



## Performance of different oxidants in the presence of oxisol: Remediation of groundwater contaminated by gasoline/ethanol blend



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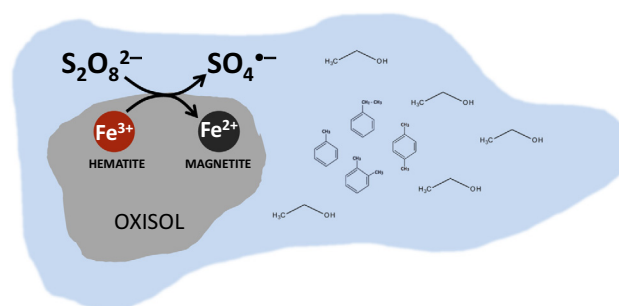
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### HIGHLIGHTS

- ISCO was tested with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, CaO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> catalyzed by iron in oxisol.
- Ethanol-blended gasoline intensifies the hazards due to high TOC and BTEX content.
- Oxidants in the presence of natural iron in oxisol lead to radical production.
- Intermediates formation suggest different remediation pathways for the oxidants.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>2</sub>O<sub>2</sub>, and CaO<sub>2</sub> were tested for the remediation of groundwater contaminated by a gasoline/ethanol blend. In fuel spills, groundwater acquires high organic carbon content and a considerable amount of BTEX (benzene, toluene, ethylbenzene, xylene), and can be treated using *In Situ* Chemical Oxidation. Batch tests were conducted to select the best oxidant, which establishes, in the presence of oxisol (soil rich in iron), the proper conditions for the generation of radicals. The results indicated that the H<sub>2</sub>O<sub>2</sub> added was scavenged in the process and that CaO<sub>2</sub>, which releases H<sub>2</sub>O<sub>2</sub> slowly, achieved the best removal results. However, this compound has low solubility, forms precipitates and increases pH to 12. Therefore, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was selected instead, once it achieved good removal results, worked at low pH values and had slow kinetics, making it suitable for groundwater remediation. Tests revealed that the concentration of iron in a ferriferous oxisol promotes proper oxidant activation, achieving 99% BTEX removal and 45% COD removal. GC–MS analysis of the oxidized samples showed the formation of intermediates (e.g. acetic acid and 1-acetic anhydride with formic acid) indicating the pathway of remediation. Despite such remarkable results, soil control sample achieved considerable DOC removal, suggesting that the use of ISCO may speed the remediation process, but the soil itself has a mechanism to degrade this kind of organic matter.

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## 1. Introduction

Groundwater has been increasingly used to supply drinking water, since the availability and quality of surface water resources

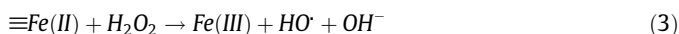
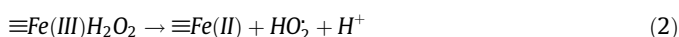
are significantly decreasing. There is, therefore, increased concern regarding the regulation of activities that affect the soil and groundwater.

Transportation, storage, and distribution of fuels deserve attention in this regard. In Europe, leakage from gas station tanks is the cause of 15% of registered contaminated sites [1]. In Canada, 11% of the annual oil spill accidents are caused by gasoline and 25% are due to diesel spills [2]. According to the American Environmental Protection Agency (EPA) benzene, toluene, ethylbenzene and xylene (BTEX), fuels and volatile organic compounds (VOCs) are found at almost 70% of the contaminated sites [3].

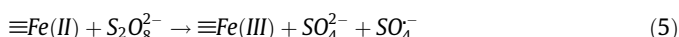
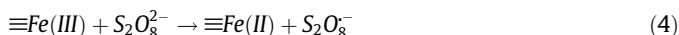
Several techniques are being studied for the remediation of groundwater (e.g. Permeable Adsorbing Barrier (PAB) [4–6], bioremediation) and *In Situ* Chemical Oxidation (ISCO) can be highlighted as a growing technique on the remediation market. ISCO introduces oxidants into the soil, causing a reaction between the oxidants and the contaminants [7]. The major oxidants used in ISCO are sodium persulfate, potassium persulfate, sodium permanganate, hydrogen peroxide and ozone [7], or a mix of these oxidants [8]. These chemicals, when dissolved in water, release chemical species with a high oxidizing power. These oxidants may be activated by heat sources [9–11], ultrasonic field [12], microwave [13], presence of metals or by chelation [14] or pH changes, which result in the formation of radicals ( $\text{SO}_4^{\cdot-}$ ,  $\text{HO}^{\cdot}$ ,  $\text{O}_2^{\cdot-}$ ,  $\text{HO}_2^{\cdot}$ ) with high reduction potentials [15].

The use of oxidant-releasing materials as the active components of a well-based permeable reactive barrier (PRB) has also been studied to evaluate their efficiency in the oxidation of methyl *tert*-butyl ether (MTBE) and benzene. The results indicated that approximately 86–92% of MTBE and 95–99% of benzene could be removed [16]. ISCO treatment has been used to degrade BTEX [17] and MTBE by using permanganate, percarbonate [18], persulfate and hydrogen peroxide [19], including activation by Fe(II) salts [20] or naturally occurring iron minerals in a Fenton-like process, in both pilot-scale [21] and large-scale applications [22].

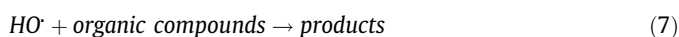
The mechanism of heterogeneous Fenton-like process in the presence of iron based compounds (mineral), is given by Eqs. (1)–(3), where  $\equiv\text{Fe}$  is a surface iron species [23].



$\equiv\text{Fe(III)}$  in Eq. (1) is regenerated through Eq. (3) and it has been suggested that the adsorption of hydrogen peroxide (Eq. (1)) is much faster than the other reactions [23,24]. The reactions between persulfate and  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  are expressed in Eqs. (4)–(6) [25,26].



The hydroxyl radicals ( $\text{HO}^{\cdot}$ ) formed in Eqs. (3) and (6) can oxidize organic compounds (Eq. (7)) or they can react with  $\text{H}_2\text{O}_2$  (Eq. (8)) or  $\text{S}_2\text{O}_8^{2-}$  (Eq. (9)) [27] in the liquid phase to form hydroperoxyl radicals or sulfate radicals that react with organic compounds at lower rates.



A majority of the studies focus on the catalytic potential of iron-oxide minerals in the oxidation of organic pollutants and used goethite [23,27–32], hematite [28–30,32,33], ferrihydrite [27–29], pyrite [30] [29], lepidocrocite [29], magnetite [29,30,33–37] and composites. Among them, the application of magnetite ( $\text{Fe}_3\text{O}_4$ ) as a catalyst in heterogeneous Fenton oxidation is gaining considerable attention because magnetite contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species, which, according to Eqs. (2) and (3), should have a positive effect on the catalytic activity.

Even being used on real sites, studies on the use of ISCO for the remediation of soil contaminated with fuel continue to be scarce. Besides that, the majority of studies uses BTEX to simulate fuel contaminants, and real fuel samples can influence on the characteristics of the contamination plume. Several countries have encouraged the blending of biofuels, such as ethanol, with gasoline in order to improve air quality and substitute harmful compounds used to boost octane ratings, such as tetraethyl lead (TEL) and MTBE. A progressive increase of ethanol in gasoline has been observed in the United States, reaching a maximum of 15% ethanol in gasoline [3,38]. In Brazil, this percentage is constantly changing, with variations ranging from 20% to 27%.

The addition of ethanol to gasoline requires attention, since changing the physical properties of the fuel modifies its behavior in the environment, generating positive and negative impacts. Regarding groundwater contamination, blending ethanol with gasoline can increase the solubility of the fuel, leading to an increased spread of downward contamination and an increase in the solubility of BTEX, which normally have low solubility in water [40–42].

The application of ISCO is growing on contaminated sites with high ethanol content (i.e. Brazil) and this study aims to clarify the mechanisms involved on the degradation of contaminants. Various oxidants were tested and this study is a preliminary investigation to define of a proper oxidant, and to clarify the interaction of the oxidant with iron present in an oxisol.

## 2. Material and methods

The experiments were carried out using “Latossolo Ferrífero” (ferriferous oxisol) samples and natural groundwater, both from the region of Minas Gerais, Brazil (Latitude: 20° 4' 48" S, Longitude: 43° 57' 36" W). Soil samples were collected at a depth of 0.7 m (in C Horizon), sieved (10 mesh) and analyzed for physical, chemical and mineralogical characterization, texture, cation exchange-capacity (CEC), total and effective Al and saturation of bases, organic matter content, concentration of remaining phosphorus and the availability of micronutrients, using the Mehlich extractor [43]. The method used to determine the total concentration of heavy metals was the 3051 method [44], while the elements were determined in an acidic solution by atomic absorption spectrometry using flame (FAAS) or graphite furnace (GFAAS).

The contaminated plume was prepared by dissolving 10% (v/v) of a commercial gasoline/ethanol blend (Brazil) in natural groundwater. This mixture was agitated for 5 min in closed bottles on a shaker, at 150 rpm and 25 ± 2 °C. After agitation, the samples were separated by gravimetric funnel separation and the soluble fraction of groundwater was collected and identified as “contaminated groundwater.”

Adsorption tests were conducted in closed flasks using 2 g of the soil in 7 mL of contaminated groundwater at different concentrations (0, 857, 1714, 5143, 6000, 6857, 8571 mg L<sup>-1</sup> DOC). The flasks were maintained in dark conditions in a shaker, at 150 rpm and 25 ± 2 °C, for 8 h. At the end of the experiment, the dissolved organic carbon (DOC; TOC-V CPN, Shimadzu) was measured on the samples (filtered through a 0.45 μm nitrocellulose membrane).

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