 well, was found to be contaminated by 548 µg/L MtBE. Hydrogen peroxide, Fe(II) sulphate and sodium citrate monohydrate as chelating agent, were then added, in different amounts as described in Table 4. Soil and liquid solutions were thoroughly mixed by means of a Vortex stirrer for few minutes, and then left reacting for 24 hours. After 24 hours, the vial content was centrifuged and the resulting liquid was analyzed for MtBE following the procedure above described. In all experimental tests the pH of the soil-water system was equal to 7.0. A blank test was performed using the same procedure above described, without any hydrogen peroxide and amendments.

Experimental design and optimization

In order to minimize the number of experiments to be carried out and to guarantee a statistical significance of the data set a Rotatable Central Composite (RCC) method was applied. This RCC method is the combination of a 2 level factorial model with a Star model. In this case the RCC method was applied to a system of 2 independent variables (hydrogen peroxide concentration and Fe(II) sulphate concentration) with 2 levels per variable (high and low concentration). Since this model assumes that experimental uncertainty is linked only to the distance from the central

point, a series of replicates of this point was carried out ([3]). The tested operating conditions, resulting from the RCC approach are reported in Table 4, and schematically shown in the RCC experimental plan shown in Figure 2.

#Test	[H ₂ O ₂] (M)	[FeSO ₄] (mM)
O	2.205	7.50
S1	2.205	1.10
S2	3.244	7.50
S3	2.205	4.00
S4	1.166	7.50
F1	2.940	10.00
F2	2.940	5.00
F3	1.470	5.00
F4	1.470	10.00

Table 4: Lab tests dosage.

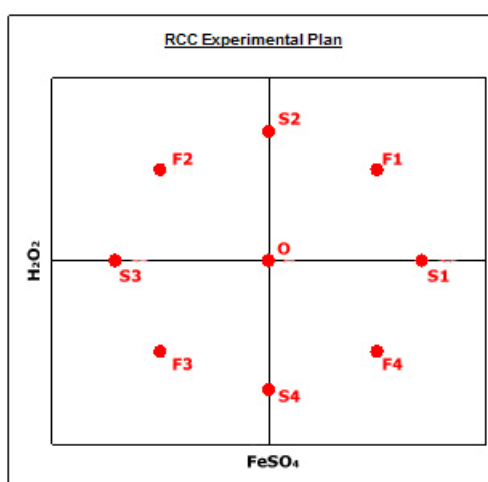


Figure 2: Rotatable Central Composite experimental plan.

Results

The results of all batch experiments are summarized in Table 5. It can be noted that all experiments were carried out in duplicate, in order to guarantee data repeatability. It has to be noted that the MtBE residual concentration was found to be 360 µg/L. Therefore, the removal efficiencies reported on Table 5 were evaluated with reference to this concentration value.

#Test	[MtBE] _{res sample A} (µg/L)	[MtBE] _{res sample B} (µg/L)	Removal (%)
O1	163.72	167.25	53.7±0.2
O2	197.98	180.35	47.3±2.5
O3	197.94	181.21	47.2±2.3
S1	120.95	121.04	66.3±0.0
S2	159.62	147.80	57.2±1.6
S3	83.70	124.87	71.0±5.7
S4	169.31	123.78	59.2±6.3
F1	54.56	48.03	85.7±1.1
F2	103.30	84.82	73.8±2.5
F3	114.42	149.88	63.2±4.9
F4	285.64	268.86	22.8±2.3

Table 5: Batch experiments results (removal was evaluated in respect with an MtBE concentration of 360 µg/L (blank sample)).

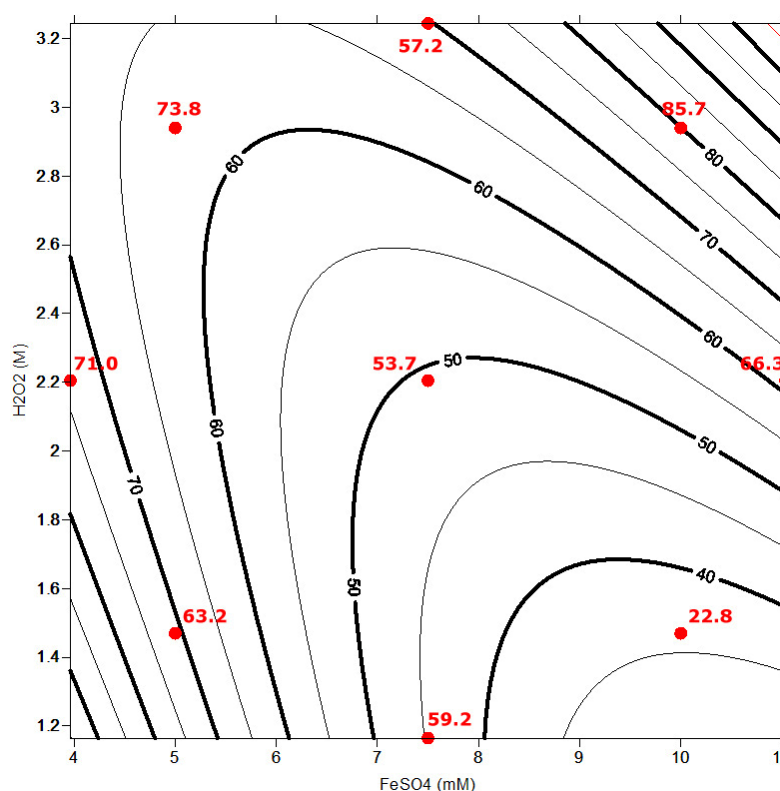


Figure 3: Iso-removal curves generated by SURFER[®] software and experimental points.

All experimental results were fitted by a quadratic polynomial regression model, using a proper software (SURFER[®]). The regression analysis of the experimental results provided a quadratic equation relating the removal efficiency with hydrogen peroxide and Fe(II) concentrations:

$$R\% = 1.45(\text{FeSO}_4)^2 + 7.14(\text{H}_2\text{O}_2)^2 - 39.22(\text{FeSO}_4) - 72.87(\text{H}_2\text{O}_2) + 7.12(\text{FeSO}_4)(\text{H}_2\text{O}_2) + 270.21 \quad (3)$$

The curves at constant MtBE removal (iso-removal curves) plotted in the experimental plan, are shown in Figure 3, together with the experimental points. By looking at Figure 3 it can be noted

that the highest MtBE removal was obtained either at low hydrogen peroxide and Fe(II) concentrations (bottom left part of [Figure 3](#)) or at high hydrogen peroxide and Fe(II) concentrations (top right of [Figure 3](#)). These two regions are also characterized by a different effect of the operating conditions on the process performance. Namely, at low Fe(II) sulfate concentrations ($< 6\text{mM}$), an increase of hydrogen peroxide concentration at constant Fe(II) concentration, leads to a reduction of the removal efficiency. Possibly, in these conditions, the amount of Fe(II) is not sufficient for activating the extra hydrogen peroxide, which follows other decomposition pathways, not effective or even detrimental for the Fenton reaction. At high Fe(II) sulfate concentrations ($> 8\text{mM}$), a big influence of hydrogen peroxide concentration on the removal efficiency is observed. It is likely that in these conditions, the amount of Fe(II) added is in excess so that any further hydrogen peroxide introduced in the system can at least in part react to form hydroxyl radicals, enhancing the MtBE removal. Finally, it is possible to detect an intermediate zone ($[\text{H}_2\text{O}_2]=1.5\text{-}2.5\text{M}$; $[\text{Fe(II)}]=6.5\text{-}8.5\text{mM}$) where the average removal efficiency is between 50 and 60%, with low sensitivity to both hydrogen peroxide and Fe(II).

Pilot-scale test

The pilot scale field test was performed by injecting hydrogen peroxide and amendments (aqueous solution of iron and chelating agent) through the PZ9 well, in order to treat the hot-spot of contamination. The oxidant movement was guaranteed by pumping water from well W1 thus also allowing to operate under hydraulic-confined conditions as prescribed by the APAT guidelines ([\[65\]](#)) which was then treated by applying an on-site Fenton's treatment, in order to reduce the residual concentration of MtBE below the limit of $10\ \mu\text{g/L}$. The on-site treatment was performed in a 500 L volume batch reactor, containing a diluted solution of hydrogen peroxide and amendments. While the pilot scale was carried out, a series of on-line and off-line measurements of certain parameters of interest (CO_2 , pressure, VOC, dissolved oxygen (DO)) were performed. The operating conditions of both on-site and in-situ treatment are reported in [Table 6](#), while [Table 7](#) summarizes the chronology of the different activities which were performed.

Parameter	Value	Notes
In-situ Pilot Scale Field Test		
[H ₂ O ₂]	1.47 M	75 L of a 30% (wt/wt) H ₂ O ₂ solution
[FeSO ₄]	10 mM	1.4 kg in 500 L
[C ₆ H ₅ Na ₃ O ₇]	10 mM	1.2 kg in 500 L
Q _{in}	10 L/min	---
On-site Pilot Scale Field Test		
[H ₂ O ₂]	0.05 M	3 L of a 30% (wt/wt) H ₂ O ₂ solution
[FeSO ₄]	0.5 mM	70 kg in 500 L
[C ₆ H ₅ Na ₃ O ₇]	0.5 mM	60 kg in 500 L
V _{batch}	500 L	---
τ	30 min	---

Table 6: Pilot scale field test setup.

Day	In-situ Test	On-site Test
0	All the wells within the contaminated area were sampled	
1	1 FRD injected	---
2	4 FRD injected	Sampling the outlet water after 30 min-treatment
3	Sampling the wells PZ9 and W1 (morning & evening)	Sampling the outlet water after 24 hours-treatment

Table 7: Pilot scale field test chronology.

(1 Fenton's Reagent Dose (FRD) = 500 L H₂O₂ sol.+500 L Fe(II):Chelate sol. ~ 2 Pore Volumes;

(ROI)_{est} ~ 50 cm).

The operating conditions of the pilot scale field test were chosen upon the results of the lab-scale feasibility test. Based on the aquifer permeability and on the hydrogen peroxide decomposition rate (which was evaluated during previous kinetic studies), a maximum Radius Of Influence (ROI) was estimated and set equal to 50 cm. ROI determination allows the so-called pore volume, as follows:

$$\text{PoreVolume} = \pi(\text{ROI})^2 H n_e \quad (4)$$

where n_e is the soil porosity (set equal to 0.40) and H represents the groundwater thickness which was interested by the injection (set equal to 2 m). During the design of the pilot scale application, Fenton's Reagent Dose (FRD) was assumed as basic unit to evaluate the total amount of reagents to be injected: it was set equal to 2 pore volumes. As shown in Table 8, a total amount of five FRD were injected during the in-situ test, corresponding to approximately 2500 L of 5% H₂O₂ solution and 2500 L of Fe(II):chelate solution. At the same time, an on-site pilot scale field test was done, in order to treat the water pumped out from the W1 well: the contact time between the Fenton system and the water was set equal to 30 min. All the water samples collected during the test were analyzed as described above (Table 3). Table 8 shows the

performances of the in-situ test where, a very high removal rate was obtained not only near the injection point but also at well W1, located approximately 3 m from the injection point. The analysis of on-line data collected during the in-situ test, shows a certain gas production (at most 100 mbar) above the injection point, thus suggesting a certain ventilation degree. The CO₂ concentration was always equal to 2-3%, meaning that a series of oxidation reactions was occurring in the subsurface. This information could not be used to close the mass balance for the contaminant since this oxidation is probably mainly due to the degradation of the natural organic matter of the soil. The Volatile Organic Compounds (VOC) concentration, was always found low, thus suggesting a very limited volatilization effect. As far as the thermal effects are concerned, it can be noted that the temperature of PZ9 well after the injection, increased up to 30 °C, but after a week decreased to its natural value (23 °C). Since iron was used as catalyst during these applications and chelating agents are generally able to mobilize metals, metals monitoring in water was carried out. Iron concentration after the treatment was equal to 1.3 mg/L, versus an initial value of 0.2 mg/L. This moderate increase, seems to suggest that, at the end of the treatment, most of the added iron precipitates. Moreover, it should be considered that, this variation is probably temporary and a normalization within few weeks is expected. It should be noted that, concerning the in-situ treatment, the data presented here are not completely exhaustive: in fact, very often, rebound phenomena can occur. This rebound depends on the aquifer properties and also on the pollutant characteristics. After a month by the pilot test, new samples from the PZ9 well were collected. Analysis on this last samples revealed an MtBE concentration of 120 µg/L, so it can be concluded that the effective removal efficiency was equal to nearly 80%. The results of the on-site test, also reported on [Table 8](#), revealed a good MtBE removal efficiency already during the first 30 min contact time; moreover, MtBE concentration after 24 hours of treatment decreased below the regulatory limit of 10 µg/L ([56]). The iron concentration was also constantly monitored: after the on-site treatment it was equal to 6.4 µg/L versus an added concentration of 22 mg/L; this decrease suggests that at the end of on-site treatment, almost all the added iron was precipitated, as a consequence of the chelating agent oxidation.

Well	Day 0	Day 1	Day 3 (Morning)	Day 3 (Evening)	MtBE Removal (%)	$\tau=0h$	$\tau=0.5h$	MtBE Removal (%)	$\tau=24h$
In-situ Test					On-site Test				
PZ9	630	442	12	13	98	630	120	81	< 10
W1	1200	---	530	487	59				

Table 8: Pilot scale field test results (all concentrations are expressed as µg/L).

Design of the full-scale remediation

The positive outcome of the pilot-scale tests was convincing enough for the final client to proceed to the design of the full-scale remediation. Such a remediation project will be based on the sequential combination of in-situ and on-site treatment. The in-situ treatment will target the hot-spot area and will be performed by injecting the Fenton's reagent through wells PZ8, PZ9 and PZ10 and other two wells to be constructed on purpose. The in-situ treatment will be performed by injection of a 10 mM solution of FeSO₄ and sodium citrate (total volume equal to 500 L), followed by injection of a 5% hydrogen peroxide solution (eventually in two aliquots each one of 250 L). A stabilizer will also be added to the H₂O₂ solution, in order to increase its stability in the subsurface and hence its ROI. The treatment will be performed in a confined environment, which will be obtained by creating an hydraulic barrier through pumping out groundwater from wells W1 and W2. Groundwater pumped out from these wells will be envied to on-site treatment unit, also based on Fenton's oxidation treatment. In particular, the on-site plant, will be as follows:

1. A reactor with a gas interceptor system, dimensioned for the immission of a 3% hydrogen peroxide solution, amendments like Fe(II) salts and chelating agent, and for an incoming flow rate of 0,6 m³/h. This reactor should be able to treat an incoming MtBE concentration of 700 µg/L;
2. Small PVC reservoirs equipped with a dosing pump for the storage of the 3% hydrogen peroxide solution, Fe(II) salt and chelating agent;
3. A calm area in the reactor for the iron sedimentation;
4. An optional unit for the iron removal
5. An inspection well before the immission to the drain collector;
6. A basin for the sludge storage
7. An activated carbon filter for the air with a capacity of 0,1 m³;

The iron precipitation system should guarantee a residual concentration of 2-4 mg/L. The monitoring operations will be carried out weekly during the first month and then monthly. During the first month different samples will be collected from the hot-spot area in order to evaluate the performance of the entire system and to calibrate the on-site plant in order to guarantee the best efficiency with the lowest consumption of amendments and hydrogen

peroxide. The remediation target level is 10 µg/L and is expected to be met in a six months time frame.

Conclusions

Both the lab-scale experimental results obtained and the field test application have shown that a Fenton-like process is feasible for the treatment of an MtBE contaminated site, whose hydrogeological properties are representative of those often encountered in Italian subsurface soils. The obtained results suggest that the drawbacks linked to the addition of hydrogen peroxide, iron catalyst and chelating agent, are of small entity until the injected volumes were small. The applied low-dosage condition may lead at most to temporary and localized variations among the water quality parameters, which could very soon come back to their normal values. The positive results of pilot-scale application performed under hydraulic confinement by activating a Pump-and-Treat system allowed to design a full scale remediation made of an in-situ treatment in order to tackle the hot-spot point.

APPENDIX B

INFLUENCE OF THE OPERATING CONDITIONS ON HIGHLY OXIDATIVE RADICALS GENERATION IN FENTON'S SYSTEMS

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Abstract: In this work, an indirect method for estimating the total amount and concentration of oxidative radicals in aqueous and slurry-phase Fenton's systems was developed. This method, based on the use of benzoic acid as probe compound, was applied for evaluating the effect of the operating conditions on the radicals amount produced, their production efficiency (i.e. moles of radicals generated per mole H₂O₂) and their concentration. A Rotatable Central Composite design (RCC) was used to select the operating conditions in order to get a statistically meaningful data set. Hydrogen peroxide and ferrous ion concentrations ranged between 0.2-1 mM and 0.2-0.5 mM, respectively; humic acid concentration between 0 and 15 mg/L, whereas the soil:water weight ratio in slurry-phase systems between 1:10 and 9:10. The probe compound concentration was 9 mM or 0.1 mM in experiments aimed to evaluate the total amount or concentration of oxidative radicals, respectively. The obtained results indicated that the amount of radicals generated in both aqueous and soil slurry Fenton's system increased with higher H₂O₂ concentration and, more specifically, that their production efficiency increased with increasing Fe(II):H₂O₂ molar ratio. Addition of dissolved organic compounds as humic acid did not notably affect the oxidative radicals amount and concentration. On the contrary, a one order of magnitude reduction in both radicals amount generated and concentration was observed when soil was added to the reaction environment.

Keywords: Oxidative radicals, Fenton's system, Rotatable Central Composite, Soil.

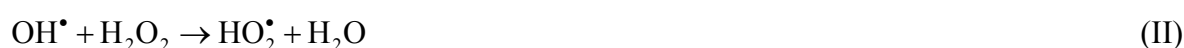
Introduction

Fenton's reaction is widely used for the remediation of contaminated soil and groundwater, with a large number of *in situ* applications. The chemistry of the Fenton's process is based upon the reaction of hydrogen peroxide ($E^0 = 1.80$ and 0.87 V at pH = 0 and 14 respectively) with a proper catalyst, leading to the generation of a pool of radicals ([37]), capable of non-selectively oxidizing a wide range of biorefractory organic pollutants such as chlorinated aliphatics, halogenated phenols, PAHs and PCBs. The radical produced in the Fenton's initiation Reaction (I) is the hydroxyl radical, whose formation can be achieved by adding an

homogeneous catalyst, such as a transition metal salt ([77],[72]), by generating the metal catalyst electrochemically by means of sacrificial steel electrodes or by using the metals naturally occurring in the environment as heterogeneous catalyst ([81]-[12]):



The hydroxyl radical generated through Reaction (I) react with hydrogen peroxide and begin a series of propagation reactions ([83]):



These propagation reactions produce a pool of radicals with different reactive properties. Namely, hydroxyl radical (OH^\bullet) and perhydroxyl radical (HO_2^\bullet) are both oxidant, although the latter is a relatively weak one; superoxide radical ($\text{O}_2^{\bullet-}$) is a weak reductant and nucleophile in aqueous systems ([83]). The oxidative properties of a Fenton's system is therefore the result of the combined activities of the different radical generated and is not strictly correlated to just one radical species. This consideration becomes more and more valid as the hydrogen peroxide concentration is increased, when Reaction (III) is more important ([83]).

Even though the Fenton's process is considered in many instances as a mature technology, with hundreds of pilot-scale and full-scale applications, mainly concentrated in the United States, the design of the operating conditions (oxidant dosage, optimal amendments concentration etc.) is still based on the evaluation of the contaminant removal efficiency, obtained through long and time-consuming lab-scale and pilot-scale feasibility tests. Recently, the possibility of using the hydrogen peroxide lifetime as an indicator of the oxidation efficiency of Fenton's and Fenton-like processes has been proposed to simplify at least the first screening phase of the experimental design activity and for selecting, among the different operating conditions, those which may be potentially effective for the oxidation treatment ([5],[6]). The obtained results demonstrated that the procedure was successful for comparing the different Fenton's process operating conditions for the same soil, but failed when applied to make a comparison between different soils, meaning that the intrinsic soil characteristics (structure, presence of both organic and inorganic substances) may modify both hydrogen peroxide stability and radicals activity with respect to the target compounds. Even though the presence of hydrogen peroxide in the reaction environment

is somehow a pre-requisite for the formation of oxidative radicals, its concentration is not necessarily related to the radicals one. A direct measurement of these radicals would allow to assess the influence of the operating conditions on the effectiveness of the Fenton's reaction. Unfortunately, the methods applied so far (i.e. electron spin resonance spectroscopy (ESR)) result unsuitable for being applied as routine procedures, due to their high-cost and time-consuming features. On the contrary, an indirect method for radical quantification looks more attractive for this kind of applications. The method hereby proposed is based upon the quantification of the products generated by the reaction between oxidative radicals and an organic probe compound, which is used as a radical scavenger. The probe compound should be characterized by few and very stable reaction products and by a well-known and established reaction constant with radicals. Dimethyl sulfoxide ([75]), salicylic acid ([31]), phenols or pyrocatechols ([35]) are among the most commonly used compounds. Recently, Lindsey and Tarr ([49]) selected benzoic acid and n-propanol as chemical probes to quantify the hydroxyl radicals production in Fenton's systems, allowing to measure both hydroxyl radical formation rate and concentration. Different systems such as pure water, aqueous solutions of fulvic acid or humic acid and natural surface waters were tested in order to determine the influence of organic substrates on hydroxyl radicals production. The reactions between hydroxyl radicals and probe compounds were performed under controlled conditions: high probe concentrations were applied to determine the radicals total amount, while low probe concentrations were used to measure the hydroxyl radicals concentration. A linear correlation between hydrogen peroxide concentration and hydroxyl radicals formation was found, while the presence of organic substrates was observed to induce an up to 4-fold reduction of OH^\bullet formation rate and OH^\bullet concentration with respect to pure water systems. The Lindsey method addresses pro forma the OH^\bullet radical but it really refers to the sum of the highly oxidative radicals generated by the Fenton's reagent in solution. Therefore, this method will be applied in this paper for the quantification of oxidative radicals generated in a Fenton's system with two main goals. On the one hand, we want to apply the Lindsey method for evaluating the influence of the operating conditions on the oxidative radicals produced during the Fenton's reaction. On the other hand, the paper is also aimed to assess the feasibility of the Lindsey method for soil slurry systems. To this purpose, experiments in aqueous phase (with and without humic acid) and in soil slurry phase are presented and discussed. The selection of the operating conditions is performed using a Rotatable Central Composite (RCC) method, in order to minimize the number of meaningful experiments to be performed and to obtain a correct evaluation of the influence of the operating conditions on the

process performances. These were evaluated by measuring the total amount of generated radicals, their concentration and their production efficiency (i.e. the fraction of H₂O₂ converted to oxidative radicals).

Experimental

Materials

Benzoic acid (BA), *p*-hydroxybenzoic acid (*p*-HBA), hydrogen peroxide (H₂O₂, 30%, w/w solution), iron(II) sulphate heptahydrate, hydrochloric acid, 1-propanol (PrOH), sodium monobasic phosphate, sodium hydroxide and acetonitrile were purchased by Sigma-Aldrich (HPLC-grade or ACS-grade). Humic acid sodium salt (HA) (technical grade, 50-60% as humic acid) was purchased by Acros Organics. All materials were used as received. Ultra-pure water was provided by a Millipore Milli-Q Plus generator.

Method for oxidative radicals detection

The total amount of generated oxidative radicals and their concentration were evaluated in both aqueous solution and soil slurry phase by using the approach developed by Lindsey and Tarr ([49]). The Lindsey method addresses pro forma the OH[•] radical but it really refers to the sum of the highly oxidative radicals generated by the Fenton's reagent in solution. For sake of simplicity the reactivity of the oxidative radicals was assumed equal to the one of the hydroxyl radicals. This made possible to follow the approach of Lindsey and Tarr ([49]), who used benzoic acid as probe compound, since its reaction rate constant with hydroxyl radicals is known ($K_{BA/OH^{\bullet}} = 4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) as well as the products obtained from their reaction, i.e. *p*-hydroxybenzoic acid (*p*-HBA), *o*-HBA, *m*-HBA and other products such as ring fission and decarboxylation products (e.g. maleic and oxalic acids, catechol and hydroquinone ([68])). Moreover, the reaction between hydroxyl radicals and benzoic acid is known to require 5.87 ± 0.18 radicals moles to produce 1 mole *p*-HBA ([87]). The amount of radicals produced during Fenton's batch scale tests was evaluated assuming that all the generated radicals reacted with BA, thus mainly producing *p*-HBA. This assumption holds true if the fraction of oxidative radicals reacting with *p*-HBA and the other secondary products is negligible with respect to the one reacting with BA, i.e. if the initial BA concentration in solution is large enough. Under this condition, the amount of radicals generated is related to the amount of *p*-HBA produced and can be measured as reported in Analytical methods section. The minimum benzoic acid

concentration to be used for quantifying the total amount of produced radicals was obtained through preliminary tests, whose results are reported in Figure 1.

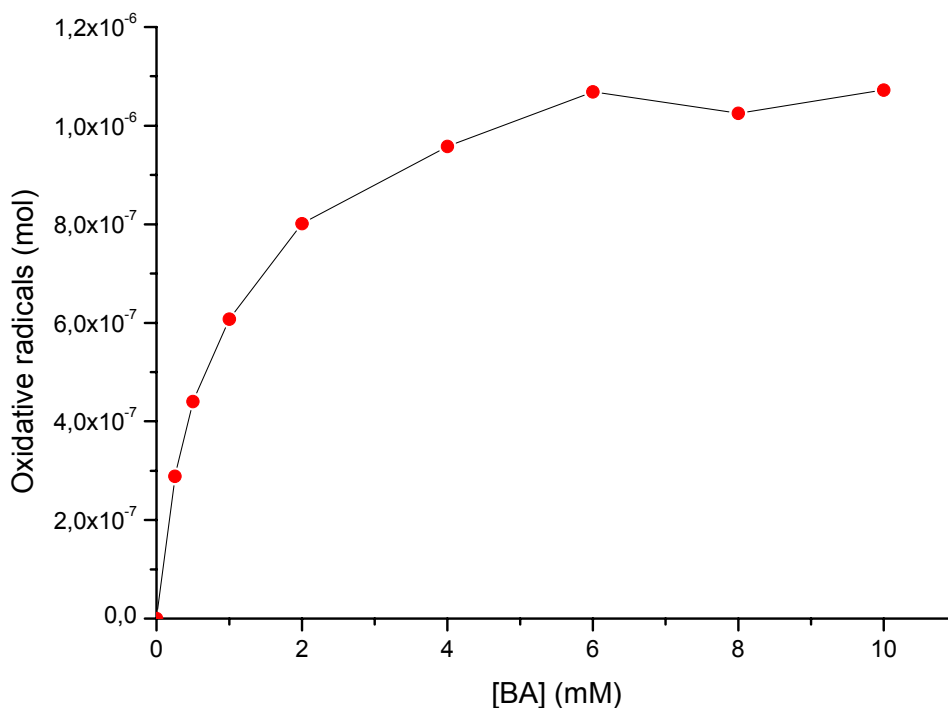


Figure 1: Results of preliminary test: trapped oxidative radicals moles versus BA concentration.

It can be noticed that the moles of oxidative radicals trapped increase with the initial benzoic acid concentration, until a threshold BA concentration, over which further increase of the BA concentration does not affect the radical amount anymore. Taking into account the results reported in Figure 1, all tests for quantifying the total amount of oxidative radicals were performed with a 9 mM BA concentration. Instead, the radicals concentration was estimated assuming that all oxidative radicals react following the same second order rate law of the hydroxyl radicals:

$$[Ox] = \frac{R_{BA}}{K_{BA/OH} \cdot [BA]} \quad (1)$$

where $[Ox]$ and $[BA]$ in Eq.(1) are the instantaneous concentrations of oxidative radicals and benzoic acid, respectively. The latter can be determined with the analytical methods reported in Analytical methods section. Since the $K_{BA/OH} \cdot$ term is known ($K_{BA/OH} \cdot = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), this method requires simply to evaluate the BA concentration at different times during a batch Fenton's test and hence the rate of BA oxidation (R_{BA}) which, over short time intervals can be

evaluated from the linear change in the BA concentration, provided that concentrations of BA and radicals do not change significantly within the time interval (steady-state conditions). Clearly, the BA concentration should be so low that the rate of reaction of oxidative radicals with BA is negligible with respect to their rate of formation. According to Lindsey method, this condition holds true when no more than 10% of the generated OH^\bullet radical is trapped by benzoic acid. Looking once again at [Figure 1](#), this means to operate with a BA concentration equal to 0.1 mM.

Analytical methods

Reaction products were evaluated by high-performance liquid chromatography (HPLC) using a Hewlett-Packard 1100 liquid chromatograph equipped with a Diode Array Detector (DAD). A Nucleodur 100-5 C₁₈ EC (5 μm particle size 250 mm length \times 4.6 mm i.d.) purchased from Macherey-Nagel, was used for all analysis. The analytes were eluted by means of a buffer solution of 50 mM NaH_2PO_4 (pH \sim 7.0) and acetonitrile (volume ratio equal to 95:5) previously filtered with a 0.45 μm membrane filter in order to eliminate all the particulates. The flowrate was set equal to 0.9 mL/min, while the oven temperature was kept to 32 $^\circ\text{C}$. Then, benzoic acid and *p*-hydroxybenzoic acid were detected by absorbance at 230 nm. The applied procedure, was taken from the Macherey-Nagel application database ([70]). Two different calibration curves were built in order to correlate the [BA] or [*p*-HBA] with the peak area; the detection range was respectively $5.0\times 10^{-6}\div 1.0\times 10^{-3}$ M for BA and $3.4\times 10^{-6}\div 1.7\times 10^{-4}$ M for *p*-HBA. Further, a preliminary test was carried out to assess the possible co-elution between the BA and the *p*-HBA: this test gave a negative result since BA and *p*-HBA retention time were estimated equal to 2.8 and 6.8 min respectively.

Design of the experiments: application of Rotatable Central Composite method (RCC)

In order to minimize the number of experiments to be performed and to guarantee a certain data set statistical significance a Rotatable Central Composite method was applied. The central composite design is probably the most widely-used experimental design for fitting a second-order response surface. An experimental design is rotatable if the variance of the predicted response is a function only of the distance of the experimental points from the center of the design and is not function of direction. Since the location of the optimum is unknown prior to running the experiment, it is useful to apply a design that provides equal precision of estimation

in all direction. Performing replicates of the central point allow to improve the model precision ([3]).

RCC method can be viewed as the combination of a 2 level factorial model (2^N) with a Star model ($2N+1$) so that the minimum number of experiments to be performed (k) is equal to:

$$k = 2^N + 2N + 1 \quad (2)$$

where N in Eq.(2) is the number of independent variables. In this case the RCC method was applied to a system of 2 independent variables (i.e. $[H_2O_2]$ and $[Fe^{2+}]$) by considering two levels per variable.

The tested operating conditions, resulting from the RCC approach are reported in Table 1, and schematically shown in the RCC experimental plan shown in Figure 2.

TEST	Fe(II) coded value	H ₂ O ₂ coded value	[Fe(II)] (mM)	[H ₂ O ₂] (mM)
O	0	0	0.37	0.60
S1	-1.41	0	0.20	0.60
S2	0	-1.41	0.37	0.20
S3	1.41	0	0.53	0.60
S4	0	1.41	0.36	1.00
F1	1	1	0.48	0.88
F2	-1	1	0.25	0.88
F3	-1	-1	0.25	0.32
F4	1	-1	0.48	0.32

Table 1: Rotatable Central Composite operating conditions.

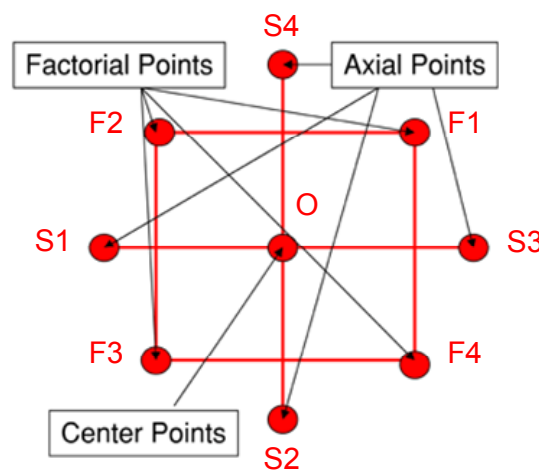


Figure 2: Rotatable Central Composite (RCC) configuration in the experimental plan.

As shown in [Figure 2](#), the experimental points which refer to factorial design were called F1, F2, F3, F4, whereas those of the Star design S1, S2, S3, S4. The central point was indicated as O. In order to simplify calculations the independent variables were expressed as coded values: namely, factorial points have values of $(\pm 1, \pm 1)$, Star points were expressed as $(\pm\alpha, 0)$ or $(0, \pm\alpha)$, while the central point had coded values of $(0, 0)$. A central composite design is made Rotatable by the choice of the α value. Its choice depends on the number of points in the factorial part of the design. In fact, as the number of factorial points is known, as the α value can be estimated by applying Eq.(3):

$$\alpha = n_f^{1/4} \quad (3)$$

where n_f is the number of factorial points ([\[55\]](#)). In this study n_f was equal to four points and then Eq.(3) gave a value of 1.41.

Fenton's experiments

Fenton's reaction was carried out in both ultra-pure water and humic acid (HA) aqueous solutions with concentration set at 5, 10 and 15 mg/L in order to assess the effect of the organic matter on the oxidative radicals production. HA solutions were prepared by dissolving a known amount of humic acid sodium salt in MQ water. All the experiments were performed in 25 mL amber glass bottles, with a reaction volume equal to 10 mL. The experiments for assessing the radicals total amount, were carried out in a 9 mM BA aqueous solution at different Fe(II) and H₂O₂ concentrations (see [Table 1](#)) and pH 2.5. The reaction time was set equal to 30 min. The 1 mL samples were immediately withdrawn from the reaction environment at different reaction times between 15 and 1800 s and immediately quenched by adding 0.5 mL of 1-propanol, whose amount was enough to compete with BA for oxidative radicals: it was assumed that this amount of added quencher had rates of reaction with oxidative radicals high enough so that, upon the addition of PrOH, no significant reaction of BA with radicals occurred ([\[49\]](#)). Then, the samples were filtered with 0.45 μ m membrane filters and analyzed by means of HPLC. All the experiments were carried out in duplicate in order to ensure data repeatability. Measurement of the oxidative radicals concentration was performed using the same procedure above described, differing only in the applied BA concentration set equal to 0.1 mM and in the total reaction time, equal to 10 min. The slurry-phase experiments were carried out with a quartz sand typically used as filter media in drinking water micro-filtration processes. Before its use, the sand was sieved (2 mm) to obtain an homogeneous media, autoclaved at 120°C for 2 minutes, allowing either

sterilization and also the reduction of enzymatic activity ([39]). Then, the sand was further characterized in terms of metal content, i.e. iron and manganese, according to acid digestion described in EPA method 3050B and analyzed by means of flame atomic absorption spectrometry (FLAA). The organic carbon content was determined according to Walkey-Black procedure; the sand presented 416 mg/kg of iron, 18 mg/kg of manganese, 0.34% of organic carbon and 0.59% of organic matter. The slurry-phase experiments were carried out in a range of operating conditions which are briefly summarized in Table 2.

PARAMETER	Oxidative radicals total amount ÷ Oxidative radicals production efficiency	Oxidative radicals concentration
Soil:water ratio	1:10, 5:10, 9:10 (g:g)	1:10, 5:10, 9:10 (g:g)
pH	2.5	2.5
Benzoic acid concentration	9 mM	0.1 mM
Total Reaction Time	30 min	10 min
Sampling Time	15, 30, 60, 120, 300, 600, 900, 1800 sec	15, 30, 60, 120, 300 sec
Quencher Volume	0.5 mL PrOH	0.5 mL PrOH

Table 2: Slurry-phase experimental setting.

The investigated H₂O₂ and Fe(II) concentrations were the same used for the aqueous-phase experiments (see Table 1). In order to remove any solid residual, the samples were filtered by means of 0.45 µm syringe filters before being analyzed following the procedure described before (see Analytical methods section). Also in this case, the experiments were carried out in duplicate.

Results and discussion

Aqueous-phase experiments

Measurement of the oxidative radicals total amount

The influence of the Fenton's operating conditions, in terms of Fe(II) and H₂O₂ concentration, was assessed with respect to oxidative radicals total amount and production efficiency (i.e. molar ratio between the measured total amount of radicals and the moles of H₂O₂ initially fed to the system). Figure 3 shows the influence of increasing hydrogen peroxide concentration on the oxidative radicals total amount at fixed iron concentration (0.365 mM).

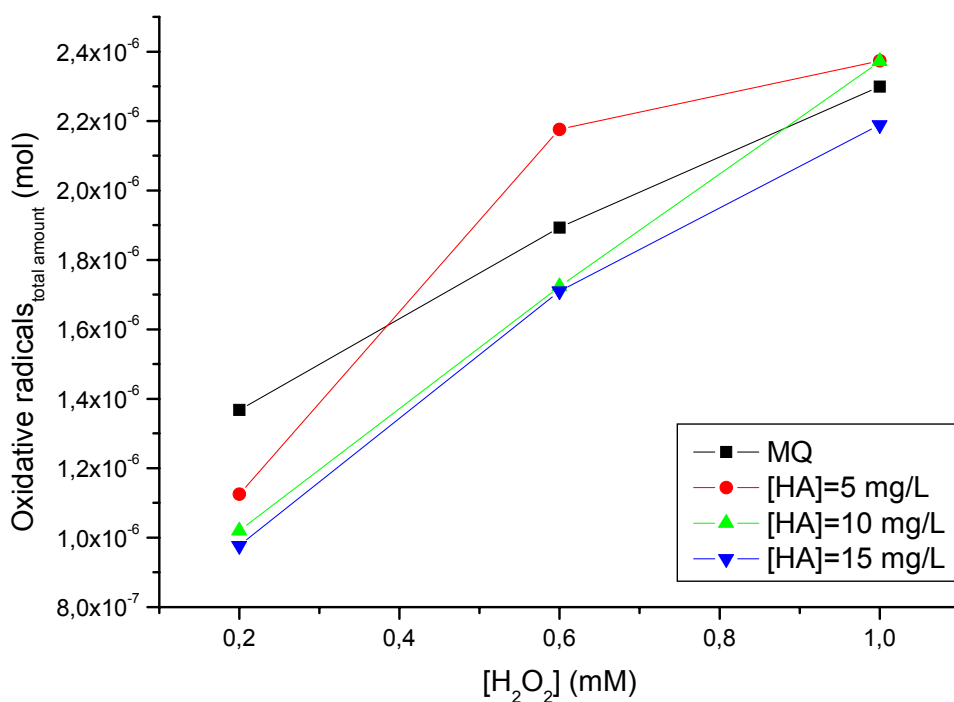


Figure 3: Influence of the hydrogen peroxide concentration on the oxidative radicals total amount: results obtained at [Fe(II)]=0.365 mM.

Within the tested concentration range, the total amount of oxidative radicals was influenced by the hydrogen peroxide concentration, with a rather linear correlation between total moles of radicals and H₂O₂ concentration. Besides, the presence of HA induced a slight decrease of the oxidative radicals total amount, even though such a decrease is also not clearly correlated to the increase of HA concentration. Anyway, the results reported in Figure 3 confirm the expected positive influence of higher H₂O₂ concentration on the radicals production. Nevertheless, one of the main tasks in the proper design of a Fenton's process consists in maximizing the amount of oxidative radicals moles produced with respect to the amount of H₂O₂ introduced in the system, i.e. the production efficiency. As shown in Figure 4 the production efficiency depends on the Fe(II):H₂O₂ molar ratio, at least up to values of this ratio around 2, where probably Fe(II) starts to act as a scavenger of hydroxyl radicals.

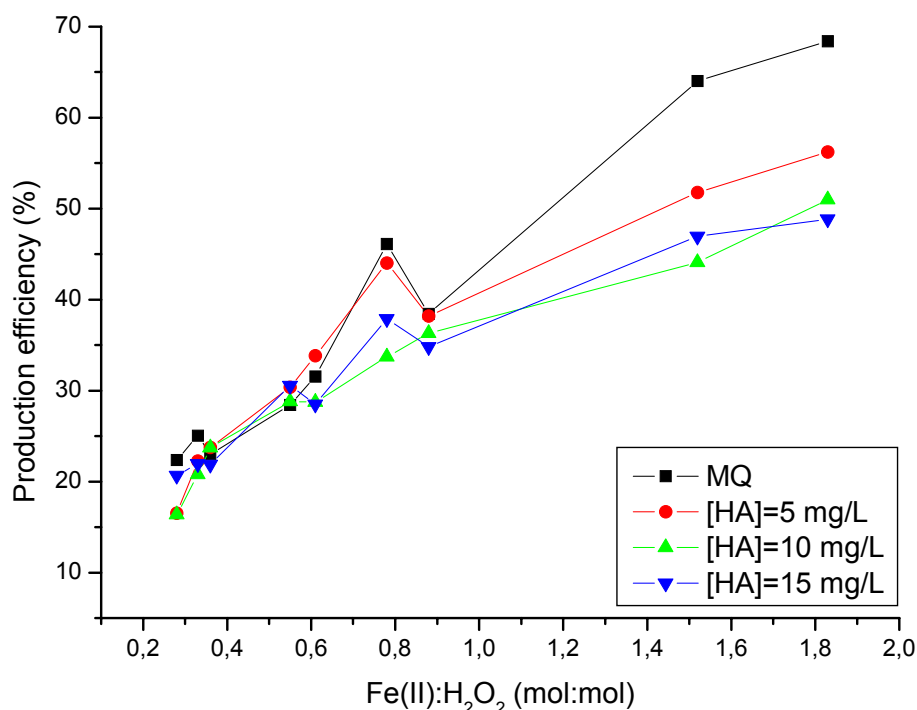


Figure 4: Influence of the Fe(II):H₂O₂ molar ratio on the oxidative radical production efficiency: comparison between tests performed in ultra-pure water and with increasing amounts of humic acid (HA).

At high Fe(II):H₂O₂ ratios, an important influence of the HA concentration on the oxidative radicals production efficiency was also observed. This results suggest that at these Fe(II):H₂O₂ ratios, competition between organic compounds and Fe(II) for hydroxyl radicals becomes important ([62],[19]).

Looking at the results obtained for the lower Fe(II):H₂O₂ molar ratios, shown in Figure 4, a decrease of the production efficiency can be noticed: in particular, for a Fe(II):H₂O₂ molar ratio of 0.28 the estimated production efficiency is 25%, i.e. about 0.25 moles of oxidative radicals per mole of H₂O₂.

Considering the Fenton's reaction stoichiometry reported in Reactions (I) and (V)



0.28 moles of Fe(II) are expected to react with 1 mole of H₂O₂ to give 0.28 moles of Fe(III) (Reaction (I)): the generated Fe(III) is then expected to further react with 0.28 moles H₂O₂ to produce 0.28 moles Fe(II) and other products (see Reaction (V)), as long as the H₂O₂ is

completely consumed. Based on our results, it seems that the amount of oxidative radicals produced (0.25 moles), closely matches the number of Fe(II) moles added as reactant (0.28 moles). This suggests that the expected recycle of Fe(III) to Fe(II) through Reaction (V) may not take place under the tested operating condition, thus stopping the radicals propagation cycle. Such conversion may be hindered for different reasons. It has been reported that the generation rate of Fe(II) is much lower than its consumption rate; thus, the amount of re-converted Fe(II) could be very low unless other compounds, such as hydroquinone-like intermediates or catechols, which are capable of quickly reducing Fe(III) to Fe(II), are present ([20]). Besides, organic acids such as maleic and oxalic acid, might scavenge Fe(III) during the process by forming stable complexes (e.g. ferrioxalate) which are not readily available to react with H₂O₂ through Reaction (V) ([68],[19]).

The above explanation would be true if only hydroxyl radicals were present in the Fenton's system. Since also other oxidative radicals are generally present in Fenton's system, it can be also argued that the fraction of oxidative radicals represented by hydroxyl radicals reacts through Reaction (II), thus producing less reactive perhydroxyl radicals, which have a less effective reaction with the probe compound.

Measurement of the oxidative radicals concentration versus time

As general result during this set of experiments, it was noticed that whichever concentration of H₂O₂ and Fe(II) was tested within the experimental plan, oxidative radicals concentration decreased of approximately 80% within 5 minutes from the addition of H₂O₂ (data not shown). This suggests that oxidative radicals production, due to hydrogen peroxide reaction, takes place in the very first seconds of the process, followed by a quite rapid radical consumption. The influence of the Fenton's operating conditions on oxidative radicals concentration was evaluated using, as performance indicator, the average radicals concentration: its value was derived from the data measured during the experiments at fixed times. The effect of increasing organic matter content was further investigated by plotting the oxidative radical concentration versus the HA:Fe(II) weight ratio as shown in [Figure 5](#).

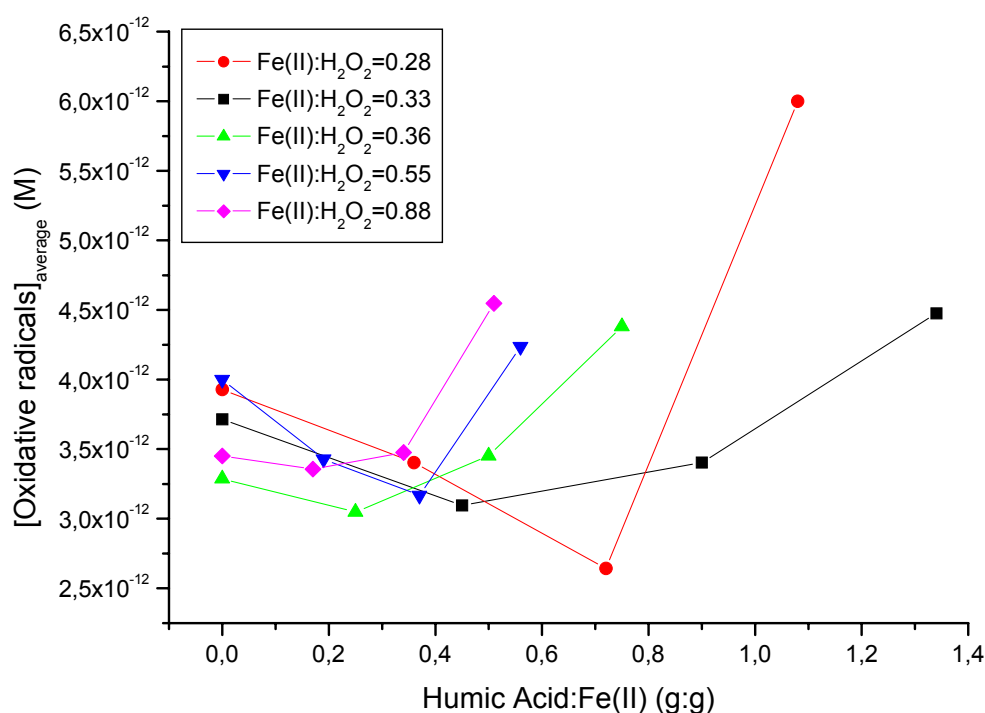


Figure 5: Effect of the HA:Fe(II) (humic acid to ferrous ions weight ratio) on the oxidative radicals concentration: comparison between different Fe(II):H₂O₂ molar ratios.

Although the effect of this ratio on the radicals concentration is not so important, the obtained results suggest that an increase of HA:Fe(II) ratio has a detrimental effect on oxidative radicals concentration for low HA:Fe(II) ratios, whereas when such a ratio increases to values around 1 or higher, the influence becomes positive. This may suggest that under given operating conditions, the organic matter may play a role in the decomposition of H₂O₂, thus increasing the radical concentration ([9]).

Slurry-phase experiments

The results reported in Figure 6 clearly indicate that whichever the soil:water ratio, the radicals generated in a soil slurry system are up to one order of magnitude lower than those measured in ultra-pure water (MQ).

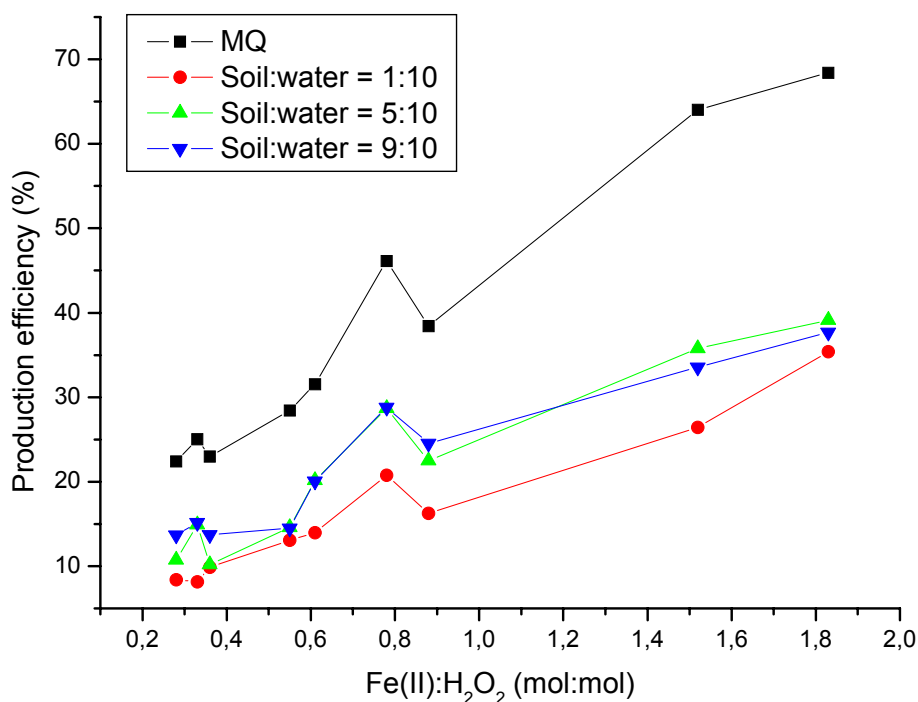


Figure 6: Influence of the Fe(II):H₂O₂ molar ratio on the production efficiency of oxidative radicals: comparison between MQ data and slurry tests at different soil:water ratios.

Besides, it is worth pointing out that the soil:water ratio has a weak influence on the radicals production efficiency. A positive correlation between the production efficiency of oxidative radicals and Fe(II):H₂O₂ molar ratio was also noted in slurry-phase experiments. As far as the effect of the Fe(II):H₂O₂ ratio on the oxidative radicals concentration is concerned, [Figure 7](#) clearly shows that in slurry-phase experiments the radicals concentration was always almost one order of magnitude lower than in aqueous phase experiments.

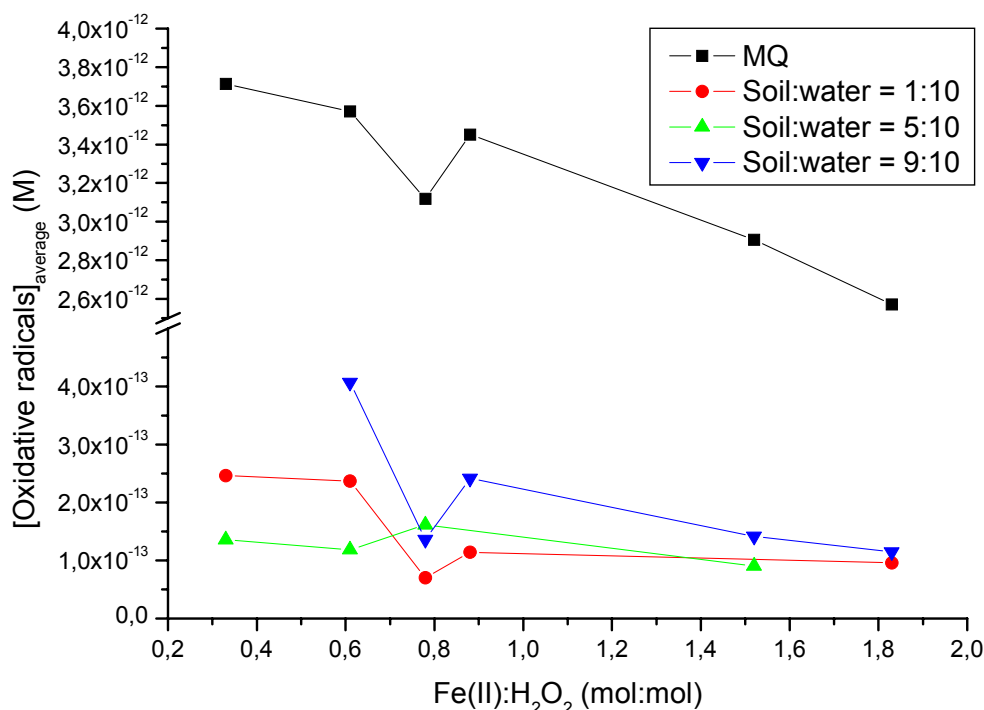


Figure 7: Influence of the Fe(II):H₂O₂ molar ratio on oxidative radicals concentration: comparison between MQ data and slurry tests at different soil:water ratios.

This means that the presence of the soil matrix has a detrimental effect on both amount and concentration of radicals available for oxidizing organic compounds, whereas it probably drives hydrogen peroxide decomposition through other pathways, such as disproportion reactions. This effect, usually accounted for in *in-situ* Fenton's application by increasing the hydrogen peroxide concentration with respect to the one used in water treatment, clearly depends on the properties of the soil matrix. The coarse sand used in this paper probably did not greatly affect the radicals production, due to its low specific surface area. A different behaviour would probably be observed in real soils, whose texture is characterized by a rather high fractions of fine particles that may have a more effective role in decomposing hydrogen peroxide to other products than oxidative radicals.

Conclusions

The application of an indirect method to quantify oxidative radicals allowed to evaluate the effect of different operating conditions on the total amount of radicals generated, their production efficiency (i.e. H₂O₂ to radicals conversion with respect to the stoichiometric one)

and finally on the fate of oxidative radicals (i.e. concentration and lifetime in the reaction environment) in aqueous and soil slurry Fenton's systems.

Within the tested operating conditions, the Fe(II):H₂O₂ ratio was observed to affect the oxidative radicals production efficiency, which achieved a maximum 70% value for the highest tested Fe(II):H₂O₂ ratio. At low Fe(II):H₂O₂ molar ratios, the production efficiency was particularly low, suggesting that either the Fe(II) was unable to complete the redox cycle generally supposed to occur during a Fenton's reaction or the hydroxyl radicals mostly reacted with hydrogen peroxide forming less reactive perhydroxyl radicals. Moreover, the organic matter content was observed to negatively affect the hydroxyl radicals production efficiency, especially for the higher Fe(II):H₂O₂ molar ratios.

Despite some weak effects were noticed and discussed, the influence of dissolved organic matter on the radicals production was of minor importance. On the contrary, a one order of magnitude reduction in both radicals amount generated and concentration was observed when soil was added to the reaction environment.

It is worth pointing out that the results discussed in this paper were obtained on a model system, where a simple silica sand was used as soil matrix. Besides, also the operating conditions selected for this study were those typically used in aqueous Fenton's systems. These choices were made in order to obtain a simplified experimental system, since no literature data on the quantification of oxidative radicals in soil slurry systems were available. Nevertheless, most of the effects that can play an important role in real world Fenton's applications were obviously not accounted for. Therefore, further research is needed to assess the feasibility of the oxidative radicals quantification method also for this kind of systems.

Acknowledgements

The authors wish to acknowledge Dr. Luigi Galeotti and Dr. Gloria Carucci of the Laboratory of Sanitary-Environmental Engineering of the Department of Hydraulics, Transportations and Roads of "Sapienza" University of Rome for their effective collaboration during the soil characterization.

APPENDIX C

FEASIBILITY STUDY AND OPTIMIZATION OF METHYL-tert-BUTHYL ETHER (MtBE) OXIDATION BY PERSULFATE IN AQUEOUS AND SLURRY SYSTEMS

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Abstract: The aim of this work is to assess the applicability of the persulfate oxidation process to remediate contaminated groundwater systems. The feasibility study consisted of a series of lab-scale experiments, carried out in order to assess the effect on the process performance of the operating parameters. The experiments were carried out on both aqueous and slurry systems. The aqueous phase tests were carried out in order to assess the performance on the MtBE removal of the persulfate activated oxidation process. Different configurations were tested, characterized by a single or a double sequential persulfate addition, and also different $\text{Na}_2\text{S}_2\text{O}_8$:amendments: MtBE molar ratios were tested in order to make a preliminary characterization of the persulfate oxidation process. The results of the aqueous phase tests were used for designing the soil slurry experimental phase. As far as the soil slurry tests are concerned, the experimental approach was based upon the Rotatable Central Composite (RCC) method which leads to define the minimum number of meaningful experiments in order to optimize the independent parameters involved in the oxidation process. The RCC method was built by taking in account two independent parameters: sodium persulfate concentration (which was varied between 1.3 and 16.2 mM) and Fe(II) sulphate concentration (which was varied between 0.7 and 32.3 mM). A Response Surface Method was applied to provide a graphical representation of the influence of the operating parameters on the process performance.

Keywords: Advanced Oxidation Processes (AOPs), Persulfate, MtBE, Rotatable Central Composite method, Response Surface Method

Introduction

The soil layer of a large number of sites has been found to be polluted with hazardous compounds which are refractory to biotic degradation processes. Among these, MtBE is the oxygenate compound most commonly used as octane-enhancing replacement for lead tetraethyl. From an industrial view point, MtBE has many positive features such as low production costs, ease of production, high octane number and favorable blending characteristics. From an environmental view point, despite a positive effect on air pollution, MtBE has a negative effect

on groundwater resources. It is a poorly biodegradable compound, with a degradation half-time life of 27 years, and is characterized by high solubility in water ($S = 48000 \text{ mg/L}$) and low Henry constant (0.022 at 25°C) ([67]). This means that, once spilled from UST (Underground Storage Tank), it will readily migrate in both vadose zone and groundwater systems with essentially no retardation with respect to underground water flow. Besides, it is worth pointing out that MtBE is characterized by a distinct odor at as low as $10 \text{ }\mu\text{g/L}$ concentration. Moreover, recent researches lead by U.S. EPA have tentatively classified MtBE as a possible human carcinogen. Despite MtBE is not included in the Italian list of priority pollutants as per D.Lgs 152/06 ([17]), a recent document issued by the Italian Health Institute (ISS) has suggested a maximum concentration of $10 \text{ }\mu\text{g/L}$ ([56]). The physical-chemical properties of MtBE also limit the remediation technologies that can be applied. Namely, Pump & Treat with adsorption by GAC is not efficient due to the poor adsorption properties of MtBE on this adsorbent; biological treatment is also not effective due to the low MtBE biodegradability; finally, air stripping treatment is also hard to apply, in view of the MtBE Henry constant. Recently, the possibility of applying In Situ Chemical Oxidation (ISCO) for treatment of MtBE contaminated groundwater has been proposed ([33],[41]).

Among these, persulfate ion was recognized as one of the strongest oxidizing agents known in aqueous solutions and capable of degrading a variety of organic compounds. The standard oxidation-reduction potential for the reaction:



is estimated to be 2.01 V . However, persulfate oxidation at ordinary temperature, in the absence of any other activating principle, is generally slow; therefore, under these conditions, persulfate is practically ineffective as oxidant. On the contrary, if properly activated, persulfate ions may readily decompose leading to the formation of sulfate radicals. The most common means of generating sulfate radicals, i.e. heat-activation, has shown to be effective above 40°C , whereas also UV irradiation may serve to the purpose ([28]). Once formed, the sulfate radical behaves as a very effective oxidant, considering that the following reaction:



has an oxidation-reduction potential of 2.6 V . Sulfate radical may also be formed at ambient temperature ($\sim 20^\circ\text{C}$), by the decomposition of persulfate anion in the presence of a transition

metal activator (e.g., Fe^{2+}) (Ebersson, 1987). The overall stoichiometric reaction between persulfate and ferrous ion is shown in the following equations (Kolthoff et al., 1951):



Through the steps:



Other than iron, the general activators found in the literatures include the ions of copper, silver (House, 1962), manganese (House, 1962; Lenka and Dash, 1983; Kislenco et al., 1997), cerium (House, 1962; Skarzewski, 1984), and cobalt (Lenka and Dash, 1983). The persulfate-ferrous ion reaction results in the rapid production of sulfate free radicals. A free radical half-life of 4 s was reported at a persulfate and ferrous ion concentration of 10^{-3} M and a temperature of 40 °C (Banerjee and Konar, 1984). Sulfate free radical converts ferrous ion to ferric ion through Eq.(5). The reaction coefficient (at a diffusion-controlled rate) for Eq.(5) has been reported to be $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Heckel et al., 1966) as was reported in a compilation by Neta et al. (1988). The rate of reaction between persulfate and ferrous ion is dependent on the concentration of each reactant. According to Eq.(3), reaction stoichiometry demands a $\text{Fe}^{2+}:\text{S}_2\text{O}_8^{2-}$ molar ratio of 2, however, the rate-determining step is the reaction between one $\text{S}_2\text{O}_8^{2-}$ and one Fe^{2+} to form $\text{SO}_4^{\bullet-}$ (Eq.(4)), which then rapidly reacts with a second Fe^{2+} (Eq.(5)) (Balabanova and Markevich, 1966). When the reactions were completed, no sulfate free radical is available for further attack of target organic contaminants. Therefore, increasing the concentration of Fe^{2+} would speed up the reactions shown in Eqs.(4) and (5) and thus lead to completion of the reaction shown in Eq.(3). The conversion of Fe^{2+} to Fe^{3+} results in the production of $\text{SO}_4^{\bullet-}$, which reacts immediately with the target organic contaminant. However, a too fast reaction between $\text{SO}_4^{\bullet-}$ and an excess of Fe^{2+} could destroy the $\text{SO}_4^{\bullet-}$, resulting in a lowering of the degradation efficiency of the target organic contaminant. This behavior can be characterized as competition for the $\text{SO}_4^{\bullet-}$ between the target organic contaminant and the excess of Fe^{2+} ions. Therefore, it should be necessary to slow down or control the reaction shown in Eq.(5), perhaps by gradually providing small quantities of Fe^{2+} activator, thereby preventing the rapid conversion of Fe^{2+} to Fe^{3+} by the $\text{SO}_4^{\bullet-}$ as shown in Eq.(5) ([44]). The aim of this feasibility study is two-fold. On the one hand, testing the performance of iron-activated persulfate for the oxidation of water systems contaminated by MtBE. On the other hand, developing a method for the selection of the

operating conditions of the persulfate oxidation process to be applied to the soil slurry systems. In order to accomplish both goals of the present paper, experiments either in aqueous and soil slurry system have been performed under different operating conditions, the production of sulfate radicals is accomplished only by Fe(II) activation, without any additional amendment. The [MtBE]:[Fe²⁺]:[Na₂S₂O₈]:soil ratios in the soil slurry system experiments, were changed in order to identify the influence of the operating conditions. The soil slurry experiments were carried out in agreement with recent guidelines issued by the Italian Environmental Agency (APAT) ([65]). The matrix selected for the soil slurry experiments was a clean soil collected within the Campus site of the University of Rome “Tor Vergata”, whereas, the MtBE contaminated groundwater was collected from a contaminated site in the Southern Italy. First preliminary experiments, either in aqueous phase or in slurry phase systems, were carried out in order to optimize the dosage of the reagents involved in the oxidation process; a Rotatable Central Composite method was then applied to the soil slurry experiments, in order to evaluate the minimum number of experiments required for the optimization procedure. Finally, a Response Surface Method was applied to provide a graphical representation of the effect of the operating parameters on the process performance.

Lab-scale feasibility study

Materials and Methods

Sodium persulfate, Fe(II) sulfate heptahydrate, sulphuric acid (96%) and methyl-tert-butyl ether (MtBE), were purchased by Fluka – Riedel-de Haën. All reagents were ACS or HPLC grade; solid-phase micro-extraction fiber (PDMS/DVB) was purchased by Supelco.

Soil and Contaminated Water Characterization

The soil, collected within the Campus area of the University of Rome “Tor Vergata”, had 24,4 % (wt/wt) moisture content and pH = 7.2.

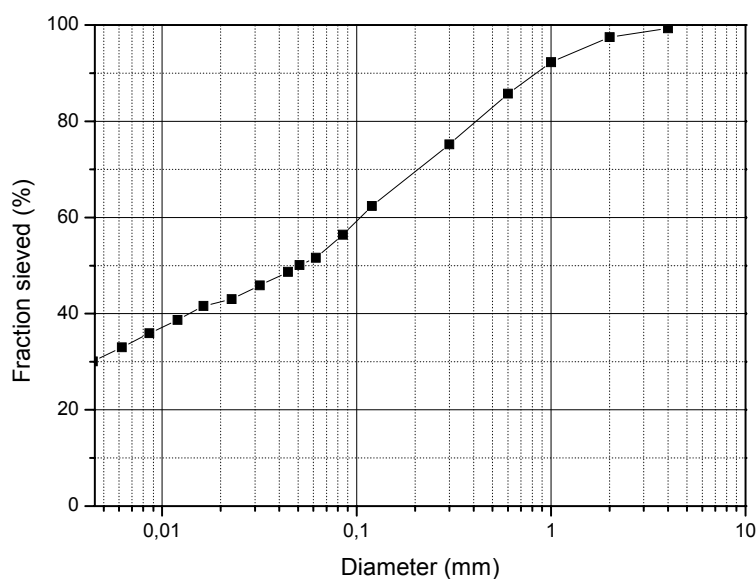


Figure 1: Granulometric curve of Tor Vergata soil.

Fraction	Value
Clay	20.00 %
Silt	30.00 %
Sand	47.50 %
Gravel	2.50 %

Table 1: Fraction distribution of Tor Vergata soil.

MtBE contaminated groundwater was collected from a site located in Southern Italy. The complete characterization of groundwater is reported elsewhere ([7]). The soil total oxidant demand (TOD), measured following the same procedure used by Haselow et al. ([27]), gave a value of 5.06 g/kg. The iron and manganese concentrations were 2967 and 842 mg/kg respectively.

MtBE determination

MtBE determination in water was performed by Headspace-SPME coupled with analysis by GC-FID as reported elsewhere ([7]).

Aqueous phase experiments

Aqueous phase tests were performed in 50 mL vials filled with 25 mL of MtBE contaminated water. The water, used in these tests, was found to be contaminated by approximately 2200 µg/L MtBE. Sodium persulfate, Fe(II) sulphate, were then added, in different molar ratios (1:0.75 and

1:1 respectively). Liquid solutions were thoroughly mixed by means of a multi-position magnetic stirrer for few minutes, and then left reacting for 24 hours. After 24 hours, the vial content was directly analyzed for MtBE following the procedure elsewhere described ([7]). A blank test was performed using the same procedure described above, without any persulfate and amendments. The aqueous phase experiments were performed at increasing $\text{Na}_2\text{S}_2\text{O}_8$:MtBE molar ratios and at two different $\text{Na}_2\text{S}_2\text{O}_8$: FeSO_4 molar ratios, 1:0.75 and 1:1 respectively.

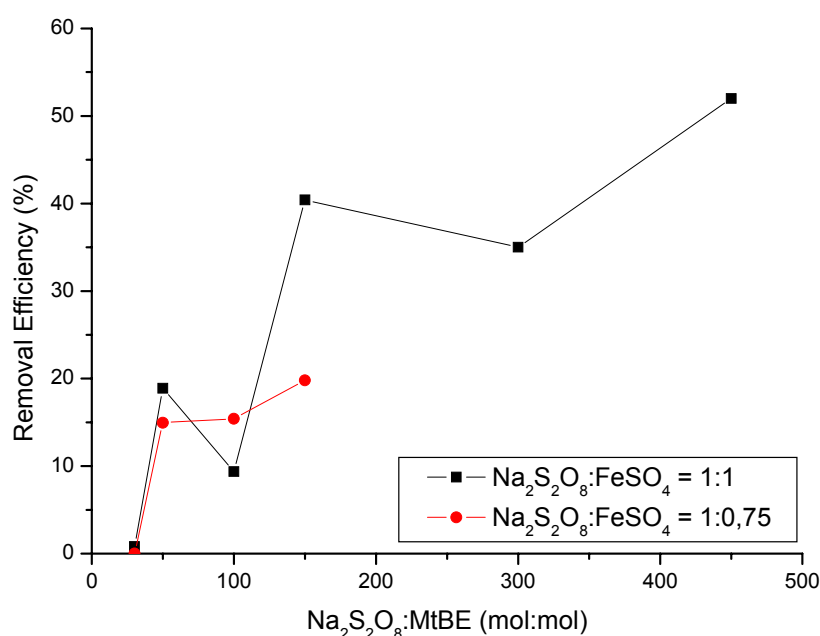


Figure 2: MtBE removal efficiency of increasing $\text{Na}_2\text{S}_2\text{O}_8$: FeSO_4 molar ratios.

The influence of the $\text{Na}_2\text{S}_2\text{O}_8$ /MtBE ratio on the MtBE removal efficiency is shown in Figure 2. It can be observed that, an increase of this ratio has a positive effect on the MtBE removal, even though this is not always univocally clear. Besides, it is worth pointing out that the removal efficiency for the test referred at FeSO_4 : $\text{Na}_2\text{S}_2\text{O}_8 = 1$ was higher than for the test characterized by a FeSO_4 : $\text{Na}_2\text{S}_2\text{O}_8$ ratio equal to 0.75.

As shown in Figure 3, the influence of the latter ratio was further investigated, showing that the best operating conditions corresponds to a FeSO_4 : $\text{Na}_2\text{S}_2\text{O}_8$ ratio equal to unity. If a higher value of this ratio is used, the excess of Fe(II) can readily react through Eq.(5), thus consuming sulfate radicals, which are not anymore available for oxidizing the target contaminant.

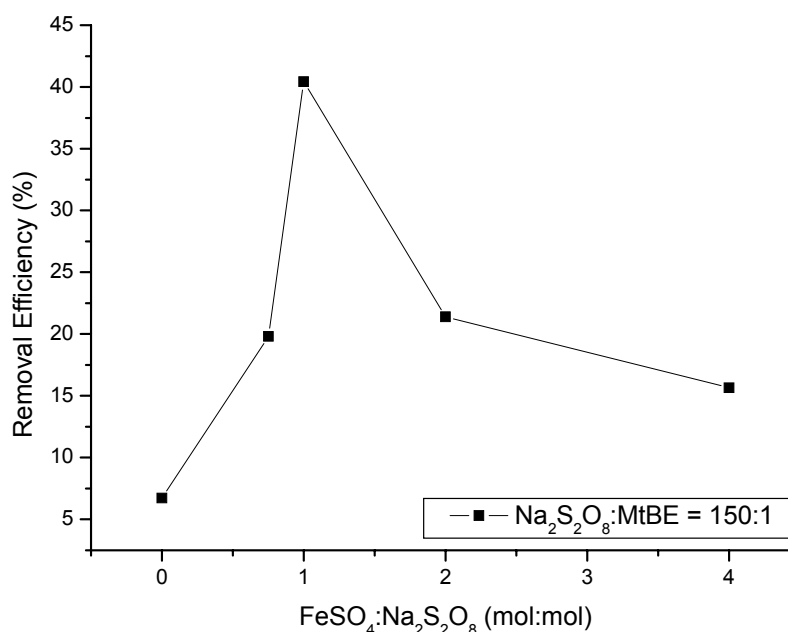


Figure 3: MtBE removal efficiency at increasing FeSO₄:Na₂S₂O₈ molar ratios, Na₂S₂O₈:MtBE = 150:1.

All experimental results except these obtained at Na₂S₂O₈:MtBE ratio higher than 150:1, where data at different FeSO₄:Na₂S₂O₈ were not available, were fitted by a quadratic polynomial regression model, using a proper software (SURFER[®]). The regression analysis of the experimental results provided a quadratic equation (Eq.(6)) relating the removal efficiency (R%) with Na₂S₂O₈:MtBE (x) and Fe(II):MtBE (y) molar ratios:

$$R\% = -0.0015x^2 - 0.0002y^2 + 0.3098x - 0.1078y + 0.0015xy - 1.026 \quad (6)$$

The curves at constant MtBE removal (iso-removal curves) plotted in the experimental plan are shown in [Figure 4](#).

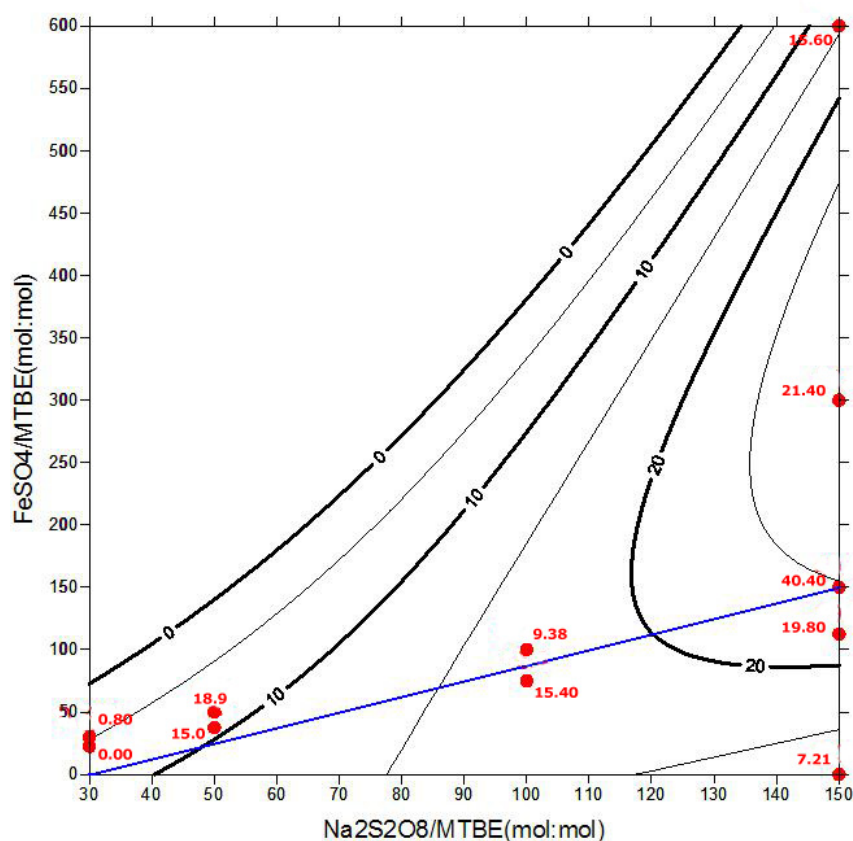


Figure 4: Iso-removal curves generated by SURFER®, and experimental points with removal efficiency.

The results shown in Figure 4 confirm that the highest removal efficiency is always found on the line characterized by a $\text{FeSO}_4:\text{Na}_2\text{S}_2\text{O}_8$ ratio equal to unity (blue line) and also the positive effect of an increased $\text{Na}_2\text{S}_2\text{O}_8$ dosage, at least within the investigated range.

Then, a further experimental set was carried out in order to assess the effect of a sequential $\text{Na}_2\text{S}_2\text{O}_8$ addition to a MtBE contaminated aqueous system; during this set, the $\text{FeSO}_4:\text{Na}_2\text{S}_2\text{O}_8$ molar ratio was kept constant to 1:1 as specified above. The sequential addition was performed as follows: a first load of persulfate and Fe(II) sulfate was added to the contaminated water and all the system was kept stirred for 3 hours; after 3 hours a new load was added and all the system was kept to react for 24 hours. It should be noted that for this experimental set it was used a contaminated groundwater whose MtBE concentration was equal to about 3200 $\mu\text{g}/\text{L}$.

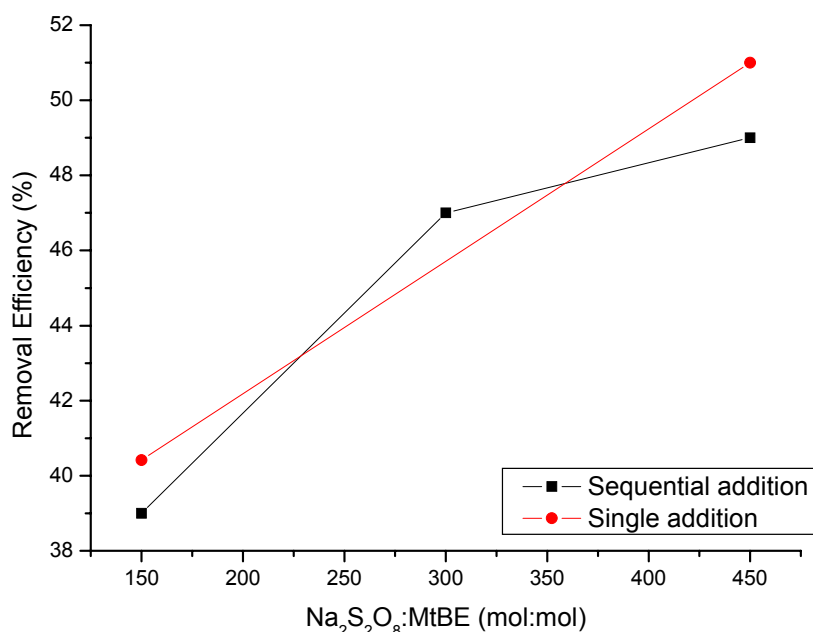


Figure 5: Comparison between single and sequential addition of activated persulfate oxidation system.

As clearly shown in Figure 5, apart from one outlier data point, the sequential addition did not increase the removal efficiency.

Soil slurry system experiments

Experimental setup

The slurry phase feasibility tests were performed in a 50 mL vial with 2 g soil in each vial and 10 mL of contaminated water; this experimental set-up was preferred to the one suggested by APAT guidelines, since it allowed to reduce the amount of MtBE adsorbed on the soil, while providing similar results in terms of MtBE removal efficiency (data not reported). The water, used in these tests was collected from an Italian contaminated site and it was found to be contaminated by approximately 2400 µg/L MtBE. Since the water used in these experiments had a different MtBE concentration, a blank test was performed in order to evaluate the percentage of adsorbed MtBE: this amount was equal to 29 %; this was an important data because it was taken in account during the calculations for the determination of the MtBE removal efficiency. The blank test was performed using the same procedure above described, without any sodium persulfate and amendments. Sodium persulfate, and Fe(II) sulphate, were then added, in different amounts as described in Table 2. Soil and liquid solutions were thoroughly mixed by means of a

multi-position magnetic stirrer for 24 hours. After 24 hours, the vial content was centrifuged and the supernatant was analyzed for MtBE following the procedure described elsewhere ([7]). In all experimental tests the pH of the soil-water system was equal to 7.0.

Experimental design and optimization

In order to minimize the number of experiments to be carried out and to guarantee a statistical significance of the data set a Rotatable Central Composite (RCC) method was applied. This RCC method is the combination of a 2 level factorial model with a Star model. In this case the RCC method was applied to a system of 2 independent variables (Sodium persulfate concentration and Fe(II) sulphate concentration) with 2 levels per variable (high and low concentration). Since this model assumes that experimental uncertainty is linked only to the distance from the central point, a series of replicates of this point was carried out ([3]). The tested operating conditions, resulting from the RCC approach are reported in Table 2, and schematically shown in the RCC experimental plan shown in Figure 6.

#Test	[Na ₂ S ₂ O ₈] _{coded value}	[FeSO ₄] _{coded value}	[Na ₂ S ₂ O ₈] (mM)	[FeSO ₄] (mM)	Na ₂ S ₂ O ₈ :FeSO ₄ :MtBE molar ratio
O	0	0	8.70	16.50	325:612.50:1
S1	0	-1.41	8.70	0.70	325:25:1
S2	-1.41	0	1.30	16.50	50:612.50:1
S3	0	1.41	8.70	32.30	325:1200:1
S4	1.41	0	16.20	16.50	600:612.50:1
F1	1	1	14.00	27.70	519.5:1027.90:1
F2	-1	-1	3.50	5.30	130.50:197.10:1
F3	-1	1	3.50	27.70	130.50:1027.90:1
F4	1	-1	14.00	5.30	519.50:197.10:1

Table 2: RCC dosage tests.

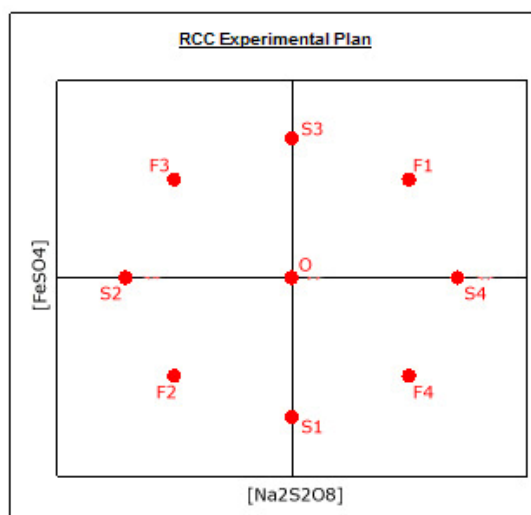


Figure 6: Rotatable Central Composite experimental plan.

Results

The results of all batch experiments are summarized in Table 3. It can be noted that all experiments were carried out in duplicate, in order to guarantee data repeatability. The removal efficiencies were evaluated making reference to the concentration of the blank sample, which was equal to 1693 $\mu\text{g/L}$.

#Test	[MtBE] _{residual, average} ($\mu\text{g/L}$)	Removal Efficiency (%)
O1	1436.55	14.63
O2	1426.64	15.23
O3	1450.37	13.82
S1	1681.39	0.09
S2	1684.38	0
S3	1303.09	22.57
S4	578.80	65.61
F1	993.37	40.97
F2	1125.98	33.09
F3	1437.39	14.59
F4	687.36	59.16

Table 3: Batch experiments results, removal was evaluated in respect with an MtBE concentration of 1693 $\mu\text{g/L}$ (blank sample).

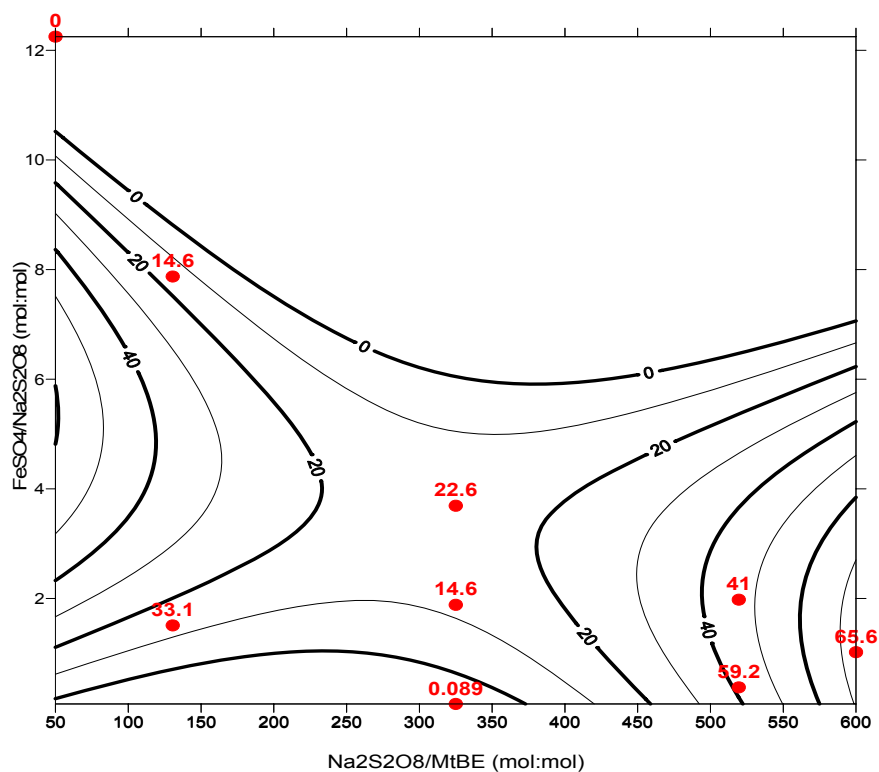


Figure 7: Iso-removal curves generated by SURFER[®] software, and slurry system experimental points.

All experimental results were fitted by a quadratic polynomial regression model, using a proper software (SURFER[®]). The regression analysis of the experimental results provided a quadratic equation (Eq.(7)) relating the removal efficiency (R%) with Na₂S₂O₈:MtBE (x) and FeSO₄:Na₂S₂O₈ (y) molar ratio:

$$R\% = 0.0006x^2 - 1.208y^2 - 0.279x + 13.400y - 0.024xy + 42.45 \quad (7)$$

The curves at constant MtBE removal (iso-removal curves) plotted in the experimental plan, are shown in Figure 7, together with the experimental points. By looking at Figure 7 it can be noted that at constant Fe(II):persulfate molar ratio, if the Na₂S₂O₈:MtBE molar ratio increases until 200:1, the MtBE removal efficiency decreases; on the other hand, for Na₂S₂O₈:MtBE molar ratio as high as 200:1, if the Fe(II):Na₂S₂O₈ molar ratio increases, it can be noted a maximum value of removal efficiency (approximately between Fe(II):Na₂S₂O₈ 1:1 and 5:1); on the contrary, at constant Fe(II):Na₂S₂O₈ molar ratio, if the Na₂S₂O₈:MtBE molar ratio increases between 400:1 and 600:1, the MtBE removal efficiency increases as high as 66%; the MtBE removal efficiency remains approximately the same, instead, by increasing the Fe(II):Na₂S₂O₈ molar ratio within the Na₂S₂O₈:MtBE molar ratio between 400:1. Moreover Figure 7 shows a region where the removal efficiency seems to reach a plateau of approximately 20% (Fe(II):Na₂S₂O₈ = 1:1-6:1; Na₂S₂O₈:MtBE = 200:1-400:1); as already noticed during the aqueous phase experiments, it

should be noted that the best removal efficiency was obtained for a Fe(II):Na₂S₂O₈ molar ratio equal to 1:1 (see the 65.6 point). When there is an excess of ferrous ions, a decrease of the removal efficiency takes place, due to the scavenging effect of the Fe(II) on the sulfate radicals (see Eq.(5)); on the other hand, when there is an excess of persulfate anions, the ferrous ions are unable to activate the excess and so, the oxidation pathway results governed by the persulfate anions and not by the sulfate radicals. By looking at the regression equation (Eq.(7)) it should be noted that the only positive term of the equation apart the constant term and the very small quadratic x^2 term, is the Fe(II):Na₂S₂O₈ linear term (y), which present a higher positive value with respect to others, meaning that Fe(II):Na₂S₂O₈ ratio is the main independent parameter to characterize the oxidation process. On the other hand, it should be noted that the regression model does not fit in a satisfactory way the entire experimental plan: in fact, by looking at the iso-response curves, it should be noted that some of the experimental points do not overlap on the right iso-response curve.

Conclusions

The experimental results obtained for aqueous and soil slurry systems have shown that iron activated persulfate process is feasible for the treatment of an MtBE contaminated groundwater, even if the obtained results suggest that a maximum removal efficiency of approximately 50% could be achieved; this is due substantially to the unproductive pathways generated by the excess either of ferrous ions and persulfate ions which substantially hinder the productive activity of the sulfate radicals. So, next researches should aim to focus on further optimization of the operating conditions involved in the persulfate catalyzed chemistry; a very important parameter should be, with respect to this, the Fe(II):Na₂S₂O₈ molar ratio rather than the Fe(II):MtBE or the Na₂S₂O₈:MtBE molar ratios. The optimization of this parameter should, by consequence, lead to a better understanding also of the mechanisms involved during the Fe(II)-chelate catalyzed persulfate oxidation process.

APPENDIX D

PEROXY-ACID AS AN INNOVATIVE OXIDANT FOR THE REMEDIATION CONTAMINATED SEDIMENTS

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Abstract: The treatment of recalcitrant organic compounds has been so far demonstrated in a number of advanced oxidation processes (AOPs) such as Fenton's reaction, permanganate, persulfate and ozone-driven reactions, even though some drawbacks do exist. Among them, the competition of formed radicals and/or reacting species with natural organic matter, the production of toxic or undesired intermediates and by-products and the instability of radical species lead to an increase of chemicals to be applied. The use of peroxy-acid, which is selective towards dense electron structures such as double, triple and aromatic bonds, could overcome the previous drawbacks. Peroxy-acids are generated by combining hydrogen peroxide with an organic acid (such as propionic or acetic acid). The break-up of peroxy-acid ring leads to the release of hydroxyl cation or even hydroxyl radicals; this process involves also the organic acid re-generation. This work aims to evaluate the feasibility of peroxy-acids as oxidant to remediate PAHs-contaminated sediments. Experiments were carried on a river sediment (A) and a marine sediment (B). Both were spiked at a PAH total concentration of 100 mg/kg, with 50 mg/kg of anthracene and pyrene. In order to evaluate the effect of different operating conditions such as hydrogen peroxide concentration, acetic acid concentration, H₂O₂:CH₃COOH molar ratio on the PAHs removal efficiency, 7g of each sediment were treated for 24 hours in a 50 mL amber glass bottle (batch reactor) by applying a mixture of different amounts of water, hydrogen peroxide and acetic acid (soil:water ≅ 1:4). A series of hydrogen peroxide decomposition experiments was carried out by varying the CH₃COOH:H₂O₂ molar ratio; the hydrogen peroxide lifetime was equal respectively to 26 hours (sediment A) and 45.5 hours (sediment B); the obtained results showed a strong decrease of H₂O₂ concentration in the first 24 hours for sediment A (1.8% Organic Carbon, Total Oxidant Demand (TOD)= 9.6 g/kg), while sediment B showed a quasi-constant value in H₂O₂ concentration during the first 24 hours (0.46 % Organic Carbon, TOD=2.9 g/kg). H₂O₂ decomposition appeared weakly affected by acetic acid content, leading to exclude a catalytic interaction between hydrogen peroxide and acetic acid. A Rotatable Central Composite design (RCC) was then applied for the design of the operating conditions to be tested, allowing to carry out the minimum number of meaningful experiments: namely, H₂O₂ concentration was in the 0.66-3.30 M range, whereas acetic acid was between 1.16-9.34 M. The obtained results confirmed the feasibility of the peroxy-acid towards the PAH removal (up to 99%), even though the

treatment performance seemed to be affected by the number of PAH-aromatic rings. Moreover, the experiments revealed that the presence of an organic acid (such as acetic acid), could enhance PAHs desorption from sediment into aqueous phase, thus enhancing its degradation.

Keywords: Peroxy-acid, sediment, Polycyclic Aromatic Hydrocarbons (PAHs).

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds made of two or more fused benzene rings which are priority pollutants, due to their widespread distribution in every environmental compartment (such as atmosphere, water and soil). They are naturally present in the environment (essentially as product of microbiological synthesis) even though their presence in the environment is mainly due to anthropogenic sources, which include all the combustion processes (such as burning of fossil fuels, coke and aluminium production, cracking of crude petroleum, incineration of industrial and domestic waste), domestic heating, cigarettes and fireplaces ([8],[24],[42],[58]). Their ubiquity leads to consider the environmental impact which can be generated by this group of organic micro-pollutants. Moreover, it is well known that some PAHs exhibit carcinogenic and/or mutagenic properties and are listed by the US Environmental Protection Agency and the European Community as priority pollutants ([8]). Concerning the PAHs chemical-physical properties, whose values for the compounds investigated in this work are summarized in Table 1, it has to be pointed out that especially the most high molecular weight PAHs, are hardly degradable and tend to accumulate especially into sediments, so that lakes, rivers and marine systems are the primary repositories for these pollutants.

PAH	Chemical Formula	Molecular Mass (g/mol)	Melting point (°C)	Boiling point (°C)	Density (g/cm ³)	Solubility (mol/L)	Henry's Constant (LPa/mol)	K _{ow}
Anthracene	C ₁₄ H ₁₀	178.23	217.5	340.0	1.283	2.51*10 ⁻⁷	3.89*10 ³	4.79*10 ⁴
Pyrene	C ₁₆ H ₁₀	202.25	145-148	404.0	1.271	6.92*10 ⁻⁷	1.17*10 ³	1.35*10 ⁵

Table 1: Chemical and physical properties for the PAHs used in this research.

The highly hydrophobic and lipophilic nature of PAHs make them strongly particle-associated in surface and groundwater systems causing sediment (and soil) contamination ([57]). There are various techniques for the degradation of PAHs in contaminated sediments. Some of them are based on thermal treatment, microbiological slurry processes, flotation, wet oxidation or solvent extraction ([42]). While nearly all organic compounds are thermodynamically amenable to transformation via oxidation, most oxidation processes, even those employing oxidants that have

favourable redox potentials (e.g. ozone), exhibit significant kinetic limitations ([25],[26]). The peroxy-organic acid oxidation is a well-known technology (since the 1940s) which was previously applied in the pulping industry during the delignification of wood pulp in order to avoid the degradation of cellulose and hemicellulose fibers. Peroxy-acids are formed by the reaction between organic acids (e.g. acetic, propionic etc.) and hydrogen peroxide. They are relatively selective oxidizing agents, so they can be targeted towards the electron dense structures like aromatic rings, double and triple bonds and ether bonds with no further competing reactions with other organic compounds (like carbohydrates) ([42],[57]). During a peroxy-acid treatment, the formation of the oxidizing agent can be seen as a cyclical process during which hydrogen peroxide reacts with an organic acid (e.g. acetic acid) in solution to form peroxy-acid. The peroxy-acid may react either directly with the target compound, or with water, by regenerating the organic acid and by forming an hydroxyl cation; hydroxyl radical may also be released during the process ([23]); Figure 1 shows a possible reaction mechanism in the case of acetic acid.

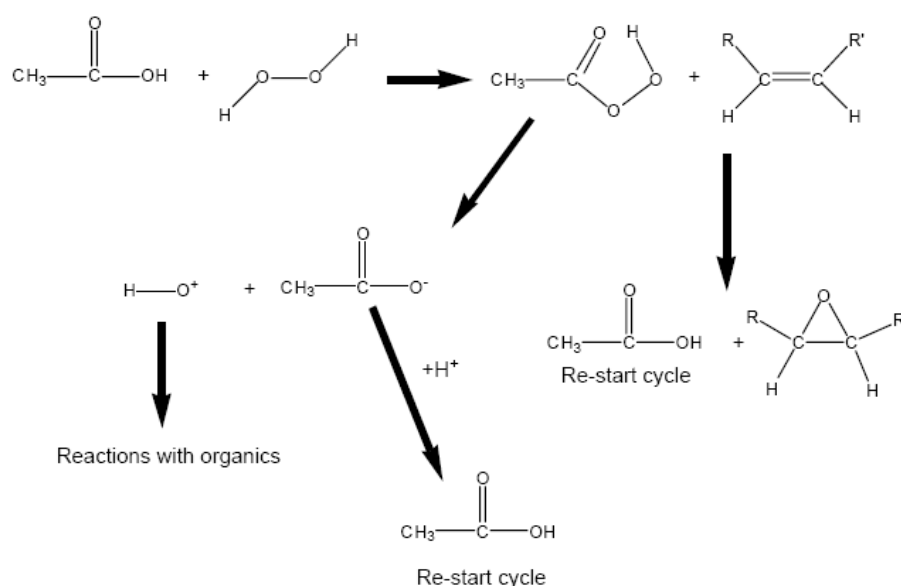


Figure 1: A possible peroxy-acid reaction mechanism in the case of acetic acid.

This research was carried out in order to reach a two-fold objective: first of all, to assess the feasibility of the peroxy-acid oxidation as fast and suitable technique to remediate PAHs-contaminated sediments and then to optimize the main operating conditions involved in the oxidation process (such as hydrogen peroxide concentration, acetic acid concentration, hydrogen peroxide to acetic acid molar ratio and soil:water weight ratio) in order to develop a cost-effective technology and to avoid any useless chemical immission into the environment.

Concerning the optimization of the different operating conditions within the experimental plan a Rotatable Central Composite method was applied, aimed to minimize the number of experiments to be performed; then, a Response Surface Method provided a graphical representation of the experimental results thus facilitating the individuation of the optimum regions within the experimental plan. The experiments were carried out on two different sediments which were properly characterized and then spiked with a mixture of two PAHs of interest (anthracene, pyrene); the total added PAH amount was equal to 100 mg/kg. Perylene was used as internal standard (added to each sample at a concentration of 50 mg/kg) during the analytical step which was carried out by means of a GC-MS technique. As far as the hydrogen peroxide and acetic acid concentrations are concerned, the tested operating conditions varied between 0.2-1 mM and 0.2-0.5 mM. Hydrogen peroxide lifetime in the reaction environment was also monitored by performing some decomposition kinetics.

Experimental

Materials

Anthracene, pyrene, perylene, acetic acid, hydrogen peroxide (30% (wt/wt) solution), sodium sulfite anhydrous, dichloromethane, acetone, sodium sulphate anhydrous were purchased by Sigma-Aldrich (HPLC-grade or ACS-grade). All reagents were used as received. Distilled water was provided by a GFL 2008 generator.

Sediments characterization and spiking procedure

The sediments were collected from two different sites: namely, the first one (named A) was collected from a river while the second one (named B) was a marine sediment. After receipt, both sediments were homogenized by means of a blender and then characterized. The characterization results are summarized in [Table 2](#).

Parameter	Sediment A	Sediment B	Notes
pH	7.85	8.90	---
Moisture content	44.54 %	20.20 %	---
Organic Carbon	1.8 %	0.46%	Walkley-Black method
Organic Matter	3.1 %	0.79 %	
SSF	95 %	99.86 %	Ignition at 550 °C
SSV	5 %	0.14 %	
Mn (mg kg ⁻¹)	191	135	EPA Method 3050B (Extraction)
Fe (mg kg ⁻¹)	12120	8340	
Cu (mg kg ⁻¹)	57	6	
Zn (mg kg ⁻¹)	418	464	
Ni (mg kg ⁻¹)	2680	126	FLAA (Analysis)
Pb (mg kg ⁻¹)	25	27	
Total Oxidant Demand (TOD) (g kg ⁻¹)	9.6 g/kg	2.9 g/kg	According to ([27])

Table 2: Characterization results.

A spiking procedure ([63]), was applied to artificially contaminate the sediments with the selected PAH congeners to get a total concentration of 100 mg/kg and a minimum contamination aging. The tested procedure consisted in spiking 250 g of sediment with 600 µL of a PAH stock solution and 10 mL of acetone. Both sediments were spiked with the PAH stock solution, thoroughly homogenized with a blender, air-dried for 24 hours, covered with aluminium foils and then kept under darkness for a week before being used for the experiments. The PAH stock solution was a mixture of two different PAH congeners (respectively anthracene and pyrene) in a 1:1 solution of dichloromethane:acetone (v/v) with a PAH total concentration of 20 g/L.

Quantification of products

Sample analysis was carried out by means of a GC-MS (Agilent 6890 Network GC System coupled with an Agilent 5973 Network Mass Selective Detector) equipped with a split/splitless programmed temperature injector. The analysis was performed in agreement with the method EPA 8270C. The GC setting parameters are summarized in Table 3.

Carrier	Helium (flowrate 1mL/min)
Column	HP-5MS (30m x 0.25 mm i.d. 0.25 µm)
Split flowrate	20 mL/min
Injector Temperature	250 °C
Oven Temperature	40 °C held 5 min. From 40°C to 290°C at 12 °C/min (held 6 min.) From 290°C to 325°C at 20 °C/min (held 5 min.)
Total time	30.58 min
Injection Volume	1 µL

Table 3: GC-MS setting parameters.

The different congeners were quantified by applying before analysis an internal standard (i.e. perylene) to each sample always in the same amount (50 mg/kg). Calibration curves for each PAH were built (5 data point each one, repeated twice), in order to correlate the ratio between the PAH congener and the internal standard peak area, with their respective concentration ratio. The calibration range for each PAH varied between 50 and 2.5 mg/kg.

Design of the experiments: application of Rotatable Central Composite method (RCC)

In order to minimize the number of experiments to be performed and to guarantee a certain data set statistical significance a Rotatable Central Composite (RCC) method was applied. The central composite design is probably the most widely-used experimental design for fitting a second-order response surface. An experimental design is rotatable if the variance of the predicted response is a function only of the distance of the experimental points from the centre of the design and is not function of direction. Since the location of the optimum is unknown prior to running the experiment, it is useful to apply a design that provides equal precision of estimation in all direction. Performing replicates of the central point allow to improve the model precision ([55]).

RCC method is the combination of a 2 level factorial model (2^N) with a Star model ($2N+1$) so that the minimum number of experiments to be performed (k) is equal to:

$$k = 2^N + 2N + 1 \quad (1)$$

where N in Eq.(1) is the number of independent variables. In this case the RCC method was applied to a system of 2 independent variables (i.e. $[H_2O_2]$ and $[CH_3COOH]$) by considering two levels per variable.

The tested operating conditions, resulting from the RCC approach are reported below in [Table 4](#), and schematically shown in the RCC experimental plan shown in [Figure 2](#) where, the experimental points which refer to factorial design were called F1, F2, F3, F4, whereas those of the Star design S1, S2, S3, S4.

Experimental Points $x_1 = \text{H}_2\text{O}_2$ $x_2 = \text{CH}_3\text{COOH}$	Coded Value		Natural Value	
	x_1	x_2	ξ_1 (mL)	ξ_2 (mL)
O	0	0	6	9
S1	0	-1.41	6	2
S2	-1.41	0	2	9
S3	0	1.41	6	16
S4	1.41	0	10	9
F1	1	1	8.8	14
F2	-1	1	3.2	14
F3	1	-1	8.8	4.1
F4	-1	-1	3.2	4.1

Table 4: RCC tested operating conditions.

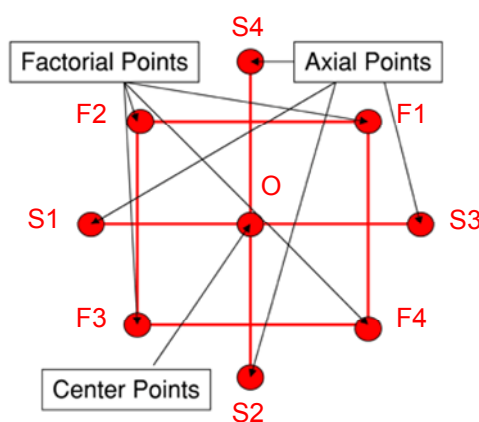


Figure 2: RCC configuration in the experimental plan.

The central point was named O. In order to simplify calculations the independent variables were expressed as coded values: namely, factorial points have values of $(\pm 1, \pm 1)$, Star points were expressed as $(\pm \alpha, 0)$ or $(0, \pm \alpha)$, while the central point had coded values of $(0, 0)$. A central composite design is made Rotatable by the choice of the α value. Its choice depends on the number of points in the factorial part of the design. In fact, as the number of factorial points is known, as the α value can be estimated by applying Eq.(2):

$$\alpha = n_f^{1/4} \quad (2)$$

where n_f is the number of factorial points ([55]). In this study n_f was equal to four points and then Eq.(2) gave a value of 1.41.

PAH oxidation experiments

A sample of 7 g of sediment was put into a 50 mL amber glass bottle with a magnetic bar. Then, in agreement with results of RCC method, different amount of water, acetic acid and hydrogen

peroxide were added to the batch in order to obtain a total volume of 30 mL (soil:water ratio approximately equal to 1:4). At time zero, a single dose of hydrogen peroxide was added by following the dosage indicated by RCC method (see Table 4), thus starting the peroxy-acid oxidation system. During all the experiments, the system was kept at room temperature (approximately 15°C). After 24 hours the oxidation was quenched by adding 6 mL of a 1 M sodium sulphite solution. The samples were left to settle, thus allowing the separation between solid and liquid phase. The liquid phase was removed by means of Pasteur pipettes and then used to measure the pH of each batch sample: the average pH value was equal to 3.30. Then, the solid sample was extracted by means of Soxhlet (sodium sulfate anhydrous was added to remove the excess of water), concentrated by air stripping and then analyzed twice by means of GC-MS. A series of tests was also performed in order to study separately the individual effect of the acetic acid and hydrogen peroxide on the PAHs removal efficiency (data not shown). The effective PAH concentration was evaluated based on blank samples which were made up only by sediment and distilled water.

H₂O₂ decomposition kinetics

Some experiments were performed in order to evaluate the hydrogen peroxide lifetime in the reaction environment. The experimental points were selected based on their CH₃COOH:H₂O₂ stoichiometric amount (high, medium and low – see Table 5) and then compared to a control which was obtained by adding only hydrogen peroxide. The decomposition kinetics were obtained by evaluating the residual hydrogen peroxide concentration in each sample after 1, 5, 10, 30 minutes and 1, 2, 6, 24 and 48 hours of reaction. Iodometric titration was applied to evaluate the residual hydrogen peroxide concentration.

Experimental Point	CH ₃ COOH (mL)	H ₂ O ₂ (mL)	Volume ratio	[CH ₃ COOH] (mol)	[H ₂ O ₂] (mol)	Stoichiometric ratio
S2	9	2	≈4:1	5.24	0.66	7.94
F2	4.10	8.8	≈1:2	2.33	2.90	0.80
S4	9	10	≈1:1	5.24	3.30	1.59
Only H ₂ O ₂	0	30	0	0	3.30	0

Table 5: Experiments for determining the H₂O₂ lifetime in the reaction environment.

Results and discussion

Hydrogen peroxide decomposition kinetics

The results of hydrogen peroxide decomposition kinetics for each sediment, are reported respectively in Figure 3-Figure 6. In particular, Figure 4 and Figure 6 show the experimental data

relative to the comparison between two different samples with the same initial hydrogen peroxide concentration ($[\text{H}_2\text{O}_2]_{t=0} = 3.30 \text{ M}$), with and without acetic acid. Concerning sediment A (Figure 3 and Figure 4) hydrogen peroxide concentration decreases sharply to below 2% within the first 24 hours of reaction. This is likely due to the high organic matter content present in the sediment A (TOC = 1.8% and TOD = 9.6 g kg^{-1}). Moreover, the presence of high metal content, and of an organic acid, could probably enhance the metal dissolution phenomena, which could further enhance the catalytic decomposition of hydrogen peroxide. This phenomenon is less present in sediment B (Figure 5 and Figure 6) due to its lower organic matter (TOC = 0.46% and TOD = 2.9 g kg^{-1}) and metal content. Due to their different features, the two sediments reacted differently with hydrogen peroxide, leading to a different H_2O_2 lifetime in the reaction environment. During the experiments, the $T_{10\%}$ parameter was defined as the time after which the residual hydrogen peroxide concentration was equal to 10% of that initially introduced into the system: namely, sediment A presented a $T_{10\%}$ equal to approximately 26 hours, while in the case of sediment B it was equal to 46 hours.

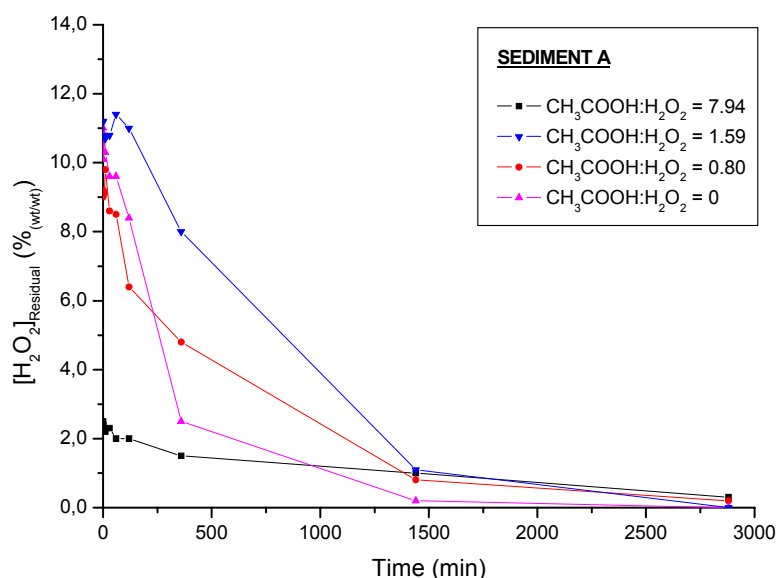


Figure 3: Results of hydrogen peroxide decomposition kinetics – Sediment A.

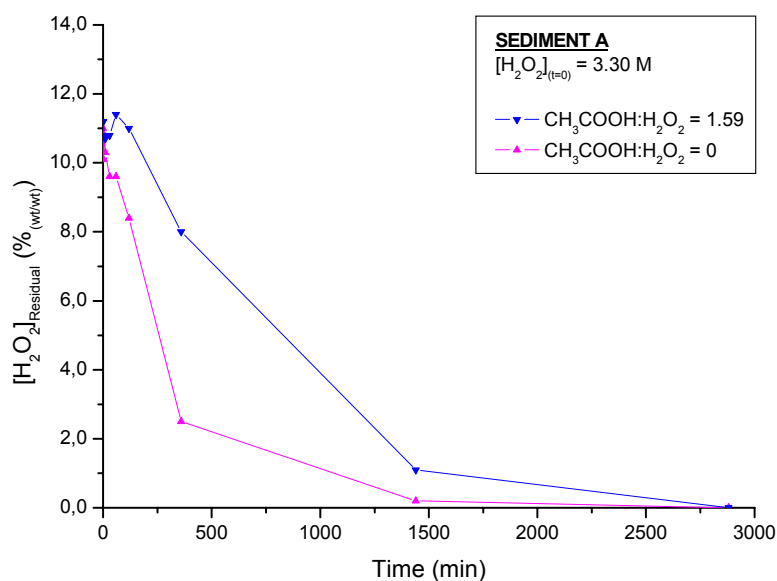


Figure 4: Results of hydrogen peroxide decomposition kinetics – Comparison between two samples with the same hydrogen peroxide concentration ($[H_2O_2]_{t=0} = 3.30 \text{ M}$).

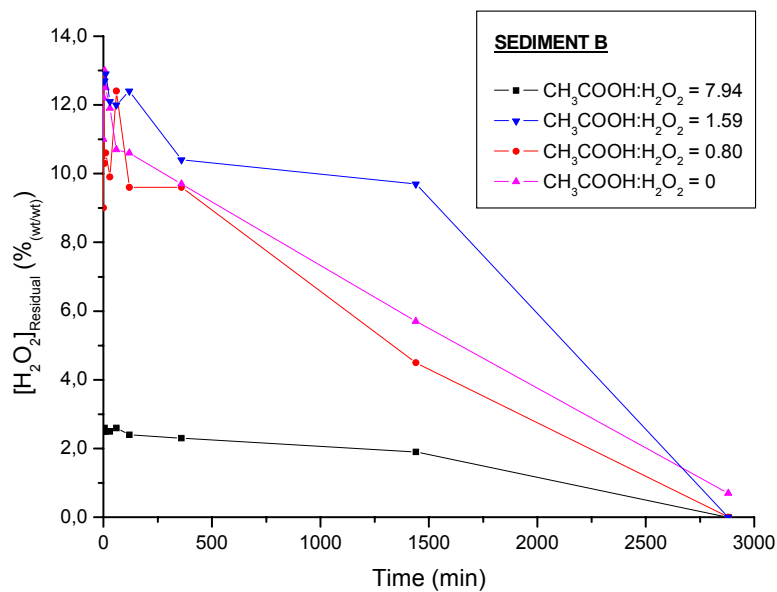


Figure 5: Results of hydrogen peroxide decomposition kinetics – Sediment B.

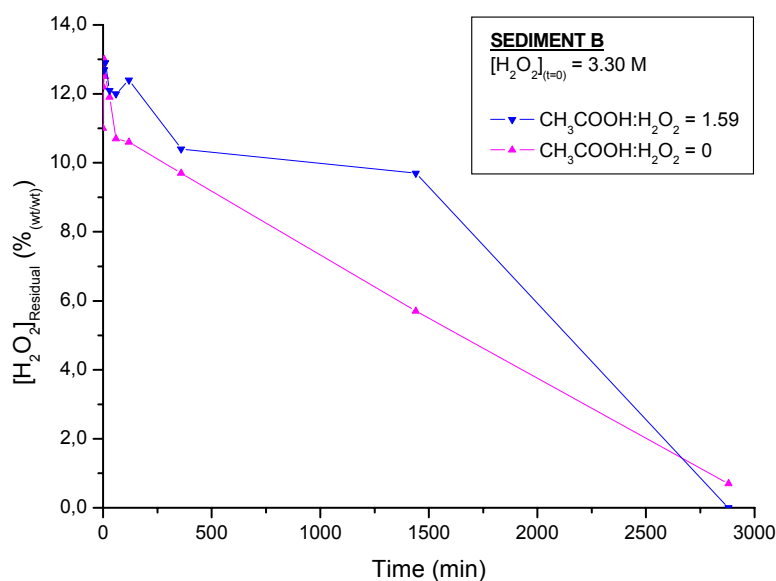


Figure 6: Results of hydrogen peroxide decomposition kinetics – Comparison between two samples with the same hydrogen peroxide concentration ($[H_2O_2]_{t=0} = 3.30$ M).

Concerning the data showed in Figure 4 and Figure 6 it can be noticed that the presence of acetic acid leads to an increase of the residual hydrogen peroxide concentration. This phenomenon could be due to the correlation between hydrogen peroxide decomposition kinetics and the pH value. This effect is particularly evident in sediment B (Figure 6) where, the presence of acetic acid allows to keep the hydrogen peroxide approximately constant for a long-time period (24 hours). Looking at the obtained results, it can be concluded that the application of peroxy-acid favour the slow release of the oxidant species, allowing to make available the applied hydrogen peroxide for a long time period, which is clearly favourable for a chemical oxidation application.

PAHs removal experiments

Sediment A

Figure 7 shows the PAHs removal efficiency versus the CH₃COOH:H₂O₂ molar ratio. It can be noticed that the PAHs removal efficiency reaches a maximum for a CH₃COOH:H₂O₂ molar ratio of 3, with a PAHs removal efficiency between 90% and 95%. This results are in agreement with other researches ([58]) where the maximum PAHs removal efficiency was obtained for CH₃COOH:H₂O₂ between 2.5-3. Moreover, it has been found ([21]) that the maximum peroxyacetic acid production efficiency was obtained with CH₃COOH:H₂O₂ of approximately

2.5 The PAHs removal efficiency seems to be influenced by the number of PAHs aromatic ring: in fact, the higher is the number of aromatic rings, the lower is the removal efficiency; pyrene, which has 4 aromatic rings, shows the lower removal efficiency with respect to anthracene.

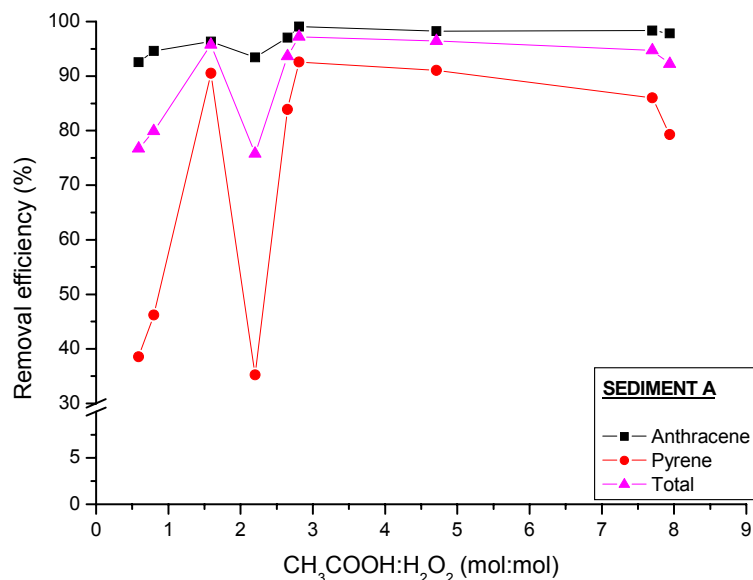
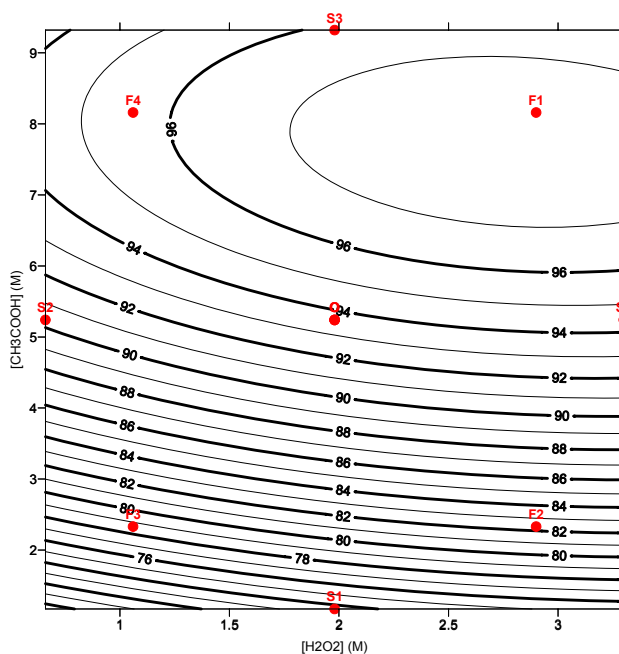


Figure 7: PAHs removal efficiency versus CH₃COOH:H₂O₂ molar ratio – Sediment A.



$$(R\%)_{\text{TOTAL}} = -0.7(\text{H}_2\text{O}_2)^2 - 0.5(\text{CH}_3\text{COOH})^2 - 0.2(\text{H}_2\text{O}_2)(\text{CH}_3\text{COOH}) + 5.2(\text{H}_2\text{O}_2) + 8.6(\text{CH}_3\text{COOH}) + 57.1$$

$$r^2 = 0.76$$

Figure 8: Iso-removal curves for the peroxyacid treatment of Sediment A.

Looking at Figure 8 which shows the iso-removal curves for the peroxy-acid treatment on sediment A, it can be noticed that, while the PAHs removal efficiency looks affected by the acetic acid concentration (PAHs removal efficiency increases linearly with acetic acid concentration), it was substantially unaffected by the hydrogen peroxide concentration (the curves look parallel to $[H_2O_2]$ axis). The PAHs removal efficiency seems to be reasonably well described ($r^2 = 0.76$) by the interpolation model.

Sediment B

Also in the case of sediment B the removal efficiency reaches a maximum value of approximately 95% in correspondence of $CH_3COOH:H_2O_2$ molar ratio of 3 (Figure 9). The PAHs removal efficiency exhibits a constant value within the $CH_3COOH:H_2O_2$ molar ratio between 3 and 8. Anthracene shows the highest removal efficiencies, while the behaviour of the two tested PAHs looks the same with respect to $CH_3COOH:H_2O_2$ molar ratio: the two trends presented the same shape, with pyrene which looks simply shifted down with respect to anthracene.

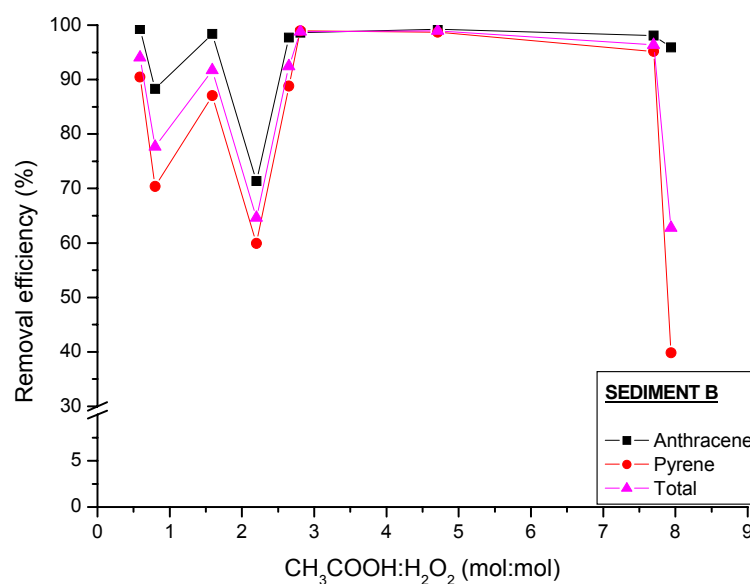
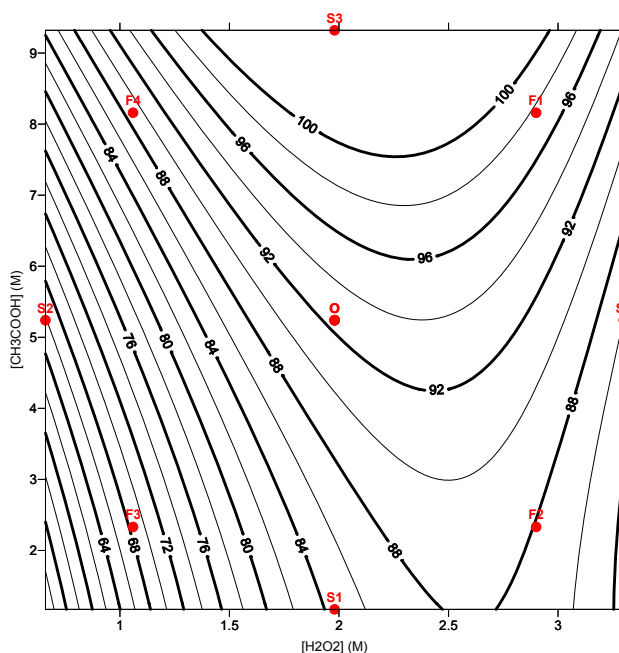


Figure 9: PAHs removal efficiency versus $CH_3COOH:H_2O_2$ molar ratio – Sediment B.



$$(R\%)_{\text{TOTAL}} = -9.5(\text{H}_2\text{O}_2)^2 + 0.16(\text{CH}_3\text{COOH})^2 - (\text{H}_2\text{O}_2)(\text{CH}_3\text{COOH}) + 50.5(\text{H}_2\text{O}_2) + 2.9(\text{CH}_3\text{COOH}) + 20.5$$

$$r^2 = 0.50$$

Figure 10: Iso-removal curves for the peroxy-acid treatment of Sediment B.

Looking at [Figure 10](#) which shows the iso-removal curves for the peroxy-acid treatment of sediment B, it can be noticed that, contrarily on what evidenced for sediment A, in this case the hydrogen peroxide concentration seems to play a crucial role in the PAHs removal process. Also in this case, the PAHs removal treatment, behaves as a first order phenomenon, even though the experimental data don't fit so good with the predicted model ($r^2 = 0.50$). The acetic acid concentration seems to play an important role only in the case of hydrogen peroxide concentrations between 2 M and 3 M. For the other tested hydrogen peroxide concentrations no specific influence on PAHs removal efficiency was observed.

Conclusions

This work aimed to assess the applicability of peroxy-acid as innovative and feasible technology to remediate PAHs-contaminated sediments. A comparison in terms of hydrogen peroxide decomposition kinetic and PAHs removal efficiency was performed between two different type of sediments (i.e. Sediment A – river sediment and Sediment B – marine sediment). Within the tested operating conditions ($[\text{H}_2\text{O}_2] = 0.66\text{-}3.30$ M, $[\text{CH}_3\text{COOH}] = 1.16\text{-}9.34$ M), the results confirmed the feasibility of this technology to remediate contaminated sediments. The obtained data were sensible and repeatable, and the applied optimized procedure led to a better

understanding of the role played by several parameters such as $[H_2O_2]$, $[CH_3COOH]$, $H_2O_2:CH_3COOH$ molar ratio, soil:water weight ratio on the PAHs removal efficiency. The hydrogen peroxide decomposition kinetics allowed to point out the role played by acetic acid in the stabilization of hydrogen peroxide. Further research should deal with optimization of the peroxy-acid treatment, in order to minimize the amount of applied chemicals and consequently to reduce possible side-effects such as soil acidification and metal mobilization. These improvements may allow to apply the process based on peroxy-acid either as on-site or as in-situ remediation technology.

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