

Chemical Decontamination Using Hydrogen Peroxide for Contaminated Soil with Hazardous Waste T.HCH

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Abstract: Soil contamination is caused by many anthropogenic activities. One of them is manufacturing and uses pesticides. Soil washing is one of the ex-situ treatment technologies for the remediation of contaminated soil. Usually in this processes most of contaminants gets concentrated in a small volume of soil that can be further treated or disposed off. When contaminated fines have been separated, coarse grain soil can usually be returned to clean site. The study was addressed to evaluating the efficacy of chemical decontamination of contaminated "fine portion" of soil using hydrogen peroxide was studied to achieve 90 percent efficiency of removal T.HCH released in the form of chlorides.

Keywords: Soil remediation, Chemical oxidation, Hydrogen peroxide

1. Introduction

Soil contamination is caused by the presence of man-made chemicals or other alteration in the natural soil environment. It typically arises from the rupture of underground storage links, application of pesticides, and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The occurrence of soil contamination is correlated to the degree of industrialization, intensity of chemical usage, and most predominantly to the waste management practices.

Pesticides are the chemicals that are used to repel or eliminate species that have an adversely affecting agricultural or horticultural production⁽¹⁾⁽²⁾. A "pesticide" can be broadly classified as an insecticide, herbicide, fungicide, nematocide, or molluscicide. These pesticides usually belong to the organophosphate and organochlorine class, depending on molecular structure of pesticides. Typical examples for organophosphorous class are chlorpyrifos, methyl parathion, azinphos methyl, and malathion; while DDT, chlordane, and T.HCH typically represent organochlorine class. Many of these pesticides are listed as Persistent Organic Pollutants (POPs) and are banned, while most of the remaining is Highly Hazardous or restricted use Pesticides.⁽²⁾⁽³⁾ Pesticides enter and pollute the environment primarily through their direct application in agricultural fields, owing to excessive and indiscriminate use. The leaching of pesticide at storage facilities is another major exposure pathway. The primary pathway of human exposure, however, is direct dermal contact and absorption. It is, therefore, necessary to remediate contaminated soil by adopting suitable measures.

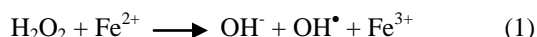
There are many different technical approaches to remediating contaminated land. These are broadly

classified as ex-situ and in-situ technologies depending on whether the contaminated soil is moved out of the land or not. In general, different technologies may be capable of treating either a wide range of contaminants, or specific ones, and are associated with certain advantages or disadvantages. Accordingly, a site-specific remedial strategy needs to be carefully selected. A number of remediation technologies to treat contaminated soils and groundwater are commercially available in many countries⁽⁴⁾. These include bioremediation, air sparging, soil vapour extraction, soil washing, thermal treatment and permeable reactive barriers. Soil washings a water based process for scrubbing soils ex-situ to remove contaminants⁽⁵⁾⁽⁶⁾⁽⁷⁾. It removes contaminant from soils in either of the ways: (i) by dissolving or suspending them in the wash solution (which is later treated by conventional waste water treatment methods), and (ii) by concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing. Soil washing systems offer the greatest promise for application to soils contaminated with various heavy metals, radio nucleotides and organic contaminants. Soil washing is most commonly used and soil fines are the residues that require further treatment. When contaminated fines have been separated, coarse grain soil can usually be returned clean to the site⁽⁸⁾⁽⁹⁾⁽¹⁰⁾. Contaminated wash water may result from soil washing will, which contain some or all of fine grained solids, (<300 mesh) contains attached and colloidal silt and clay materials such as heavy metals free floating petroleum hydrocarbons requiring removal.

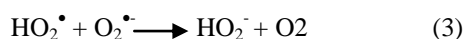
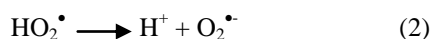
Soil washing technology can be used in conjunction with other treatment technology such as physical treatment, chemical treatment and biological treatment for decontamination of fine fractions of soil remaining after soil washing processes, applied for contaminated soil with pesticides. Several technologies such as chemical, biological and microbial are reported for the treatment/decontamination of T.HCH. The chemical methods

include treatment using ozone, hydrogen peroxide, sodium persulfate, hydrogen peroxide and Fenton's reagent and permanganate. α -, β -, and δ - isomer of HCH being non-biodegradable, chemical oxidation may be considered as an appropriate treatment method for such soils fraction contaminated with these pesticides. (C.P. Huang, *et.al.*, 1993).

Hydrogen peroxide is one of the most successfully used remedial chemical for contaminated soil remediation. Oxidation with Hydrogen peroxide can be direct and/or through the generation of free radicals (Hydroxyl radicals OH^\bullet). The latter relies on the decomposition of hydrogen peroxide catalyzed by most ions of transition metals (Fe, Cu, Zn, etc.) and by natural minerals of those metals (hematite, goethite, etc.) present in soil. The basic reaction is:



Superoxide anion (O_2^\bullet), hydroperoxyl radical (HO_2^\bullet) and hydroperoxide anion (HO_2^-) can also act as desorbing oxidizing agents in soil remediation. These species are created during the propagation reactions with high ($\geq 2\%$) H_2O_2 concentration:



Treatment with hydrogen peroxide has several advantages over other soil remediation methods. Hydrogen peroxide oxidation is relatively fast, taking only days or weeks. The contaminants are treated *in-situ*, converted to innocuous and/or natural occurring compounds (e.g. H_2O , CO_2 , O_2 , halide ions). By acting/ reacting up on the contaminant in place, the reagent serves to eliminate the possibility of contaminant vertical movement other than resulting from the act of vertical injection itself, which is often a concern in other remediation technologies (B.R. Petigara, 2002).

As a side advantage, aerobic biodegradation of contaminants can benefit from the presence of oxygen released during H_2O_2 decomposition, if large quantities of chemical needed to be applied. H_2O_2 can be electrochemically generated on site, which may further increase the economic feasibility and effectiveness of this process for treated contaminated sites. Natural iron oxide minerals (hematite α - Fe_2O_3 , goethite, magnetite Fe_3O_4 and ferrihydrite) present in soil can catalyze hydrogen peroxide oxidation of organic compounds. Thus, the treatment of contaminated soil would require no addition of soluble iron catalyst (W.W. Eckenfeld, 1992).

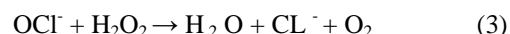
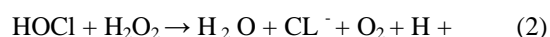
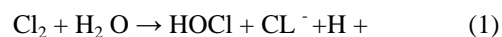
Disadvantages include the need for pH control in some cases and difficulties controlling *in-situ* heat and gas production. The efficacy of hydrogen peroxide oxidation may be limited by low soil permeability, incomplete site delineation, subsurface heterogeneity, and highly alkaline soil where carbonate ions are free radical scavengers. Advanced oxidation processes (AOPs) are a promising unit process for the degradation of trace organic pollutants in drinking water and wastewater. AOPs generate highly

oxidative hydroxyl radicals that destroy a broad variety of contaminants. In an AOP that combines ultraviolet light (UV) with hydrogen peroxide, hydrogen peroxide (H_2O_2) is photolyzed forming hydroxyl radicals. Because of the low molar absorption of H_2O_2 , the concentration required for efficient generation of hydroxyl radical is high (2 to 10 mg=L), and not all of it gets photolyzed. As a result, about 75 to 90% of the influent H_2O_2 remains after UV photolysis at UV doses appropriate for drinking water or water reuse. The residual H_2O_2 will react with chlorine and must be quenched before it is possible to generate chlorine residual required for full-scale disinfection (R.J. *et.al.*, 1992).

In the case of bench-scale disinfection byproduct (DBP) formation testing, H_2O_2 also must be quenched for the same reason. Other common post-AOP bench-scale tests such as toxicity assays also require H_2O_2 quenching, although for a different reason (e.g., because H_2O_2 may interfere with the biological culture used in the assay due to its oxidative properties).

This technical note compares two H_2O_2 quenching techniques, free chlorine and bovine catalase (BC, an enzyme from the liver of a cow), and provides insight into the advantages and disadvantages of each for specific applications. Issues with conventional oxidant quenching agent, thiosulfate and sulfite are also reviewed. The results will help UV/ H_2O_2 AOP practitioners and researchers select the quenching.

Quenching with Free Chlorine: Reaction between H_2O_2 and free chlorine is very rapid and proceeds according to the following stoichiometry:



Each mole of free chlorine reacts with one mole of H_2O_2 which translates into 2.09 mg/L of free chlorine for 1 mg/L of H_2O_2 .

The objective of present study was to determine the efficacy of decontamination of fine fractions of soil remaining after soil washing using strong chemical oxidant. The scope of work comprised mainly the following: (i) collection & characterization of soil samples in central region of India, (ii) spiking of fine portion of soil with T.HCH (T.HCH), and (iii) decontamination of fine fractions of soil remaining after soil washing using strong chemical oxidant viz. hydrogen peroxide⁽¹¹⁾⁽¹²⁾⁽¹³⁾⁽¹⁴⁾.

2. Material and Method

The present study was addressed mainly to study treatability studies on use of hydrogen peroxide as a chemical oxidant to degrade the pesticide retained on residual clay. The materials and methods used in the research are briefly described below;

Materials:-Samples of Murom, Pesticide i.e. Technical HCH, Water, filter paper, Glass fiber filter paper (Whatman) etc.

Equipment: - Sieves with different mesh sizes, Plastic bucket, Rotary evaporator, Soxhlet extractor, Separating funnel, Oven, Bottles, Gas Chromatograph, Weighing machine, burrette, pipette, measuring cylinder etc.

Solvent and Chemicals: Acetone, Hexane, H₂O₂, NaCl, NaHCO₃, K₂CrO₄ and AgNO₃.

Soil Sample Collection and Analysis: - Representative soil samples Murom which is predominantly available in and around Nagpur, situated in central India, was collected from different locations. The soil sample was subjected to sieve analysis with a view to knowing the proportions of soil fractions in different size range. Four sieves viz. ISS 400 (4mm opening), ISS 236 (2.36mm), ISS 170 (1.7mm), ISS 30(0.3mm) were used to determine the fractions in the category silt and clay. Approximately 5 kg representative sample of Murom was subjected to characterization for significant physico-chemical parameters such as pH, content of sodium, potassium, phosphate, nitrogen, specific gravity, moisture content, organic matter, ash, organic carbon, and heavy metals. The analysis was carried out in accordance with the procedure prescribed in Standard Methods and USEPA Manuals (SW-846).

Sample Preparation, Soil spiking and Analysis: - The following procedure was adopted for soil spiking with T.HCH. Initially 100gm of soil sample of size <0.3 mm (clay) was taken in different beakers and spiked with T.HCH in concentrations of 1000 mg/kg and 500 ml water was added and retained for one week for maximum adsorption. After one week soil samples were almost dry, these samples were used for chemical treatment, subjected to soil extraction processes using mixture of N-hexane and acetone (80:20). Soxhlet extractor was used and utmost care was taken to extract maximum T.HCH to minimize errors. To find out concentration of T.HCH for crosschecking.

In these experiments, above said spiked samples of clay samples were treated using hydrogen peroxide. Ten gm of spiked clay sample with T-HCH dose of 1000 mg/kg i.e. 10 mg in 10 gm of clay sample was diluted with 250 ml distilled water in a volumetric flask having capacity 500 ml and stirred for 24 hours. After stirring, 25 ml supernatant was taken from each flask for estimation of chlorides by titrimetric analysis to know the initial chlorides concentration in clay before treatment by hydrogen peroxide. In these flasks, hydrogen peroxide was added in varying dosages from 1 ml of H₂O₂/mg of T.HCH/gm of soil to 50 ml of H₂O₂/mg of T.HCH/gm of soil. After addition of hydrogen peroxide, the flasks were kept under stirring condition to achieve intimate contact between clay sample and hydrogen peroxide. All these samples were analyzed for estimation of chloride concentration by titrimetric analysis using N/142 (0.00705 N) silver nitrate with potassium chromate as indicator at time intervals of 10, 30, 60, 120 and 240 minutes. Results are reported in Table 1.

Table 1: Percent Release of Chlorides (equivalent to % decontamination) at Different Time Intervals for Various Hydrogen Peroxide Dosages

Sample	Dose of H ₂ O ₂ in ml/mg T.HCH	% Release of Chlorides at different time intervals			
		0.5 Hr	1 Hr	2 Hr	4 Hr
1	10	77.47	84.57	85.54	86.50
2	11	78.44	85.54	87.79	88.76
3	12	80.05	87.15	88.12	89.73
4	13	81.34	87.80	88.76	90.29
5	14	82.31	88.44	89.41	90.83
6	15	83.28	90.01	90.83	90.83
7	20	88.76	90.38	90.83	90.83
8	30	90.06	90.83	90.83	90.83
9	40	90.38	90.83	90.83	90.83
10	50	91.02	91.02	91.35	91.35

For cross checking clay samples were spiked with T.HCH dosage 1000 mg/kg and 3 different dosage of Hydrogen peroxide 10 ml, 15 ml and 30 ml per mg of T.HCH was added for contact period of 10 min, 30 min and 60 min. Soil fraction and water are analysed for chloride release by titration method and T.HCH retention using Gas Chromatography. Results are furnished in Table.

Table 2: Percent Retention of T.HCH on Soil and Wash Water

Sr. No.	Time in Min	% Retention of T.HCH on Soil and Wash Water* (W/W)								
		Dose 10 ml			Dose 15 ml			Dose 30 ml		
		Soil	Wash Water	Total	Soil	Wash Water	Total	Soil	Wash Water	Total
1	10	40.68	54.34	95.02	52.9	42.2	95.21	23.31	71.5	94.8
2	30	17.41	76.82	94.23	11.4	83.43	95.01	4.95	90.26	95.21
3	60	14.73	80.19	94.92	4.59	90.37	94.96	4.11	91.17	95.28

Based on GC Analysis (W/W=Weight/Weight)

3. Results and Discussion

From above studies clay fractions < 0.3 mm of Murom needs treatment for decontamination. Spiked sample of clay were subjected to chemical treatment for decontamination of T.HCH from clay as per method given above. The procedure for chemical treatment was followed as described earlier. The resistivity of the T.HCH to biodegradation is primarily due to chlorine atom, which needs high energy to get released out of organic molecule. In chemical treatment, due high energy of oxidizing radical, chlorine is relatively quickly released. T.HCH molecular residue sans chloride is not POP. Therefore, the decontamination of the soil and wash water was assessed on the basis of increase in chloride and how close it was to the stoichiometric maximum. For example, initial chloride content in soil was observed as 43.09 mg/kg. A dose of T-HCH (chemical formula C₆H₆Cl₆)@1000 mg/kg is equivalent, on the basis of stoichiometry, to 731.17 mg/kg chloride⁽⁶⁾. Therefore, the maximum chloride content in contaminated clay samples could be considered as 774.26 mg/kg. The results of chloride concentration for various

dosages and contact times are given in Table I, that shows for a soil sample contaminated with T-HCH dose of 1000 mg/kg, hydrogen peroxide dose of 1.5 ml per gm of soil per mg of T.HCH dose sample for a contact time of 60 minutes was found to release more than 90 % of chlorides. The increase in this efficiency for a contact times greater than 60 minutes was insignificant for all H₂O₂ doses applied. All these results are indicative and may vary for different soil types under different climatic conditions. Nevertheless, these results form the basis for deciding the appropriate soil remediation strategies for T.HCH contaminated sites, which are common in India. These results of decontamination were based on titrametric method of chloride determination.

4. Conclusions

The study has conclusively established that

- H₂O₂ is effective in decontamination of the T.HCH contaminated soil fractions and wash waters.
- Studies on chemical oxidation of pesticide retained on fine fractions of soil and in used wash water using different dosages of chemical i.e. hydrogen per oxide and for different contact period reveal that a hydrogen per oxide dose of 15 ml per mg of T.HCH spiked per gram of soil for 60 minute retention time and a hydrogen per oxide dose of 30 ml per mg of T.HCH spiked per gram of soil for 30 minute retention time is adequate to break the bond of T-HCH and remove chlorides in wash water to the tune of 90 %. Further increase in the dose of hydrogen peroxide or contact time does not lead to substantial improvement in removal of T.HCH.
- Studies on chemical oxidation of pesticide using hydrogen per oxide with different dosage indicates that the decontamination in initial phase i.e. up to 5 minute is rapid to the extent of about 40 to 60 percent removal depending upon the dose of hydrogen peroxide. The rate of removal reduces with time and becomes insignificant after duration of 60 minutes.
- The results of quantity of T.HCH determined by titrimetric method after oxidation using hydrogen per oxide and by GC after soxhlet extraction are quite comparable. The level of accuracy, as judged on the basis of mass balance of chlorides in soil, is observed to be 91 % to 95 %. Hence, it can reasonably be stated that the process of soil washing and estimation of T.HCH in soil fractions and used wash water is acceptable.
- The soil washing technology along with chemical oxidation using hydrogen per oxide is proved to be effective in remediation of both red soil and Murom contaminated with T.HCH as large volume of soil can be cleaned up only by plain washing and only small volume of soil fractions needs further treatment with hydrogen per oxide for decontamination.

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