

Comparison of Effectiveness of Two Remediating Agents on Hydrocarbon Contaminated Soil/ Groundwater in the Laboratory

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Abstract

Bench-scale tests of various potential remedial technologies were performed on samples of diesel contaminated soil and groundwater. Two remediating agents Molecular Potentially Chain Disintegrator (MPCD) and Potassium Permanganate (KMnO₄) were tested in a laboratory setting to determine the most effective and viable remediating agent that is capable of remediating the specific contaminants and concentrations found in the 3-D sand tank model. Groundwater and soil samples were collected from the sand tank during remediation operation to evaluate performance of the two remediating agents. Total Petroleum hydrocarbon (TPH) tests using Gas Chromatography with flame ionization detector (GC-FID) were carried out on both the sand and water samples. Other tests such as Conductivity and Dissolved Oxygen tests were also carried out on the water samples. The results show that both MPCD and KMnO₄ solutions are viable in remediating diesel contaminated soil and groundwater, but MPCD appears more effective than KMnO₄. However, MPCD exhibited destructive reactions in the laboratory 3-D sand tank model dissolving the epoxy used to glue the plexiglass and melting the plexiglass while KMnO₄ has no effect on the epoxy and the plexiglass.

Keywords: conductivity test, dissolved oxygen, gas chromatography, hydrocarbon contamination, molecular potentially chain disintegrator, potassium permanganate

1. Introduction

The use of chemical oxidants for the destruction of Volatile Organic Compounds (VOCs) began in the wastewater treatment field, and was applied as a remediation technology to treat contaminants in situ in early 1990s (Gates & Siegrist, 1993; Gardner et al., 1996; Jerome et al., 1998). Initial efforts focused on the use of the oxidants permanganate, catalyzed hydrogen peroxide (CHP, also known as modified Fenton's reagent), and ozone. Persulfate, percarbonate, and ozone catalyzed with hydrogen peroxide (Known as peroxone) have also been studied increasingly in recent years.

In Situ Chemical Oxidation (ISCO) using permanganate may reduce the permeability of the aquifer due to the formation of insoluble byproducts. During the reaction with organic compounds, permanganate becomes reduced, and forms manganese dioxide (MnO₂) solids (Perez-Bonito & Arias, 1991; Yan & Schwartz, 1999). The precipitation of manganese dioxide solids has been a concern in that it has been the cause of permeability reduction in treatment areas and in injection well filter packs at field sites (West et al., 1998; Lowe et al., 2000; Palaia et al., 2004) and stimulated laboratory scale studies (Reistma & Marshall, 2000). However, Siegrist et al. (2002) performed calculations showing that manganese dioxide would fill less than 1% of the pore space during permanganate degradation of TCE at concentrations up to 54 mg/l. Experiment by Lowe et al. (2002) with NaMnO₄ also shows that generation of reaction intermediates and products (e.g., chlorinated organic acids or partially degraded chlorocarbons), or reduction in formation permeability were observed. Other authors have noted minimal reductions in permeability in field-scale tests, even in areas of intense manganese dioxide staining (Chamber et al., 2000; Mott-Smith et al., 2000; Nelson et al., 2001).

The chemistry of the destruction of organic compounds by chemical oxidation has been investigated for over a century (Fenton, 1894). In the last twenty years, much research has been conducted specifically on the use of oxidants to destroy VOCs and other contaminants. Some of the research included exploration of contaminant-oxidant reaction pathways and kinetics, interactions of oxidants with soil matrices, the formation of reaction byproducts, the mobilization of metals, and impacts of microbial communities. The results of these

studies are summarized in guidance documents and review papers such as Siegrist et al. (2001), Block et al. (2004), ITRC (2005), Watts and Teel (2005), and Huling and Pivetz (2006)

Molecular Potentially Chain Disintegrator (MPCD) is a relatively new innovative product that is non flammable, colloid type, water-based, biodegradable cleaner of hydrocarbon based contamination via the dilution of the surfactants in water, sodium bicarbonate and sodium meta-silicate. MPCD is an aqueous solution, which is pink in colour and it is slightly denser than water.

The MPCD solution contained the following composition at different proportions, tetrasodium EDTA, sodium carbonate, sodium metasilicate, nonylphenol ethoxylate (9 mole), lauramine oxide, quaternary ammonium compound, other elements which are less than 0.1%, dye water, one of the major components of MPCD is sodium nonylphenol, which emulsifies the contaminate, another major component is sodium metasilicate, as with all alkaline silicates, when coming in contact with heavy metals, it allows the formation of a metallic silicate compound. This metallic silicate compound has the characteristics of a compound with very low solubility; it is non-toxic and it does not easily become soluble again. In addition, the alkaline silicate allows the micro-impermeabilization of the capsule through the formation of a gelatinous film that catches grains of precipitation that will emulsify, and encapsulate molecules of the contaminant.

The third principal component of MPCD is sodium carbonate. This component stabilizes the precipitation and trapping of the pollutant agents, once the pollutant is encapsulated MPCD now becomes a nutrient for local bacteria, it ingest the hydro-carbon pollutant. Within 72 hours MPCD will break down the molecular chain of the contaminate and between 7 to 15 days the environment will start to regenerate. The bacteria and microorganisms present in the environment being treated by MPCD penetrate the encapsulated pollutant and exit the capsule after the nutrients have been consumed. The encapsulated material becomes a nutrient for the bacteria and microorganisms which in turn return to the environment as nutrients. The capsule remains stable and “inert” sediment that does not have to be removed. (Vanguard Technology, 2012)

This paper compares the effectiveness of two remediating agents (MPCD and KMnO_4) on hydrocarbon contaminated soil/ groundwater in 3D sand tank in the Laboratory.

2. Materials and Methods

2.1 3-D Sand Tank Model

The experimental aquifer is 140 cm long, 30 cm wide and 80 cm high. The middle chamber was filled with a tropical saturated alluvial porous medium (Owena River sand), and chamber at both ends with water to maintain constant heads. Variable level overflow outlets were incorporated in the constant head reservoirs, to facilitate varying of hydraulic gradient across the porous media chamber. A 20 cm chamber was created between the cluster of multilevel wells (OW_B , OW_C and OW_D) and the last multilevel well (OW_E) (Figures 1 and 2). In the middle chamber of the sand model, alluvial sand was packed, while the diesel contaminated soil was packed in the 20 cm chamber. Water was allowed to flow freely through the sand medium from the inlet chamber, which was being fed continuously from the storage elevated tank. The preferred discharge port was opened (1st Port) (Figure 2) with the flow rate of 58 ml/min, while the other three (3) ports were closely locked.

2.2 Experiment Description

The oxidants were injected through the multilevel injection wells A, B, C and D. Water samples were taken via the multilevel well E (OW_E) (i.e., OW_E Top is at the depth of 420 mm from the top of the Sand Tank, OW_E Middle is at the depth of 620 mm from the top of the Sand Tank and OW_E Bottom is at the depth of 820 mm from the top of the Sand Tank) at 7th day and 15th day of the experiment and were analysed for Total Petroleum Hydrocarbon (TPH) with the aid of gas chromatography apparatus with flame ionization detector (GC FID), Conductivity and Dissolved Oxygen (DO) test. On 15th day of the experiment soil samples were also taken at different depths from the top of the sand tank (i.e., 200 mm, 400 mm, 600 mm and 800 mm from the top of the sand tank) in the 20 cm chamber created in the sand tank and analyzed for Total Petroleum Hydrocarbon (TPH) test.

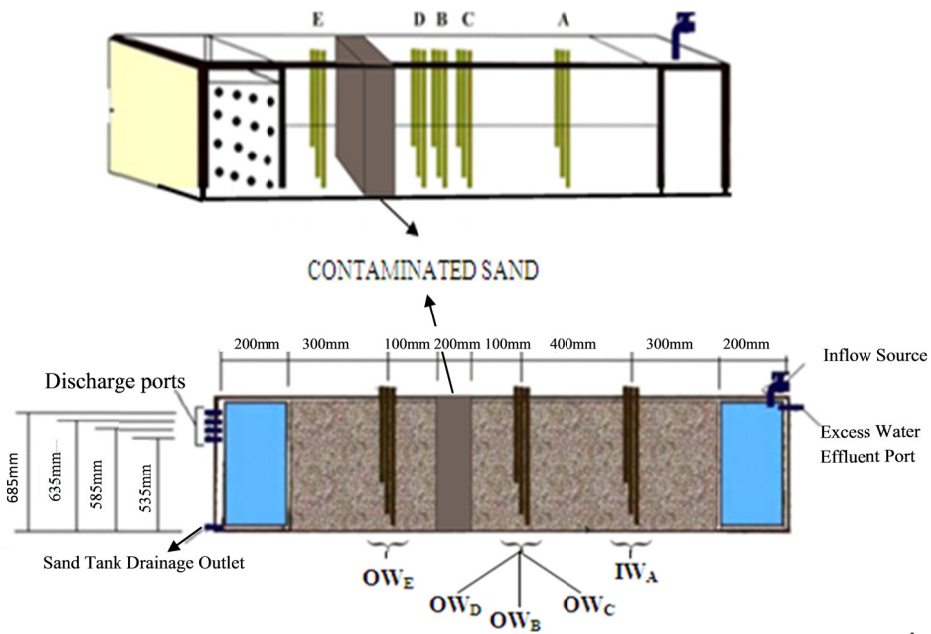


Figure 1a. Isometric and Sectional View of 3D Laboratory Sand Tank Model

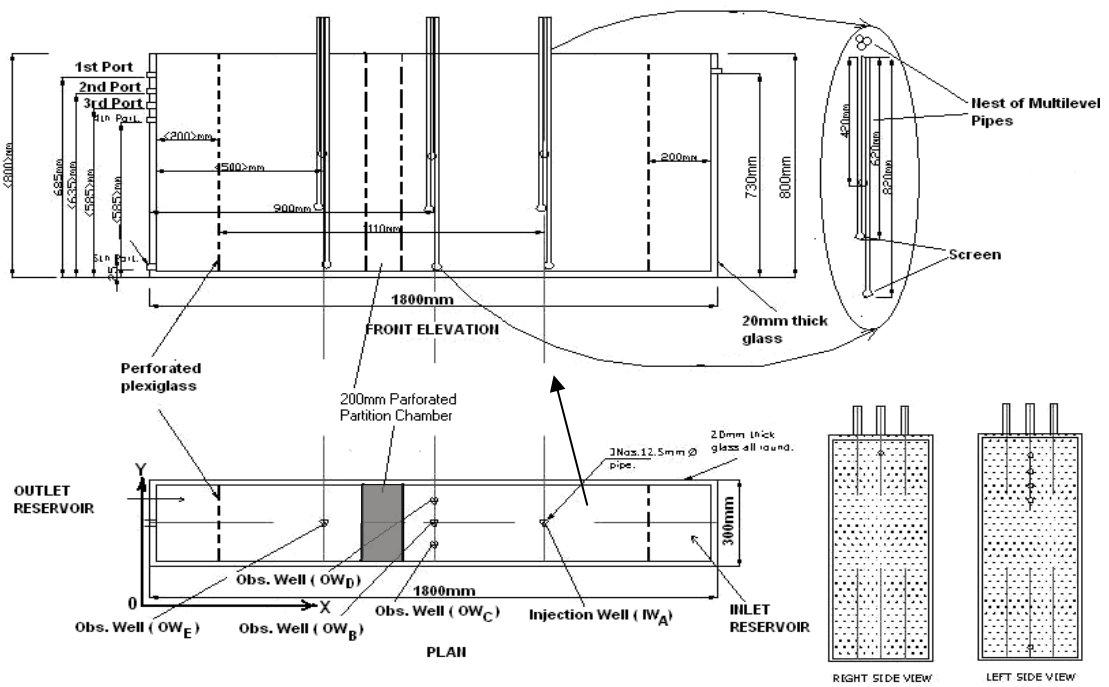


Figure 1b. Schematic Diagram of 3D Laboratory Sand Tank Model



Plate 1. Sample A

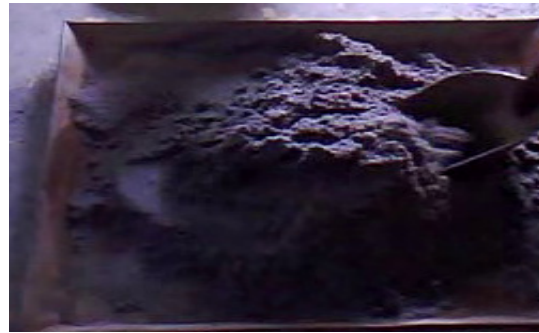


Plate 2. Sample B

Key: Sample A: Alluvial Sand without Diesel Contaminant;
 Sample B: Alluvial Sand mixed with 10.5% Diesel Contaminant.

2.2.1 Sample Preparation for MPCD Remediation Experiment

2.2.1.1 Soil Sample Preparation

Contaminated soil was prepared as follows:

Mass of air dried alluvial soil 20kg

Mass of Diesel 2.1kg

Percentage by mass of Diesel used

$$\frac{2.1}{20} \times 100 = 10.5\%$$

= 1.05 × 10⁵ mg of diesel/kg of the porous media.

Sample A is the air dried alluvial soil without diesel contaminant while Sample B is the alluvial sand contaminated with 10.5% diesel (Plates 1 and 2).

2.2.1.2 Soil Sample Preparation for KMnO₄ Remediation Experiment.

The same method used in the preparation of soil samples for the sand tank in the MPCD remediation experiment was adopted for the experiment with KMnO₄.

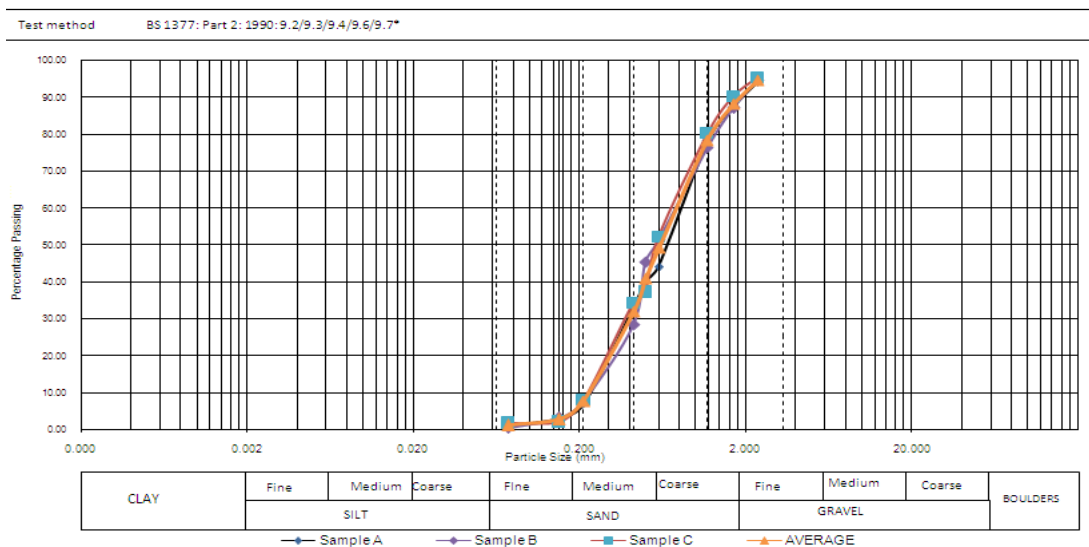


Figure 2. Granulometric Distribution Curve for Samples A, B and C

The granulometric characteristic of Owena river sand material gives a coefficient of uniformity $C_u = 2.60$, coefficient of gradation $C_z = 1.06$ and the median grain diameter $D_{50} = 0.70$ mm. The coastal river sand (Owena sand) material is relatively homogenous coarse-to-medium- grained sand. Silt and clay size fractions are almost absent i.e., less than 0.7 percent (Figure 2), the Owena sand contains grains of mostly one size, it is poorly graded (SP).

2.3 Injection of Diluted Molecular Potentially Chain Disintegrator (MPCD) Solution

0.5 L of concentrated Molecular Potentially Chain Disintegrator (MPCD) was diluted with 3 L of water. Thereafter, 3.5 L of diluted MPCD solution was evenly injected (i.e. approximately 0.29 L per injection well) into the Sand tank via the 4 nest multilevel injection wells IW_A , OW_B , OW_C and OW_D . (i.e., IW_A Top is at the depth of 420mm from the top of the Sand Tank, IW_A Middle is at the depth of 620mm from the top of the Sand Tank and IW_A Bottom is at the depth of 820 mm from the top of the Sand Tank. etc)(Figures 1a and 1b)

2.4 Injection of $KMnO_4$ Solution

175 g of $KMnO_4$ was measured and dissolved in 3.5 L of distilled water (equivalent to ratio 50 g of $KMnO_4$ to 1L of distilled water) stirred for about 20 minutes to obtain well dissolved solution of $KMnO_4$. Thereafter, the dissolved $KMnO_4$ was evenly injected (i.e. approximately 0.29 L per injection well) into the Sand tank via the 4 nest multilevel injection wells IW_A , OW_B , OW_C and OW_D . (i.e., IW_A Top is at the depth of 420 mm from the top of the Sand Tank, IW_A Middle is at the depth of 620mm from the top of the Sand Tank and IW_A Bottom is at the depth of 820 mm from the top of the Sand Tank. etc) (Figures 1a and 1b)

3. Results and Discussion

3.1 Conductivity Tests

The conductivity test result of the background water sample (water sample without diesel contaminant) is 1.67×10^2 S/m while the result of the conductivity test carried out on the water sample contaminated with diesel gives 3.89×10^2 S/m, the results of conductivity test carried out on the MPCD and $KMnO_4$ water samples at 7th day and 15th day are summarized in Table 1. Comparing the conductivity result of sample with diesel contaminant with the 15th day remediated sample of MPCD, it can be deduced that on the 15th day of the experiment with MPCD, the remediated water sample conductivity result has reduced by 23%, while experiment with $KMnO_4$ water remediated sample has reduced by 18%, the more conductive the water is, the more impurities there are in the water, thus the lower the quality of water.

Table 1. Results of Conductivity Test on Water Samples at the Background, Contaminated Water Samples without Remediation with any Oxidant, Contaminated Water Samples Remediated with Molecular Potentially Chain Disintegrator (MPCD) and $KMnO_4$ Solution

Sample	Conductivity (us/cm)	
A (Background)	1.67×10^2	
B (Diesel Contaminated)	3.89×10^2	
	MPCD Solution	$KMnO_4$ Solution
C (7 th day)	3.01×10^2	3.45×10^2
D (15 th day)	3.00×10^2	3.20×10^2

Sample A: Water Sample without diesel contaminant (Background), Sample B: Water sample contaminated with diesel, Samples C and D are water sample remediated with MPCD and $KMnO_4$ taken at 7th day and 15th day respectively.

3.2 Dissolved Oxygen

Dissolved Oxygen (DO) is the amount of oxygen that is present in the water, it is probably the most significant water quality test to determine the suitability of the water. The result of the dissolved oxygen test carried out on the background water is 5.48 mg/L, while the result of the dissolved oxygen test carried out on the water sample contaminated with diesel before the injection of any remediating chemical gives 0.59 mg/L (Table 2).

The MPCD and $KMnO_4$ remediated water samples, on the 7th day, the DO of the sample remediated with MPCD is 2.14 mg/L and increases to 3.43 mg/l on the 15th day. This is an increase of 263% on the 7th day, and 481% on the 15th day. The DO of the diesel contaminated samples remediated with $KMnO_4$ solution on 7th day is 2.43 mg/L and

increases to 3.63 mg/L on the 15th day. This is an increase of 297% on the 7th day and 515% on the 15th day. The DO increases with day with the two remediating agents, it is obvious that KMnO₄ had more dissolved oxygen than MPCD in the reaction.

Table 2. Results of Dissolved Oxygen (DO) Test on Water Samples at the Background, Contaminated Sample without Remediation with any Oxidant, Contaminated Water Samples Remediated with MPCD and KMnO₄ Solution

Sample	Dissolved Oxygen (mg/L)	
A (Background)	5.48	
B (Diesel Contaminated)	0.59	
	MPCD Solution	KMnO ₄ Solution
C (7 th day)	2.14	2.43
D (15 th day)	3.43	3.63

3.4 Total Petroleum Hydrocarbon (TPH)

Tables 3 and 4 respectively show the results of the TPH test carried out on the water and soil samples remediated with MPCD and KMnO₄ solution.

Table 3. Results of TPH Test on Soil Samples Remediated with MPCD and KMnO₄ Solution in mg/kg

Depth (m)	Using MPCD Solution	Using KMnO ₄ Solution
0.2	596.4	704.7
0.4	676.1	969.9
0.6	428.8	480.8
0.8	346.5	416.3

Original TPH of contaminated soil before start of remediation is 10.5% (1.05×10^6 mg/kg).

Table 4. Results of TPH Test on Water Samples Remediated with MPCD and 50 g/l KMnO₄ Solutions in mg/L

Days	Top Well		Middle Well		Bottom Well		Outlet Chamber	
	MPCD Solution	KMnO ₄ Solution	MPCD Solution	KMnO ₄ Solution	MPCD Solution	KMnO ₄ Solution	MPCD Solution	KMnO ₄ Solution
7 th	2.96×10^4	3.24×10^4	4.2×10^3	1.24×10^4	4.66×10^3	1.44×10^4	26.1	28.55
15 th	2.12×10^2	1.061×10^4	8.85×10^2	6.2×10^3	1.07×10^3	7.42×10^3	3.19	5.52

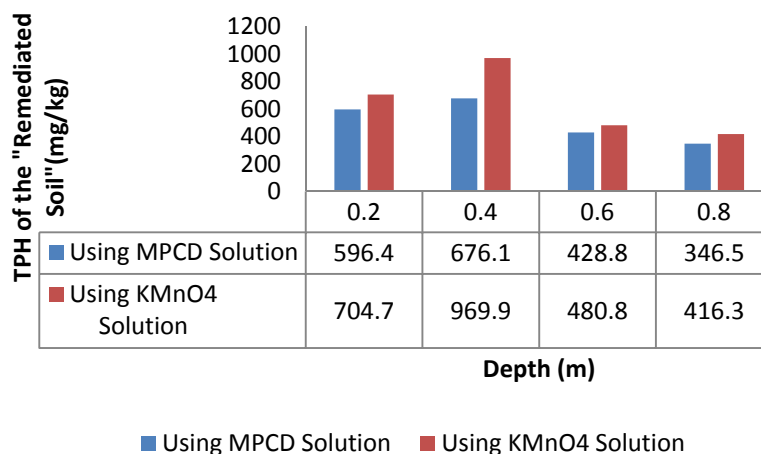


Figure 3. Results of MPCD and KMnO₄ Remediated Soil Samples after 15 days of Remediation

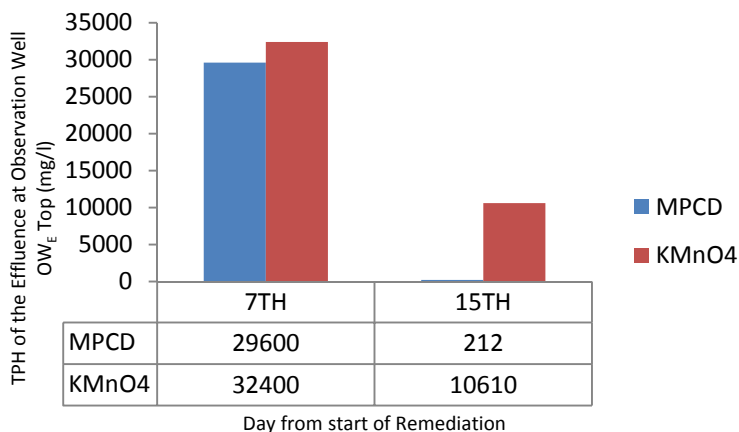


Figure 4. Graph of MPCD and KMnO₄ Remediated Water Sample Taken at the Top Observation Well E (Depth of 420mm from the top of the Sand Tank Model)

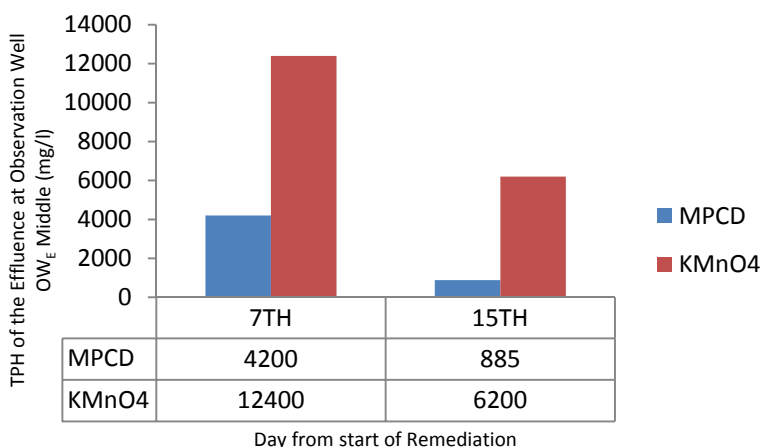


Figure 5. Graph of MPCD and KMnO₄ Remediated Water Sample Taken at the Middle Observation Well (Depth of 620mm from the top of the Sand Tank Model)

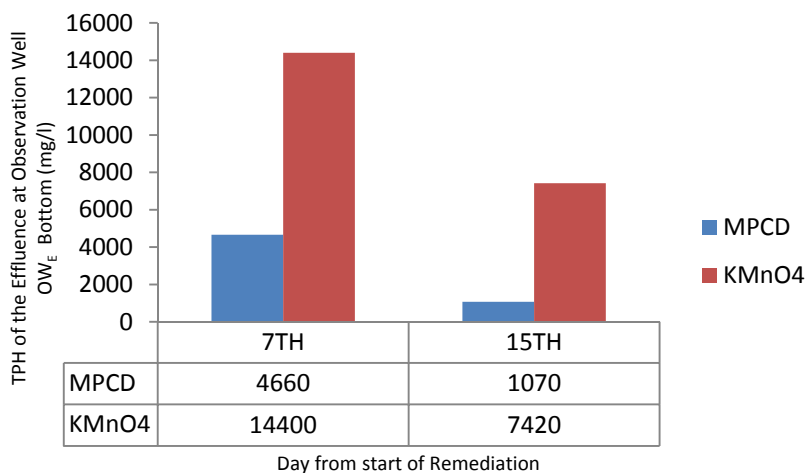


Figure 6. Graph of MPCD and KMnO₄ Remediated Water Sample Taken at the Bottom Observation Well (Depth of 820mm from the top of the Sand Tank Model)

The results of the Total Hydrocarbon Tests (TPH) for the soil and water samples are presented in Tables 3 and 4 for MPCD and KMnO_4 solution respectively. Figure 3 shows the plot of TPH results of the MPCD and KMnO_4 remediated soil samples taken at depth of 0.2 m - 0.8 m after 15 days. At 0.8 m, the results of MPCD remediated TPH is 346.5 mg/kg and for the KMnO_4 sample the TPH result is 416.3 mg/kg. The result in Table 4 indicates that the remediating fluids are more effective with depth. The TPH results for soil samples showed a significant remediation of the diesel contamination ranging from 99.94% to 99.95% for KMnO_4 and MPCD respectively within 15 days.

The results of contaminated water samples remediated with MPCD for 15 days vary between 212 and 1070 mg/L from the various wells (Table 4). This is a significant reduction from the original contamination of about 1.05×10^6 ppm. The reduction in the TPH concentration by using 50 g/L KMnO_4 solution varies from 6.2×10^3 to 10.6×10^3 mg/L within 15 days. Table 4 and (Figures 4-6).

3.3 Corrosive Action of MPCD and KMnO_4

It was observed that the plexiglass and the adhesive joining the plexiglass as partitioning in the sand tank were severely attacked by the reaction of the Molecular potentially chain disintegrator with the hydrocarbon contaminant starting from the third day of the experiment, at the end of the experiment with MPCD, the plexiglass was totally destroyed and broken into pieces (Figure 8) whereas, such destructive reaction was not experienced during the experiment with KMnO_4 . The material Safety Data Sheet MSDS confirms that it is a corrosive material, contact with skin causes chemical burns and possible tissue destruction, contact with eyes can cause blindness, if swallowed causes lung injury, liver damage and kidney injury. The HMIS rating for health is 3 (High hazard).



Figure 7. Broken Plexiglass after MPCD Remediation

4. Conclusions

From the study, although, Molecular Potentially Chain Disintegrator (MPCD) solution shows a promising remediating strength that is persistent in subsurface of the laboratory 3-D tank and this shows feasibility of its potential in a large scale remediation (Field Scale) to oxidize the Contaminant of Concern under specific field condition, but, the destructive reaction exhibited during the experimental study in the laboratory could be harmful to human health and animal in the environment in the course of using the solution in the pilot scale (on site) whereas KMnO_4 is safe and easy to apply to the contaminated subsurface without the health and safety concerns and lingering environmental issues that are associated with MPCD. In view of this corrosive and high health hazards, MPCD is not recommended for remediation of groundwater remediation such as in wells where the water is used for human and animal consumption.

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