Efficiency of modified chemical remediation techniques for soil contaminated by organochlorine pesticides

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Abstract. This study reports the optimization of innovation chemical techniques in order to improve the remediation of soils contaminated with organochloride pesticides. The techniques used for remediation were dehalogenation and chemical oxidation in soil contaminated by pesticides. These techniques were applied sequentially and combined to evaluate the design optimize the concentration and contact time variables. The soil of this study was collect in cotton crop zone in Agustin Codazzi municipality, Colombia, and its physical properties was measure. The modified dehalogenation technique of EPA was applied on the contaminated soil by adding Sodium Bicarbonate solution at different concentrations and rates during 4, 7 and 14 days, subsequently oxidation technique was implemented by applying a solution of KMnO₄ at different concentration and reaction times. Organochlorine were detected by Gas Chromatography analysis coupled Mass Spectrometry and its removals were between 85.4- 90.0 % of compounds such as 4, 4'-DDT, 4,4'-DDD, 4,4-DDE, trans-Clordane y Endrin. These results demonstrate that the technique of dehalogenation with oxidation chemistry can be used for remediation soils contaminated by organochloride pesticides.

1. Introduction
In Colombia, in the municipality of Codazzi, Cesar; still manifest in the environment of organochlorine compounds used in the cultivation of cotton between the 60s and 80s. At the beginning the 90s this agricultural activity declined for various reasons as the El Niño phenomenon, the illicit crops and the economic crisis facing the country at that time [1], these conditions in addition to economic losses, led to pollution of soil resources due to burial of agrochemicals and improper disposal of the remaining chemicals (especially organochlorine pesticides) on adjacent land to the plantations [2]. In addition to the burial of these pesticides a public health problem appear with increasing cases of cancer and congenital diseases. The municipality of Codazzi was considered one of the cities with the highest rate of cancer in the country [3].
Today, much of the affected area is abandoned and neglect by the municipality. It’s important to consider that exist studies showing the soil contamination and its effects and has not made any alternative solution to the problem. Therefore, in this study chemical treatments were applied on a laboratory scale, to enable removal of organochlorine in soil. Chemical treatments applied to contaminated soil were based on chemical dehalogenation techniques followed by chemical oxidation. To perform these treatments was applied chemicals in the soil getting results between 80 and 90% removal of pesticides. The soils were characterized by physicochemically and biologically. After that we apply the treatment of dehalogenation and oxidation with soil contact time and concentration of the substance as variables. Analysis of chlorides present in soil were performed using atomic absorption techniques. The analysis to determine the removal of pesticides in soil were performed by gas chromatography coupled to mass spectrometry.

2. Experimental part
Samples of soils contaminated by pesticides were taken at the cotton area located in northern Colombia in the nearby of the city of Agustin Codazzi, Cesar. In this paper we present three stages for remediation of soil contaminated with pesticides. In the first stage physicochemical properties of the soil of interest were identified. In the second stage the techniques of chemical oxidation and dehalogenation were optimized. Finally the removal efficiency of each of these techniques was determined. The sampling procedure was carried out following the methodology proposed by Corpoica [4]; the affected area was demarcated in two quadrants of 50 x 50 meters with zigzag sampling. The sampling achieved a total of 80 samples collected at 40 cm deep and with a volume of approximately 3 kg per sample. In the laboratory the soil samples were processed by crushing, screening and homogenization to achieve a composite sample.

2.1 Soil physicochemical characterization
For the analysis of the physicochemical characteristics of soil relevant evidence based on standardized methods were performed. The parameters measured were: texture, moisture content, moisture loss, density (apparent and real), total porosity, pH, electrical conductivity and cation exchange capacity (CIC) [5]. The soil was submitted to analysis for the detection of organochlorine compounds and their concentrations in the Laboratory of Gas Chromatography and Mass Spectrometry (CROM-MASS) of the Industrial University of Santander (UIS). This analysis was performed using the dispersion technique solid phase matrix (MSPD), using as reference material certified mixture of organochlorine pesticides part No. OCP508-1JM (Chemservice, West Chester, PA 19381 PO BOX 599, USA). The chromatographic analysis was performed on a gas chromatograph AT 6890 Series plus (Technologies Agilent, Palo Alto, California, USA) coupled to a mass selective detector (Agilent Technologies, MSD 5973) operated in SIM mode [monitoring ions selected]. The column used for analysis was DB-5MS [5% -phenyl-poly (methylsiloxane), 60 m x 0.25 m x 0.25 microns]. The injection was performed in splitless mode ($V_{inj} = 2 \mu L$).

2.2 Degradation techniques organochlorine
The treatment implement of two chemical techniques applied sequentially on the ground to make the respective decontamination. The techniques used were chemical dehalogenation followed by a chemical oxidation. The optimization of these two techniques was carried out by implementing a $2^2$ factorial design (two factors on two levels), which allow to select the best parameters to decontaminate the soil. In both designs the object of study was the soil contaminated with organochlorine pesticides and the response or dependent variable was the concentration of organochlorines.

2.2.1 Chemical Dehalogenation
The technique used was a variation of the chemical dehalogenation by bases catalyzed decomposition developed by the Agency for Environmental Protection (EPA), the method 542-F-96-020 [6]. In the applied modified Sodium Bicarbonate (NaHCO₃) solution it was added in different concentrations
between 0.5, 1, 5.0 and 10% w/v and further maximum and minimum flow of 0.4 mL/min and 0.10 mL/min respectively in the contaminated soil. The contaminated soil was heated in a temperature range between 38 °C and 40 °C simulating the temperature at which the soil is exposed in their home area. These modifications were made in order that the technique has a bigger applicability and less costs in the area of interest. For dehalogenation process for laboratory scale we used 100 g of contaminated soil in a beaker heated to 38 °C using an electric hot plate, dosing the soil with a solution of sodium bicarbonate (NaHCO$_3$) with concentrations between 0.5 and 10%. The containers with contaminated soil were sealed with parafilm and connected with distilled water in bottles sealed conditions, in order to collect the gases generated by applying the technique. After the dehalogenation chlorides analysis was performed in water by the volumetric method according to Standard Methods numeral 4500-Cl B to confirm the presence of free chlorides from the soil layers as gas and condensed in water. The amount of sodium bicarbonate applied to each test was approximately 70% of field capacity soil.

The 2$^2$ factorial design allowed us to determine the main effects of the concentration of sodium bicarbonate, the flow rate, and the effect of the interaction of both factors in decreasing concentration of organochlorine pesticides. Each test had three replicas.

The results obtained by the chloride method allows to select the concentrations of sodium bicarbonate and flow rates to be used in contaminated soils. The analyses of removal of contaminants from soil to best conditions selected were submited to the detection of dehalogenated compounds by gas chromatography-mass spectrometry.

### 2.2.2 Chemical Oxidation

After the implementation of chemical dehalogenation, the soil was treated by chemical oxidation process by applying potassium permanganate as an oxidizing agent [7]. To optimize this technique $2^2$ factorial design was implemented and the factors were chosen based on what is reported in literature. The factors to be evaluated were the concentration of the oxidizing agent [KMnO$_4$] and reaction time of soil contaminated with KMnO$_4$. For this technique we used analyzes of samples by gas chromatography.

In the application of oxidation technique on the contaminated soil it consisted of a galvanized metal base with nine carrying vessels of PVC. This material was used for the oxidizing character of potassium permanganate used in the process of soil decontamination using this technique. The dimensions of the vessels of PVC were similar to those of the containers used in the prior art, so that the dehalogenated soil was transferred to these vessels to apply oxidation. PVC cups had an outlet pipe made of the same material for collecting leachate, the output was controlled by a valve and deliver into glass beakers of 100 mL. The aggregate of potassium permanganate for oxidation chemistry correspond to the 30% of the field capacity remaining available in each soil sample. Thus the soil was 100% field capacity, tests were also performed in triplicate. The factorial structure $2^2$ applied to the oxidation of organochlorine compounds allow to identify the main effects of the concentration of the oxidizing agent (KMnO$_4$) between 1, 0.5, 0.25 and 0.01% p/v, the reaction time, and the oxidant interaction effect of both factors in decreasing concentrations of organochlorines. The samples with different concentrations of KMnO$_4$ were evaluated 7 days after the application of the oxidizer to the ground in accordance with the literature recommendation. Once determined the concentrations of potassium permanganate we proceeded to determine the reaction time for the optimization of oxidation were between 1, 0.5, 0.25 and 0.01% p/v. The results of gas chromatography analysis allows to choose the best combination for chemical oxidation.

### 2.3 Determination of the efficiency of removal of organochlorine

The gas chromatography analysis allows to determine the efficiency of removal of organochlorine compounds to each of the techniques implemented. In chemical dehalogenation, they were selected factorial design variables by determining chlorides in soil samples latter were submitted to gas
chromatography analysis to establish the efficiency of removal of each variable. Similarly, the removal efficiency of chemical oxidation was calculated from the results obtained by gas chromatography. To calculate the removal techniques we consider the baseline concentrations of pesticides, determined by the soil chromatographic analysis.

3. Results and discussion

3.1 Physical and chemical Soil characterization

The physicochemical analysis of the soil favourably loamy described for vegetation [8], with a neutral pH optimum of 6.68 for the solubility of essential nutrients for plants and electrical conductivity irrelevant, however signs of degradation evidenced by compacting the value the Du (1.604 g / cm3) and total porosity (23.45%), along with a low content of organic matter (1.08%) Average cation exchange capacity (17.6 meq / 100 g soil) nutrient deficiency and (P and N).

| PROPERTY | PARAMETER | RESULT | INTERPRETATION |
|----------|-----------|--------|----------------|
| PHYSICAL | Texture   | Well graded Franco | Intermediate particle size and wide variation. |
|          | Humidity (%) | HG: 2.43; HV: 3.9 | low moisture |
|          | Density (g/cm³) | Dr: 1.93; Da: 1.604 | Degradation by light compaction to medium |
|          | Porosity (%) | 23.45 | |
|          | Field capacity (mLH₂O/KgS) | 227.7 | Medium liquid retention |
| CHEMICAL | pH (U) | H₂O: 6.68; KCL: 6.26; ΔpH: -0.42 | Neutral negative colloid charge and cation exchange |
|          | Conductivity (µS/cm) | 204.6 | Negligible in altering plant growth. |
|          | CIC (meqg/100gS) | 17.6 | CIC Media, limiting availability of essential cations |
|          | CO y MO (%) | CO: 1.06; MO: 1.802 | Low content of organic component |
|          | Nutrients (mg/Kg) | N total: 1025.55; P total: 1.33 | Poor content of nutrients |

According to the results of the soil is classified as low or mineral ore with low content of organic matter. Notably, the climate of the area where the soil is important for the percentage of organic matter, for warm climates or where there are high temperatures, organic matter is degraded more rapidly due to microbial activity present [9]. Moreover, low in organic matter in the soil as associated with the limited capacity of cationic exchange of the soil. The soil shows poor fertility therefore low organic matter, signs of degradation by compaction. Table 2 organochlorine pesticides found in the soil sample under study and their concentrations, obtained by analyzing chromatography coupled with mass spectrometry gases occurs.

| Compound | Concentration of pesticide in sample (mg/kg) |
|----------|--------------------------------------------|
| trans-Clordano | 0.1 |
| 4,4'-DDE | 1.1 |
| Endrin | 1.9 |
| 4,4'-DDD | 2.4 |
| 4,4'-DDT | 9.1 |
The results show the presence of concentrations of the pesticide DDT and its metabolites DDD and DDE degradation, and other pesticides such as trans-chlordane and endrin. The present study has a primary focus on DDT to be the most toxic compound and its two metabolites DDD and DDE degradation.

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3.2.1 Chemical deshalogenation in soil

In Figure 1, a progressive increase in chloride concentrations in soil with increasing concentration of sodium bicarbonate is recorded, indicating that there is a correlation between the two parameters. In the analyzed results with high variability values are recorded, this may be because the Cl- ions in the soil were released by the dehalogenation of organochlorine compounds in the course of time and may be associated with Cl₂.

Removal concentration of chlorides in soil was obtained at different concentrations of sodium bicarbonate solution in range of 0.5% w/v (lowest) to 10% w/v (highest). Additional different flow rates corresponding to 0.4 ml/min (Fmin) and 10 ml/min (Fmax) was applied. Analysis of chlorides in soil under these conditions was presented in Figure 1.

![Figure 1. Chemical deshalogenation treatment according sodium bicarbonate concentration and the flow rate factor.](image)

The presence of chlorides after application dehalogenation confirms breaking the molecule organochlorine and release of halogen (Cl), reducing the toxicity of pesticides in soil. The results for the initial concentrations of trans-Chlordane, 4,4'-DDE, Endrin, 4,4'-DDD and 4,4'-DDT demonstrated the decrease evident in the compounds concentrations in all samples analyzed. The values obtained by applying the bicarbonate solution 0.5% w/v were the most significant in both high and low flow with minimal difference in concentrations suggesting that the flow rate factor is not representative. However, the combination of sodium bicarbonate NaHCO₃ [0.5%]-Fmax, presented better results in the dehalogenation of all organochlorine compounds evaluated.
The 4,4’-DDT in the effect of the concentration of sodium bicarbonate (NaHCO$_3$) and the effect of flow rate are positive, suggesting that increasing the concentration of sodium bicarbonate and the flow rate will increase the concentration of this pollutant, also the effect of the interaction of both factors is positive suggesting same effect generation of increased concentration of 4,4’-DDT in soil. On the other hand it is important to emphasize that the results greater magnitude in the most significant effect is the concentration of NaHCO$_3$ used.

To summarize the results of the application of design 2 for the three organochlorine compounds of interest suggest that the factor concentration of sodium bicarbonate (NaHCO$_3$), is the most important in the removal of these compounds at lower concentrations their decline in soil. After applied dehalogenation were proceeded to testing chemical oxidation technique. For determination of this factor four trials using different concentrations of KMnO$_4$ (1, 0.5, 0.25, 0.01% w/v) and analyzed after seven days contact between the oxidant [10] and the contaminated soil is made, the analysis of they performed by gas chromatography. Table 3 shows the contaminant concentration occurs den soil after applying a removal with potassium permanganate oxidant at different concentrations.

Table 3. Chemical oxidation treatment applied to contaminated soil by pesticides

| Compound          | Concentration of Potassium Permanganate |
|-------------------|----------------------------------------|
|                   | [1%]  | [0.5%]  | [0.25%] | [0.01%] |
| trans-Clordano    | 0.09  | 0.05    | 0.05    | 0.05    |
| 4,4’-DDE          | 0.65  | 1.3     | 0.74    | 0.61    |
| Endrin            | 0.64  | 2.78    | 0.74    | 0.68    |
| 4,4’-DDD          | 8.45  | 1.99    | 0.96    | 0.84    |
| 4,4’-DDT          | 1.46  | 3.23    | 1.18    | 1.08    |

According to the results of Table 3 oxidation with KMnO$_4$ to 0.25 and 0.01% w/v shows that the concentrations of the compounds had a uniform descending behavior, whereas oxidation with KMnO$_4$ and 0.05 to 1% w/v report outliers where concentrations of contaminants up again or rebound. According to the EPA this occurs when oxidants injected had no contact with any contaminated area or the oxidant is exhausted before trying all evidenced based contamination. In concentrations chosen for the oxidation process were 0.25 and 0.01% w/v.

The concentrations selected of potassium permanganate to 0.25 and 0.01% w/v were evaluated at three times 4, 7 and 14 days. Table 4 present the pesticide concentrations after applying oxidation with KMnO$_4$ in soil with pretreatment of dehalogenation.

Table 4. Concentrations of pesticides in soil by oxidation treatment using 0.25 and 0.01% KMnO$_4$. 

| Compound    | Chemical Oxidation by KMnO$_4$ 25% | Chemical Oxidation by KMnO$_4$ 0.25% |
|-------------|------------------------------------|-------------------------------------|
|             | 4 days  | 7 days | 14 days | 4 days  | 7 days | 14 days |
| trans-Clordano | 0.02    | 0.08   | 0.06    | 0.06    | 0.08   | 0.05    |
| 4,4’-DDE      | 0.54    | 1.05   | 0.93    | 0.74    | 1.08   | 0.59    |
| Endrin        | 0.6     | 0.93   | 0.72    | 0.52    | 0.74   | 0.48    |
| 4,4’-DDD      | 0.82    | 1.41   | 0.75    | 1.16    | 1.52   | 0.84    |
| 4,4’-DDT      | 1.82    | 3.08   | 2.82    | 1.33    | 2.99   | 1.61    |
The results of chemical oxidation with potassium permanganate show inconsistency in the behavior, for this reason was chosen as the criterion for selecting the combination of factors for the chemical oxidation which showed more favorable results for the elimination of the compound with increased toxicity, 4,4’-DDT. Table 4 shows that the sample with KMnO₄ [0.01%] analyzed after 4 days reports the best result for the 4,4’-DDT, however does not generate the same effect for 4,4’-DDD and 4, 4’-DDE.

As shown in Table 4, the samples in a contact time of 7 days with concentration of sodium permanganate and 0.25 to 0.01% w/v increasing concentrations recorded for the compounds tested and significantly with respect DDT a contact time of 4 days and 14 days. The results demonstrating the phenomenon of increased concentrations of contaminants referenced by the EPA, which in turn is disadvantageous for the removal of compounds.

3.3 Efficiency of removal of organochlorine

Based on the concentrations detected by gas chromatographic analysis of each applied techniques and the initial concentrations of pesticides in soil, the trend removal of organochlorine interest soil was analyzed. Figure 2 shows the trend of reduction the concentrations of organochlorine compounds by comparison the techniques applied previously selected conditions.

![Figure 2. Concentration of organochlorine pesticides during chemical treatment phases.](image)

In comparison by other techniques in specific biology treatments, the deshalogenation treatment applied in soil contaminated by pesticides is more effective in short times from 4 to 7 days. Biological techniques achieve the same removal percentages but in times of 3 to 9 months. However the chemical techniques can cause loss of soil’s microorganisms and require the application of additional techniques. The application of chemical oxidation is more effective than dehalogenation technique, but obligate to move exsitu the soil, which implies increasing cost and additional treatments.

4. Conclusions

The physicochemical analysis of the soil described for greening loam with a neutral pH optimum of 6.68 for the solubility of essential nutrients for plants and electrical conductivity irrelevant. However signs of degradation by compaction highlighted by the value of the Da (1.604 g/cm³) and total porosity (23.45%), along with a low content of organic matter (1.08%), average cation exchange capacity (17.6 meq/g / 100 g soil) and deficiency of nutrients (P and N).
Deshalogenation technique proposed has favorable results for the lower concentrations of organochlorine in the ground reaching up to 81.8%. The analysis suggested that the analysis 2 factor sodium bicarbonate concentration is more significant than the flow rate used, revealing that the lower the level of the chemical concentration greater reduction was obtained in all organochlorine.

In chemical oxidation with KMnO₄ increases, it is evident in the organochlorine concentrations in some samples, attributing this phenomenon to incomplete distribution of the oxidizing agent in the matrix of the contaminated soil. In the 2² factorial design it was determined inconsistency in the behavior of this technique, however oxidation can remove the 4,4'-DDT, DDE 4,4'- and 4,4'-DDD to different conditions each.

The removal percentages obtained in the first phase of treatment comprised dehalogenation technique were 79.0% for 4,4'-DDT, 41.8% for 4,4'-DDE and 62.9% for 4,4'-DDD. The second phase comprised by chemical oxidation favored continuous reduction of the compound 4,4'-DDT reaching up to 85.4% removal, but generated a decrease of the previously obtained removals of 4,4'- and 4,4'-DDE y DDD to values of 32.7% and 51.7% respectively.

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