



Sodium hypochlorite oxidation of petroleum aliphatic contaminants in calcareous soils



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HIGHLIGHTS

- Ex-situ NaClO oxidation of C10–C50 soil contaminants.
- NaClO oxidation yield is boosted by CO₂ absorption.
- Oxidation mechanism might involve transition metals.
- Constant specific NaClO consumption over the entire decontamination range.

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ABSTRACT

This research project investigated the sodium hypochlorite (NaClO) oxidation of aliphatic petroleum contaminants (C10–C50) in a calcareous soil (average 5473 ppm C10–C50, 15 wt% Ca), which had been excavated from a contaminated industrial site. The decontamination objective was to lower the C10–C50 concentration to 700 ppm. CO₂ acidity was used in the project to boost the NaClO oxidation yield and seems to have played a role in desorbing the natural organic matter. The experimental conditions were a 2- to 16-h reaction time, at room temperature, with a 1 to 12.5 wt% NaClO oxidative solution and a fixed 2:1 solution-to-soil ratio. With a 3 wt% NaClO solution and with a CO₂ overhead, the NaClO dosage requirement was maintained below 60 g NaClO/g of oxidized C10–C50 over the entire decontamination range. The strong chlorine smell remaining after the reaction was completed suggests that part of the NaClO requirement can be recycled. Except traces of chloroform, there were no regulation-listed organochloride contaminants detected on either the treated soil samples or leachates and the total count of chlorinated compounds in treated soil samples was below the detection limit of 250 mg/kg. The NaClO oxidation mechanism on aliphatic substrates might be triggered by transition metals, such as manganese, but no attempt has been made to investigate the oxidation mechanism. Further investigations would include a constant-fed NaClO system and other techniques to lower the required NaClO dosage.

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1. Introduction

Industrial activities are susceptible to contaminate the soil surrounding its operating sites. This soil has to be decontaminated when the industrial activities cease. This decontamination effort has a high cost and thus many former industrial sites are left contaminated. This contamination poses a burden to further develop these sites most often located on valuable real estates. Every major urban center in North America faces this situation. As an example, 350 M\$ would be required to decontaminate the

amount of unused industrial sites in the east island of Montreal estimated to 8.5 million square meters (CEM, 2013). There is therefore a high incentive to develop an economical process to decontaminate these sites.

Commercial-scale soil remediation of petroleum-based compounds is most often performed in soil piles and the remediation treatment is either biological or chemical oxidation. The soil piles suffer certain disadvantages in spite of their simplicity. First, the efficiency of the pile treatment is strongly dependent on the soil permeability. For this reason, a clay or loamy soil is much harder to decontaminate than a sandy soil. Other disadvantages are the large land area required to place the soil piles, the constant monitoring of humidity, biological activity and temperature. These disadvantages add to the extended time required to complete the reaction.

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Moreover, soil treatment could be more economical in a permanent treatment center rather than on the contaminated site (Toffoletto et al., 2005). Based on these considerations, there is an opportunity to develop a decontamination process that would speed up the remediation of petroleum-contaminated soils.

Almost all reported works on soil contaminant oxidation use the following strong oxidants: H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$, KMnO_4 and O_3 . H_2O_2 is used in Fenton and Fenton-like oxidation reactions. These reactions require soluble Fe to be activated and therefore the reaction rate is minimal at pH 8 (Buragohain et al., 2013) due to the low Fe solubility. $\text{Na}_2\text{S}_2\text{O}_8$ shows a very low oxidation yield and is particularly inefficient to oxidize n-alkanes (Yen et al., 2011; Usman et al., 2012). Furthermore, the free hydroxyl radicals generated by H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$ oxidation mechanisms are neutralized by the soil carbonates found in calcareous soils. In the case of O_3 , reported experiments are most often run dry and thus the impact of the natural soil humidity is not taken into account (Li et al., 2014). Few of these published works specifically report C10–C50 oxidation with a particular emphasis on C25–C50, which are not diesel contaminants. Moreover, few published results targeted a contamination level suitable for soil reuse (usually 700 TPH mg/kg or less).

NaClO is a relatively weak oxidant and most often has been neglected in the literature on soil remediation. The literature on the NaClO oxidation of petroleum contaminants is therefore scarce and basically reports that this avenue does not provide good results (Renneberg and Dudas, 2002; Ferguson et al., 2004). A few reasons explain why NaClO didn't attract more interest. First, there is the risk of synthesizing organochlorides from the petroleum contaminants that are more tightly controlled than petroleum contaminants. Second, NaClO solutions causes an odor nuisance due to the hypochlorous acid (HClO) desorption that would necessitate an odor abatement device in a field practice. Third, a liquid waste stream is generated from the NaClO oxidation of soil contaminants. This liquid stream would have to be neutralized or reused in a field practice. There are advantages to use NaClO in a field practice. First of all, NaClO is a low cost oxidant less expensive than KMnO_4 solutions. Also, diluted NaClO solutions can be synthesized on-site from an affordable NaCl supply with a commercial electrolytic kit. These advantages have to be weighed against the above-listed disadvantages and uncertainties.

The objective of the article is to present a NaClO-based oxidation process to treat soils contaminated with petroleum aliphatic compounds (C10–C50). The article is organized to provide experimental data on the NaClO oxidative reaction and possible strategies to improve its reaction yield. These strategies are the use of CO_2 -assisted oxidation, a soil pre-treatment consisting in neutralizing the soil with lime prior to oxidation and multiple-batch oxidation. The NaClO instability over time and the ageing of the soil sample are addressed in this research project.

2. Theoretical background

2.1. Interference of Ca in the oxidation of soil content

A pH neutral soil with a high Ca content limits the oxidation reaction of strong oxidants. First, naturally occurring carbonates in neutral soils interfere with the hydroxyl radicals that are generated by the H_2O_2 mechanism. $\text{Na}_2\text{S}_2\text{O}_8$ also follows a radical oxidation mechanism and are reported less efficient to oxidize petroleum contaminants in Ca- or Na-rich reaction media (Liang and Guo, 2012). The Ca content also constitutes preferential adsorption sites for hydrocarbon contaminants that would become occluded and thus be less accessible to biodegradation (Besalatpour et al., 2010). Based on these reported results, a high Ca content means a higher resistance to biological or chemical oxidation.

2.2. NaClO non-catalytic oxidation of substituted substrates

NaClO with no catalyst reacts with substituted molecules. This mechanism seems to be dependent on the substrate to be oxidized, the pH and the NaClO concentration. The overall oxidation kinetics would be 1st order with respect to the substrate provided that NaClO is available in high excess. Depending on the substrate composition, the reaction steps might include the formation of a transition chlorinated intermediate (Eliason et al., 1991). Under neutral to basic pH, the oxidized product does not bear any chloride, the end product is NaCl (Weast and Astle, 1980) and the O atom is transferred to the substrate's end products. On the other hand, organochlorides are synthesized by NaClO oxidation under acidic pH (Nadupalli et al., 2011). Most of these general features certainly apply to NaClO soil oxidation but they don't explain why a saturated hydrocarbon bearing no substitution can be oxidized by NaClO.

2.3. NaClO catalytic oxidation of saturated substrates

The non-catalytic mechanisms do not indicate how the reaction initiates when the substrate is an alkane. An undefined initial chlorination step could also be involved in the NaClO oxidation of alkanes. The clay transition metals might play a role in this initial chlorination step. Based on the data available in the literature, Mn organocomplexes (Liu and Groves, 2010; Asadullah et al., 1998) and Ni organocomplexes (Querci et al., 1990) could catalyze the halogenation of C–H bonds to form C–Cl bonds in the presence of NaClO at ambient temperature. Soluble inorganic Mn salts could also generate hydroxyl radicals from NaClO as it was measured in a 20-ppm NaClO solution (Liu et al., 2012a,b). The clay contains trace amounts of Mn, which catalyzed the $\text{Na}_2\text{S}_2\text{O}_8$ oxidation of an artificially diesel-contaminated soil (Do et al., 2010). This catalysis could also apply to NaClO oxidation of weathered soil. The hypothesis of a possible catalytic role played by the soil Mn complexes has to be weighed against the fact that trace heavy metals rapidly degrade NaClO into NaCl (Church, 1999). From another point of view, humic acids bearing hydrophobic sites could also be involved in facilitating petroleum contaminant chlorination by NaClO (Georgi et al., 2007). The search for an explanation is on-going.

2.4. Organochloride formation potential

The formation of organochlorides due to the bleach mechanism is a concern. According to chemistry references (Ege, 1994; Huot and Roy, 1999), organochlorides undergo nucleophilic substitution or elimination when the reaction media is at a neutral/basic pH. In this research project, this nucleophilic substitution is warranted by the soil natural alkalinity (Ca, K, Na, Mg). Furthermore, long-lasting organochlorides would only be produced in very diluted NaClO solutions as organochlorides have not been detected in 1-wt% NaClO solutions (Jackman and Hughes, 2010).

3. Experimental

3.1. Materials

The aged contaminated soil comes from a 10-ton pile on a dumping pad. A bucket was filled with this soil and named "soil A". The soil sample was then dried at room temperature for a week and sifted using a 2.5 mm sieve to recover the fines. During the entire research project that extended over more than a year, the soil sample was kept at room temperature in a closed cabinet. The composition and some other properties for soil A are shown in Table 1. This hexane soluble content in Table 1 shows that about

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