



Laboratory Evaluation of the Efficacy of Chlorine Dioxide (ClO₂) Composite Powder for Remediation of Petroleum Hydrocarbon-Contaminated Soils

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Abstract

The evaluation of efficacy of ClO₂ composite powder as a chemical oxidant for remediating petroleum hydrocarbon in soils has been explored. The main purpose of this study is to investigate the oxidative degradation capacity of ClO₂ and the resulting effects on soil chemistry. The most economical dosage was a ratio of 1g product:27g of contaminated soil. Destruction efficiency in the samples ranged from 7 to 41%. Decrease in soil samples pH ranged from 0.08 to 0.80 and 0.04 to 1.01, respectively. Increasing trend in hydrocarbon degradation was $F_1 \approx F_2 \approx F_3 > F_4$. The degradation mechanism of the hydrocarbon constituents was postulated to occur in two stages. The first fast-reaction stage involves ClO₂ (aq) in initial electron transfer and in the second-stage, the generation of hypochlorous acid (HOCl) and itself partially dissociates, forming hypochlorite anion, ClO⁻, which would recurrently react with the soil contaminants. SAR values remained unchanged relative unchanged. SO₄⁻² level increases in all samples due to oxidative transformations of sulfur containing compounds by ClO₂. Soil EC rises as ClO₂ dosage increased and was attributed to higher levels of Cl⁻ and SO₄⁻². As a direct benefit, SO₄⁻² provides a source of nutrient fertilizer in the soil for plants.

Keywords: Contamination; Hydrocarbon; Chlorine dioxide

Introduction

Anthropogenic activities and mismanagement can often lead to spilling of petroleum hydrocarbons in the soil, with real risks to human health and negative affect on the soil ecosystem [1-3]. In addition, the spillage can give rise to unwanted and uncontrollable migration of petroleum hydrocarbon substances in the air, surface and ground water bodies. Petroleum represents one of the most important sources of energy and a raw material in the chemical and manufacture industries. From a strict chemical perspective, the term petroleum hydrocarbons refer to a complex mixture of organic compounds consisting predominantly of hydrogen and carbon atoms, and containing small quantities of oxygen, nitrogen, sulfur as well as trace of metallic constituents. The impacts of petroleum hydrocarbons on environmental ecosystems have been examined and documented [4-6], including unwanted changes to soil physicochemical properties, toxicity to biota, recalcitrancy to natural degradation, bioaccumulation, degradation of water and

air quality, destruction of flora, exposure to airborne contaminants, loss of productive land and economic activities [7-9]. As such, the predicament of petroleum hydrocarbons contaminated soils and their remediation is among the most urgent and complex tasks facing many countries around the world in terms of environmental protection and financial aspects.

Petroleum hydrocarbons is regarded as the most recurring environmental contaminant. Scientists have recognized the potential dangers of petroleum hydrocarbons accidental released on land and devoted to the development of various remediation technologies. The soil remediation approaches available can be classified as *in-situ* or *ex-situ* while falling under the treatment category of chemical, physical, biological, electrochemical, or thermal treatments. However, the relative success of these various remediation methods will depend mainly on their large-scale applicability in the field and low-cost effectiveness.

Interactions between soil-hydrocarbon contaminant tend to be highly complex. Consequently, affected by hydrocarbon constituents and characteristics, soil solution surface tension, soil mineralogy, biological, chemical and physical properties, soil aqueous regime, extent of sorption and desorption processes, nature of mechanism of the soil-contaminant interactions as well as contaminant mobilization [10-12]. Solid state oxidation or creation of chemical oxidation in soil has emerged as one of the most practical remediation strategies to degrade organic pollutants in soil media [13-15]. Chemical oxidants are contacted with the contaminated soil. This starts off chemical reactions resulting in oxidative breakdowns via electron transfer processes

or generation of free radical species. Hydrogen peroxide, persulfate, ozone, calcium peroxide, and permanganate are deployed as common oxidants (Table 1). The chemical activation methods are generally activated by metals, change in soil pH, or heat that creates free radical oxidants that further oxidize the organic pollutant. The sensitivity of treatment to matrix conditions will vary with different oxidants and types of contaminants [16] (Table 2). In practice, many of these remedial techniques require additional activation methods. However, they have drawbacks, including high costs, toxicity to organisms, and detrimental effects on soil properties.

Table 1: Common oxidants used in solid state oxidation in soil.

Oxidant	Available Form	Activator	Reactive Species
Hydrogen peroxide (H ₂ O ₂)	Liquid	None, Fe(II), Fe(III)	HO ₂ •, OH•, O ₂ ^{•-} , H ₂ O•
Persulfate (Na ₂ S ₂ O ₈)	Powder	None, Fe(II), Fe(III), H ₂ O ₂ , heat, high pH	SO ₄ ^{•-} , SO ₄ ⁻²
Ozone (O ₃)	Gas	None	O ₃ , OH•
Calcium peroxide (CaO ₂)	Powder	None	H ₂ O ₂ , HO ₂ •
Permanganate	Powder, liquid	None	MnO ₄ ⁻

Table 2: Common oxidant species properties.

Reactive Species	E° (V)
Hydroxyl radical [OH•]	+2.8
Perhydroxyl radical [HO ₂ •]	+1.70
Ozone [O ₃]	+2.1
Sulfate radical [SO ₄ ^{•-}]	++2.6
Hydrogen peroxide [H ₂ O ₂]	1.77
Superoxide radical [O ₂ ^{•-}]	-2.4
Permanganate anion [MnO ₄ ⁻]	+1.77
Persulfate anion [S ₂ O ₈ ⁻²]	+2.1
ClO ₂	+0.954

The remediation of hydrocarbon or other organic contaminants in soil and water with stabilized chlorine dioxide (ClO₂) represents an attractive solution. Due to its reaction selectivity and a strong chemical oxidizing agent, ClO₂ has been reported to be an efficient oxidant of organic pollutants [17]. ClO₂ is commonly referred to as a paramagnetic radical that is safe, economic and environmentally friendly to use in remediation applications. Contrary to many chemical oxidation techniques, the ClO₂ oxidation systems does not require changing the soil pH to achieve a high degree of oxidation level. As a strong, water-soluble oxidant, it remains effective at a broad pH-range from 4-11 and does not hydrolyze in aqueous solution [18]. Furthermore, a paramount advantage of ClO₂ is that it does not react with the treated system matrix to form halogenated by products compared to using free chlorine as an oxidant.

The reaction mechanism of organic pollutant by ClO₂ has been investigated [19,20]. ClO₂ reacts with a high degree of oxidation

with the pollutant by attacking the atoms with the highest electron density. The pollutant loses electron and produces reactive intermediate. Subsequently, the unstable intermediate product participates in the ensuing reaction by undergoing molecular rearrangement and binding to ClO₂ or itself, which results in the formation of oxidation products.

At present, the evaluation of efficacy of ClO₂ composite powder as a chemical oxidant for remediating petroleum hydrocarbon in soils has not been explored. Thus, the main purpose of this study is to examine the oxidative degradation capacity of ClO₂ and the resulting effects on soil chemistry.

Material and Methods

Measurement of soil moisture

The measurement of the soil moisture was determined by the gravimetric method. A representative soil subsample was

collected, weighed before drying at $105^{\circ}\text{C} \pm 2$ for 72 hours and then reweighed. The percent soil water is given according to Equation 1:

$$\% \text{ soil water} = \left(\frac{\text{weight of wet soil (g)} - \text{weight of dry soil (g)}}{\text{weight of dry soil (g)}} \right) 100 \quad (\text{Eq. 1})$$

Dutridy-10 when mixed into the moist soil is expected to generate ClO_2 radicals. In order for ClO_2 to be active under the current investigation, it must be able to absorb moisture present in the soil to yield the following reaction: $5\text{NaClO}_2 + 4\text{HCl} \rightarrow 4\text{ClO}_2 + 2\text{H}_2\text{O} + 5\text{NaCl}$.

Chemical

Dutridy-10 is a composite powder that contains 10% ClO_2 , moisture absorbing powder, sodium chlorite and natural silicates. The product is manufactured by Duka Production LTD. To carry out the study, 400 g of contaminated soil was weighed and treated at room temperature with Dutridy containing 10% ClO_2 as the source of ClO_2 and tap water as well. The mixture was then homogenized mechanically in a 72 Oz Ninja Blender for 15 seconds to simulate the Micro-Enfractionater™. The treated

matrix was then transferred into a 500mL glass, labelled with a permanent marker, and its temperature measured with a laser thermometer and recorded as a result of heat released by the exothermic reaction. The glass jar was sealed and the system was allowed to react overnight in the dark. The treated samples were subsequently delivered to a licensed laboratory in Calgary for analysis.

Soil samples collection and analyses

The two soils samples impacted with petroleum hydrocarbon were collected from two different sites located in northern Alberta. The samples were transferred into 20L plastic pails, labelled, mechanically homogenized, sealed and then transported to Calgary where they were stored in a fridge at 6°C . The hydrocarbon analyses were conducted by a licensed laboratory located in Calgary. Additional soil physical and chemical properties were conducted internally [21] and are summarized in Table 3. Quality assurance and quality control were maintained throughout the study and conducted as specified by manufacturer. All the internal analyses were conducted in duplicate with the average value reported.

Table 3: Characteristics of the investigated soil samples.

Parameter	Sample ID	
	Sample 1	Sample 1
pH (CaCl_2 extraction)	7.72	7.82
Ec^{a} (dSm)	13.20	11.10
Saturation (%)	76	46
Cl^- (mgkg^{-1})	1760	1170
Na (mgkg^{-1})	2050	635
Ca (mgkg^{-1})	366	397
SO_4^{-2} (mgkg^{-1})	2770	1320
SAR^{b}	26.8	10.1
Moisture (wt%)	26%	17%
Clay (%)	22	14
Sand (%)	38	50
Silt (%)	40	36
USDA ^c name	Silt loam	Silt
USCS ^d name	MH (Liquid limit >50%)	MH (Liquid limit <50%)
TPH ^e (mgkg^{-1})	19360	31800
$\text{C}_6\text{-C}_{10}$ (F1)	200	1020
$\text{C}_{10}\text{-C}_{16}$ (F2)	5090	8010
$\text{C}_{16}\text{-C}_{34}$ (F3)	11000	17100
$\text{C}_{34}\text{-C}_{50}$ (F4)	3070	6290

^aElectrical conductivity (Saturation paste); ^bSodium adsorption ratio; ^cUnited State Department of Agriculture; ^dUnified Soil Classification System; ^eTotal petroleum hydrocarbons

Carbonates screening test

The hydrocarbon contaminated soil matrices were screened for the presence of carbonates. The test was performed using 0.1N and 1N HCl, respectively. Samples of the contaminated soil material were placed in a Pyrex spot plate to which 1mL of each HCl solution was added. The extent of effervescence was visually determined as an indication for presence of carbonates. The

qualitative test was carried out in triplicate.

Experimental Design

The experimental design for treatment with Dutridry-10 involving the two soil samples is depicted in Table 4. The set up consisted of three distinct systems with four treatments within a given system. Inorganic analyses and moisture determination were conducted in duplicate, and the average reported.

Table 4: Experimental design for the study.

System Treatment A	Treatment ID
400g soil sample + 0ml moisture added + 0g Dutridry-10 added	Control
400g soil sample + 0ml moisture added + 5g Dutridry-10 added	TRT#1
400g soil sample + 0ml moisture added + 15g Dutridry-10 added	TRT#2
400g soil sample + 0ml moisture added + 30g Dutridry-10 added	TRT#3
System Treatment B	Treatment ID
400g soil sample + 15ml moisture added + 0g Dutridry-10 added	Control
400g soil sample + 15ml moisture added + 5g Dutridry-10 added	TRT#1
400g soil sample + 15ml moisture added + 15g Dutridry-10 added	TRT#2
400g soil sample + 15ml moisture added + 30g Dutridry-10 added	TRT#3
System Treatment C	Treatment ID
400g soil sample + 30ml moisture added + 0g Dutridry-10 added	Control
400g soil sample + 30ml moisture added + 5g Dutridry-10 added	TRT#1
400g soil sample + 30ml moisture added + 15g Dutridry-10 added	TRT#2
400g soil sample + 30ml moisture added + 30g Dutridry-10 added	TRT#3

Results and Discussion

Soil moisture

Moisture content in the samples were 26% in sample 1 and 17% in sample 2, respectively. In sample 2, this value represents 104g of initial water content in the matrix and in sample 2 matrix, it was calculated to be 68g of initial water content. Therefore, Dutridry-10 when incorporated in the contaminated soil matrices was able to absorb the soil moisture to activate the formation of ClO₂. An exothermic reaction was produced by the reaction of the oxidant with the soil matrix and measured with a laser thermometer. Heat produced increased with incremental treatment with Dutridry-10. In the experimental systems delta temperature in TRT#1 was on average 3°C while in TRT#2 and TRT#3, it was 5 and 14°C, respectively.

Carbonate mineral screening test

The intensity of the effervescence reactions in presence of HCl is an indication of the level of carbonate minerals such as calcium carbonate (CaCO₃) or magnesium carbonate (MgCO₃) or

other types of carbonate minerals in the soil samples. Carbonate minerals do not appear to be present in significant concentration level in either of the hydrocarbon contaminated soil matrix. At 0.10 N HCl, no effervescence reaction was denoted in the samples. The 1N HCl yielded a very weak fizzing reaction in both samples.

Chemical oxidation of hydrocarbon by ClO₂

Results of petroleum hydrocarbon destruction by ClO₂ is depicted in Table 5. Average TPH concentration in sample 1 was 19,360 while in sample 2, it corresponded to 31,800mg/kg. Destruction efficiency on a percent basis (%DE) of hydrocarbon in a treatment was determined by Equation 2:

$$\%DE = \left[\left(\frac{\text{concentration in control} - \text{concentration in treated sample}}{\text{concentration in control}} \right) 100 \right] \quad (Eq. 2)$$

Across the experiments, heat, pH, and soluble salts were parameters also followed. The pH values fractional decreased with increasing moisture and ClO₂. EC values increased linearly across all treatments with higher levels of Dutridry-10. The reaction of ClO₂ with the contaminated matrices produced an exothermic reaction. Average delta temperature was +3°C in

systems treated with 5g of Dutridry-10. For systems treated with 15g of Dutridry-10, the average delta temperature was +5°C while an average delta temperature of +14°C was denoted in all systems treated with 30g of Dutridry-10. ClO₂ radical formation is activated when the substance contacts with the soil moisture. As a strong oxidizing reagent, ClO₂ transformed the petroleum hydrocarbon compounds into less harmful intermediates or end-products such as CO₂. Although complete mineralization is the primary objective, partial chemical oxidation by ClO₂ radical resulting in long-chain of the petroleum hydrocarbon compounds converted into less-complex, more dissolvable, and easily biodegradable substances or intermediates should be regarded also as a beneficial outcome. A comprehensive analysis of the % destruction efficiency trend is depicted in Figure 1 & 2, for the respective soil samples.

Destruction efficiency ranged from 7 to 41% in sample 1 and from 14 to 30% in sample 2. The effectiveness of ClO₂ radicals at transforming the soil hydrocarbon contaminants in sample 1 increases with increasing dosage of Dutridry-10 and soil moisture of the system. However, it was observed in sample 2 that contaminant degradation efficiency by ClO₂ was rather higher at low soil moisture and increased Dutridry-10 dosage. According to this study, 5 g of Dutridry-10 combined with a soil mass water (i.e., 104g + 30g = 134g H₂O) ratio 3:1 is the most appropriate combination to avoid using more water and achieving economical dosage of Dutridry-10 for treating sample 1. On the other hand, sample 2 is represented by a soil mass water (i.e., 68g + 0g = 68g H₂O) ratio 6:1 with a dosage of 5g of Dutridry-10.

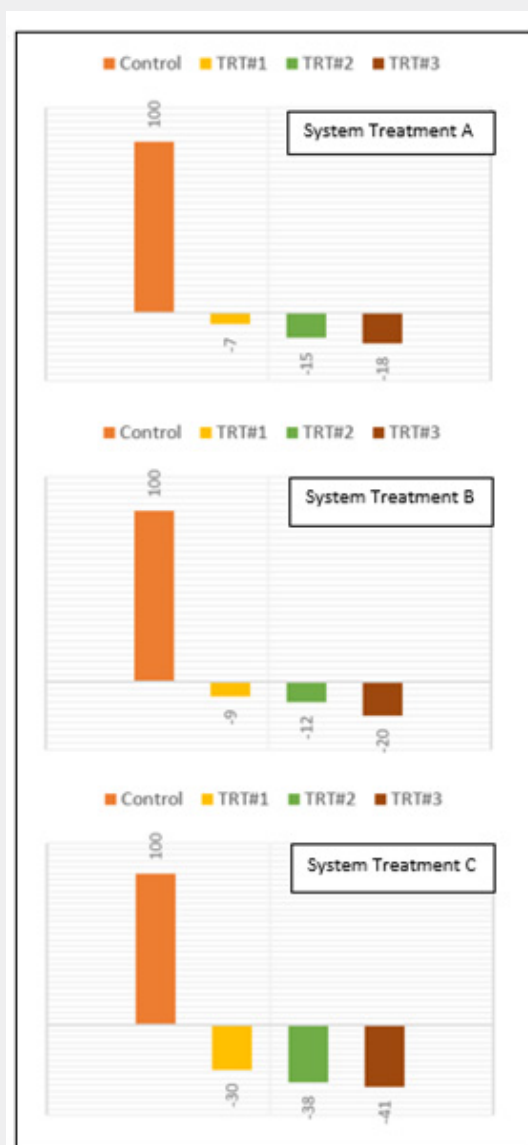


Figure 1: Graph of hydrocarbon destruction efficiency in Systems Treatment A, B, and C for soil Sample 1.



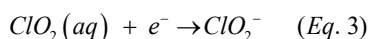
Figure 2: Graph of hydrocarbon destruction efficiency in Systems Treatment A, B, and C for soil Sample 2.

Table 5: Hydrocarbon loss by ClO₂ oxidation.

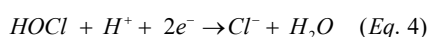
System Treatment A	Treatment ID	Sample 1		Sample 1	
		HC loss (mg kg ⁻¹)	% Destruction	HC loss (mg kg ⁻¹)	% Destruction
400g soil sample + 0ml moisture added + 0g Dutridry-10 added	Control	-----	-----	-----	-----
400g soil sample + 0ml moisture added + 5g Dutridry-10 added	TRT#1	1000	7	6900	22
400g soil sample + 0ml moisture added + 15g Dutridry-10 added	TRT#2	2200	15	9400	30
400g soil sample + 0ml moisture added + 30g Dutridry-10 added	TRT#3	2600	18	9300	30
System Treatment B	Treatment ID	HC loss (mg kg ⁻¹)	% Destruction	HC loss (mg kg ⁻¹)	% Destruction
400g soil sample + 15ml moisture added + 0g Dutridry-10 added	Control	-----	-100	-----	-----

400g soil sample + 15ml moisture added + 5g Dutridry-10 added	TRT#1	1200	9	4300	14
400g soil sample + 15ml moisture added +15g Dutridry-10 added	TRT#2	1600	12	4900	15
400g soil sample + 15ml moisture added + 30g Dutridry-10 added	TRT#3	2600	20	6200	20
System Treatment C	Treatment ID	HC loss (mg kg⁻¹)	% Destruction	HC loss (mg kg⁻¹)	% Destruction
400g soil sample + 30ml moisture added + 0g Dutridry-10 added	Control	-----	-----	-----	-----
400g soil sample + 30ml moisture added + 5g Dutridry-10 added	TRT#1	3000	30	5300	18
400g soil sample + 30ml moisture added + 15g Dutridry-10 added	TRT#2	3800	38	6900	23
400g soil sample + 30ml moisture added + 30g Dutridry-10 added	TRT#3	4000	41	7800	26

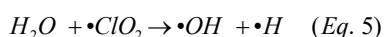
Hydrocarbon constituents' interactions with soils are specific, dynamic, can be reversible or irreversible, and affected by soil solution tension and chemistry, organic matter, and types of soil mineralogy [22,23]. Taking into account the higher sand content as well as the soil mass water rater ratio, and higher F1 and F2 fractions content in sample 2 relative to sample 1, may have contributed to more hydrocarbon mass transfer into the soil solution phase. The dissolved constituents are characterized by labile bonds that can readily be attacked and broken by the ClO₂ radicals in the solution. All fractions seemed to have been degraded within each soil sample. In relative term of concentration, increasing trend in degradation in both samples was $F1 \approx F2 \approx F3 > F4$ as indicated by the chromatograms data and higher ClO₂ concentration resulted in higher degradation. This clearly illustrates the non-specific nature of ClO₂ at degrading various organic substances. Similar results have been reported elsewhere [24]. The degradation mechanism of the hydrocarbon constituents may be occurring in two stages. The first fast-reaction stage involves initial electron transfer by Equation 3:



Correspondingly, residual ClO₂ and the generated hypochlorous acid (HOCl) partially dissociates, forming hypochlorite anion, ClO⁻ and would recurrently react with the contaminants. The process is illustrated through Equation 4 as determined by the relative remaining reaction time.



Chlorine dioxide radicals can also cause non-ionized hydrolysis of water, Equation 5, which gives rise to the formation of •OH in the ClO₂ oxidation system [28].



ClO₂ has been substantiated as one of the most auspicious oxidants and disinfectants. It has more oxidative capability and disinfection power than chlorine and able to react with a variety of organic substances. The most common and simplest components of petroleum hydrocarbons are alkanes with formula C_nH_{2n+2}. C-C bonds are non-polar and C-H bonds are also relatively non-polar. ClO₂ reactions with organic compounds almost does not produce hazardous byproducts such as trihalogenomethanes. The possible pathway for the degradation of the organic compounds by ClO₂ is mainly electrophilic. Essentially, ClO₂ reacts with the hydrocarbon constituents as a pure oxidant functioning primarily as a one-electron acceptor [29]. In practical term, the reaction from the formation of the C=O and O-H bonds is exothermic and generates CO₂ and H₂O. Many studies have reported that the degradation of organic compounds by ClO₂ were not pH dependent within the range 4.5-9.5 [25] in which both soil samples fall. However, ionizable organic compounds degradation by ClO₂ are generally pH-dependent while pH has no effect on non-ionizable organic compounds [26,27]. Since most of the hydrocarbon constituents in both investigated soil samples are non-ionizable organic compounds and non-polar, one should expect that the degradation process to be pH independent. The effect of the various treatments on soil pH of the soil samples are plotted in Figure 3 & 4, respectively. There has been a decrease in the soil pH in all treated systems. The delta changes in the soil slurries (i.e., initial soil pH-final soil pH) increase with increasing ClO₂ concentration and moisture addition. Additionally, delta changes in soil pH in sample 1 ranged in decrease from 0.08 to 0.80 while in sample 2, it was from 0.04 to 1.01. The results imply the formation of HOCl as a secondary oxidant during the oxidation of ClO₂, which could cause a decrease in the soil pH in both samples. It was also denoted a greater change in soil sample 2 pH in contrast to soil sample 1. This difference could be ascribed to greater HOCl formation in soil sample 2, which could not be offset by the lower

soil buffering capacity. There was no contribution to soil salinity of the soil samples by the various ClO₂ treatments. The effects of the ClO₂ various treatments on the soil samples salinity were analyzed. Sodium adsorption ratio (SAR) affects water intakes of soil and is given by the formula: $[Na] / (([Ca] + [Mg])/2)^{1/2}$, where all concentrations are expressed as milliequivalents of charge per liter is an indication of the amount of Na relative to Ca and Mg in the soil solution. SAR values within and across treatments for each soil sample remained relatively unchanged relative to the controls. Soil electrical conductivity (EC), a measure of the

amount of salts, increases equally in both samples as ClO₂ dosage increased. The biggest contribution to increase in the soil EC values was attributed to higher levels of Cl⁻ and SO₄⁻². Oxidative transformations of sulfur containing compounds by ClO₂ has been documented [30]. As a direct effect of ClO₂, concentration of SO₄⁻² increases in the soil samples with increasing ClO₂ dosage. Increase in SO₄⁻² level in sample 1 ranged from 54% to 100% while in sample 2, it was from 90% to 100%. As a direct benefit, SO₄⁻² can serve as a source of nutrient fertilizer in the soil for plants during reclamation.

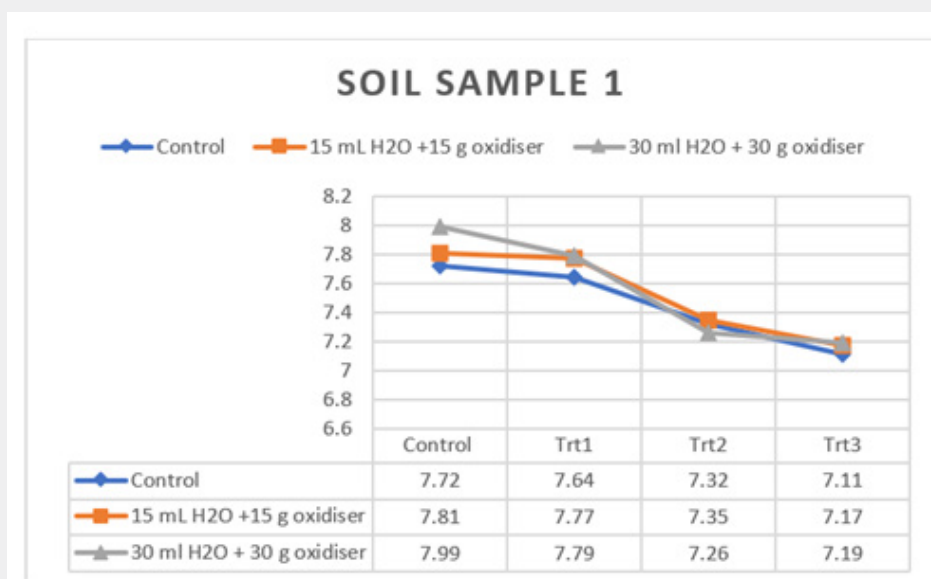


Figure 3: Soil pH as affected by treatments in soil sample 1.

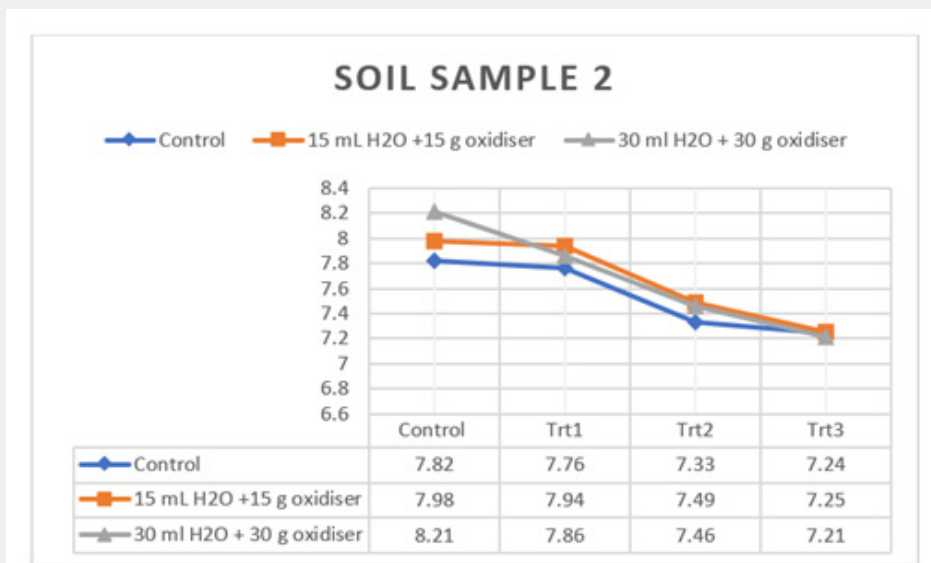


Figure 4: Soil pH as affected by treatments in soil sample 2.

Cost analysis

Dutridry-10 is typically sold in bulk for \$10/kg. At an effective application rate of 2.5g: 400g of hydrocarbon contaminated soil (i.e., 6.25g: 1kg of hydrocarbon contaminated soil), the cost of the product will be \$0.0625/kg per 2000 ppm hydrocarbon oxidized. The typical hydrocarbon concentration a contaminated soil matrix is 120,000mg/kg. Therefore, for a target reduction (TR) of hydrocarbon concentration to 20,000mg/kg in the post treated soil matrix entailed a reduction, Equation 6:

$$\%TR = \left\{ \frac{(\text{Hydrocarbon concentration} - \text{Targeted concentration})}{(\text{Hydrocarbon concentration})} \right\} 100 \quad (\text{Eq. 6})$$

$$\text{Hence, we obtain } \%TR = \left\{ \frac{(120,000 - 20,000)}{(120,000)} \right\} 100 = 83\%$$

Furthermore, the ensuing calculation was also performed to determine the amount of dutridry-10 product (Kg) that should be applied to achieve the above 83% reduction assuming 1kg of hydrocarbon contaminated soil, Equation 7:

$$\text{Kg of product} = \left\{ \frac{(\text{Hydrocarbon concentration} - \text{Targeted concentration})}{(\text{Hydrocarbon concentration})} \right\} \text{effective dosage} \quad (\text{Eq. 7})$$

and yields

$$\text{Kg of product} = \left(\frac{118,000}{2000} \right) 6.25 \frac{\text{product}}{\text{kg}} = 0.37 \text{Kg of Dutridry} \frac{\text{mg}}{\text{kg}} \text{ of contaminated soil at } 120,000 \frac{\text{mg}}{\text{kg}} \text{ of hydrocarbon}$$

Strategically, the product could be easily incorporated mechanically with on-site equipment at no additional operational cost to the remedial program. The author believed that mixing Dutridry with the Micro-Enfractionator™ would have the potential to increase the efficiency of the oxidizer by as much as 20-35% through improved contact surface area for reaction. Hence, an overall reduction in treatment cost.

Conclusion

It appears that ClO₂ has the potential of oxidizing hydrocarbon in contaminated soils. The effectiveness of ClO₂ radicals at transforming the soil hydrocarbon contaminants increases with increasing dosage and soil moisture of the system. However, the most economical dosage was a ratio of 1g product:27 g of contaminated soil. Destruction efficiency ranged from 7 to 41 % in sample 1 and from 14 to 30% in sample 2. Increasing trend in hydrocarbon degradation in both samples was F1 F2 F3 > F4. There has been a decrease in the soil pH in all treated systems. The delta changes in the soil pH slurries increase with increasing ClO₂ concentration and moisture addition. The results imply the formation of HOCl as a secondary oxidant during the oxidation of ClO₂, which could cause a decrease in the soil pH in both samples. Soil buffering capacity will influence the extent of soil pH lowering.

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Conflict of Interest

The authors acknowledge that the preparation of this paper was free of any conflict of interest.

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