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In situ chemical oxidation of BTEX and MTBE by ferrate: pH dependence and stability

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HIGHLIGHTS

- BTEX and MtBE are some of the most common and serious hazards to groundwater reservoirs.
- ISCO has high cost-effectiveness for soil remediation and contaminated groundwater.
- Ferrate is an oxyanion with high oxidation power and does not generate hazardous waste.
- BTEX are degraded between pH 7 and 9 within the range of greatest stability of ferrate.
- MtBE is recalcitrant to degradation by ferrate.

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ABSTRACT

Gasoline spills from underground storage tanks are a worldwide environmental problem. BTEX and MtBE are the compounds of gasoline that present the highest degree of migration due to their chemical properties, and are therefore able to impact groundwater reservoirs. In situ chemical oxidation (ISCO) is an emerging technology for groundwater remediation. Several compounds such as permanganate and hydrogen peroxide among others have been used as oxidants, a strong impact of pH on the relative stabilities and reduction potentials having been in each case determined. This paper presents a study of stability and degradation of BTEX and MtBE at different pH ranges of a novel oxidant for ISCO, potassium ferrate (K_2FeO_4). To carry out this study, BTEX and MtBE solutions were prepared in different phosphate buffers (pH 5,8; 7; 9; 10 and 11) in concentration ratio of $(FeO_4{}^{-2})/(BTEX + MtBE) = 100:1$. Each solution was analyzed at different times by gas chromatography with photoionization and tandem mass spectrometer detector. The results show a higher degree of degradation at pH 7 for Benzene and Toluene, and at pH 9 for Ethyl benzene and Xylenes, while MtBE proved recalcitrant to degradation by ferrate. The most favorable pH for stability of $FeO_4{}^{-2}$ solution was confirmed in 9–10.

1. Introduction

Petroleum hydrocarbon spills are a common source of groundwater contamination where the remediation of aquifers has always been presented as a difficult, expensive and slow process. Furthermore, in populations that are far from major courses of surface water or lakes, groundwater is the only source of water supply [1]. A study carried out between 1999 and 2000 by the United States Geological Survey (USGS) and sponsored by the American Water Work Association Research Foundation (AWWARF) reported that of 954 sources of drinking water analyzed and randomly selected in 50 states of the USA, 8.9% presented Methyl *tert*-Butyl Ether (MtBE) in concentrations ranging from 0.2 to 20 micrograms per liter (μg/L) [2]. MtBE is an unregulated drinking water contaminant for Environmental Protection Agency of United States (US-EPA), although its Maximum Contaminant Levels (MCL), set by California Department of Public Health (CDPH), are 13 μg/L (primary MCL) and 5 μg/L (secondary MCL) [3]. In turn, US-EPA estimates that 35% of underground storage tanks for petroleum hydrocarbons have losses, which corresponds to 2 million tanks, of which 40% has resulted in the contamination of groundwater [4,5]. The last report of the US-EPA Office of Underground Storage Tanks (USTs) about performance measures conducted between October 1, 2014 and September 30, 2015 informs that of 94,287 on-site inspections there were 6830 confirmed releases. At the present time, US-EPA's

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Table 1
pH of working solutions.

	Initial pH	Final pH (40 days)
Buffer solution pH 5.8 blank	5.80	5.77
Buffer solution pH 5.8 with ferrate	5.80	5.87
Buffer solution pH 7 blank	7.00	6.98
Buffer solution pH 7 with ferrate	7.00	7.03
Buffer solution pH 8 blank	8.00	8.00
Buffer solution pH 8 with ferrate	8.00	8.16
Buffer solution pH 9 blank	9.00	9.01
Buffer solution pH 9 with ferrate	9.00	9.46
Buffer solution pH 10 blank	10.00	9.90
Buffer solution pH 10 with ferrate	10.00	10.55
Buffer solution pH 11 blank	11.00	11.24
Buffer solution pH 11 with ferrate	11.00	11.34

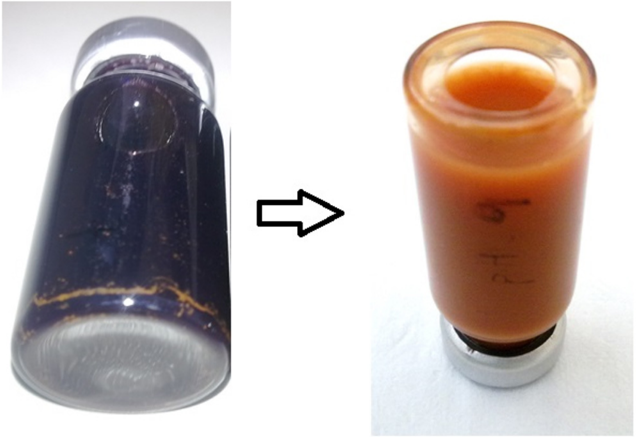

Fig. 1. O_2 generation during $FeO_4{}^{-2}$ decomposition with vial explosion to release pressure at the end.

UST program includes approximately 204,000 sites with 565,956 active tanks and 528,521 releases reported since the beginning of the UST program in 1984 [6]. In Argentina there is no statistical data freely accessible associated with these events; however, of 284 USTs tested during 2008–2009 period in the province of Córdoba, Argentina, 12% did not pass the leakage tests with possible impact on the vadose zone or groundwater [7].

In sites contaminated by leaks or spills of hydrocarbons such as gasoline or diesel, it is common to find that compounds with higher migration in the unsaturated media and even reaching the adjacent water layer are monoaromatic organic compounds. This is so because these chemicals have low adsorptivity on the soil and high solubility in water compared with aliphatic compounds that constitute the majority of a fuel. Among these aromatic compounds a family of great environmental importance is BTEX, which is an acronym for Benzene, Toluene, Ethyl benzene and all isomers of Xylene (ortho, para and meta).

BTEX have attracted much attention in recent years because they are one of the most common and serious threats to groundwater reservoirs as well as to the confined environments that are set up in sites contaminated with hydrocarbons [8,9].However, combined results from four studies encompassing 604 sites showed that approximately 75% of petroleum hydrocarbon plumes are below 61 m. On the other hand, BTEX plumes (width and length) are much smaller than other types of plumes (e.g., chlorinated ethene plumes, chlorinated solvent plumes, chloride salt water plumes) [10]. From the point of view of environmental risk, the most important chemical compound is Benzene because it is highly mobile in soil and groundwater due to its low K_{oc} and high solubility, and has been classified as a carcinogen by the US-EPA [11] and the International Agency for Research on Cancer (IARC) [12]. In drinking water, the potential effects on health from long-term exposure above 0.005 mg/L are anemia, decrease in blood platelets and increased risk of cancer [13].

Another organic compound that has even greater solubility in water than BTEX and that is also very persistent in the environment is MtBE [14,15], used since the early 90's as a gasoline octane enhancer in replacement of tetraethyl lead. Under normal conditions of aquifer, MtBE is generally resistant to biodegradation, although some bacteria can adapt to its degradation; therefore the application of active remediation technologies is necessary to decrease their concentration to acceptable risk levels to human health [16,17]. The US-EPA classified MtBE as a potential carcinogen for humans exposed to high concentrations [18] but currently such classification has been removed and it is presented as "under study", while the IARC considers it as not classifiable as carcinogenic for humans [19].

BTEX are considered in the standards for water quality in Argentina through the National Law N° 24051, Regulatory Decree 831/93, Table 1: Guide Levels of Quality of Water as Source of Drinking Water, which establishes the following guide levels: Benzene (10 µg L^{-1}), Toluene (1000 µg L^{-1}), Ethyl benzene (700 µg L^{-1}) and total Xylenes (10000 µg L^{-1}) [20].

In 1997, US-EPA established for MtBE a draft lifetime health advisory limit based on criteria of taste and odor in drinking water, in that concentrations in the range of 20–40 µg L^{-1} or lower probably do not cause odors and flavors, acknowledging that the sensitivity of different people may vary [18].

Initially, most mechanisms of groundwater remediation with organic contaminants were based on the application of Pump and Treat (P&T) technology [21]. Between 1982 and 1992, 73% of the cleanups at Superfund sites with contaminated groundwater specified the use of P&T technology [4]. This method consists in treating contaminated groundwater extracted from impacted saturated media on the surface. Usually, activated carbon is used as a treatment system where organic compounds are adsorbed [22].This method has the drawback of having high operating costs due to energy consumption required for continuous pumping for long periods of time, the required constant presence of qualified staff to control the system, and the generation of hazardous waste (activated carbon saturated with organic compounds). Like any method of on-site or active treatment, it also causes disturbances associated with the extraction of water to be treated on the surface, and has drawbacks associated with the disposal of wastewater in those places where reinjection of treated water into the aquifer is not allowed (Figs. 1 and 2).

Over time, studies undertaken by the US-EPA showed that P&T technologies commonly used for the treatment of contaminated groundwater rarely restore this medium to baseline conditions [21]. Furthermore, few places in the USA have been remediated to regulatory levels using P&T, which is why the effectiveness of this technology is being questioned [23].

In the last 10 years, in situ technologies have gained popularity due to their higher efficiency compared with P&T systems [24]. In situ chemical oxidation (ISCO) is an emerging technology with the best cost-effectiveness ratio for the remediation of soil and contaminated groundwater. ISCO consists in the introduction of chemicals into the subsurface in order to destroy contaminants in the vadose zone and the saturated zone and thus to reduce the potential risk to human health and environment. Chemicals oxidants currently used are: hydrogen peroxide (H_2O_2), sodium or potassium permanganate ($NaMnO_4$ or $KMnO_4$), sodium persulfate (NaS_2O_8) and ozone (O_3) [25–27].

Most ISCO projects involve the concurrent use of other in situ remediation technologies, such as soil vapor extraction in the vadose zone and ISCO in the saturated zone [28].

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