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TREATMENT OF PETROLEUM-HYDROCARBON CONTAMINATED SOIL THROUGH SORPTION AND ADVANCED OXIDATION PROCESSES

THESIS

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En espera de su respuesta, reciba mis más altas y distinguidas consideraciones.

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ABSTRACT

Soil contamination due to hydrocarbon spills is common in Mexico. According to the Federal Office of Environmental Protection in Mexico (PROFEPA), in 2015 over a thousand environmental emergencies in the country were caused by hydrocarbon spills. Puebla is one of the most affected states in Mexico due to these spillages. To avoid the negative consequences of this contamination it is necessary to implement treatments that lower the contaminant concentration in the soil and allow the recovery of its productivity.

Although biological methods have proven to be effective in soil treatment, they require long periods of time to complete. Other cost effective and considerably faster technologies can be applied in order to reduce hydrocarbon concentrations to the maximum permissible limits established in the corresponding regulations. To this end, a sorption-oxidation treatment for hydrocarbon contaminated soils was evaluated through batch sorption tests using a valorized activated carbon (AC) residue, paired with advanced oxidation tests using hydrogen peroxide (H_2O_2) and potassium persulfate ($K_2S_2O_8$) as oxidants.

Soil samples were obtained from an agricultural area in the municipality of San Martín Texmelucan, Puebla. The characterization of these samples showed that the texture of the soil is loamy sand, impacted by diesel fuel, and a total petroleum hydrocarbons (TPH) concentration of 55 141 mg/Kg. The degradation and removal of hydrocarbons from soil was determined by gravimetric analysis of initial and final TPH concentrations in the soil.

Even though both treatments, sorption and oxidation, achieved good performances by themselves, none of them was able to lower the TPH concentration enough to meet the maximum permissible limit of 1 200 mg/Kg. However, by pairing both treatments in two steps, first sorption and then oxidation, a final TPH concentration of 1 075 mg/Kg was reached. Important changes were observed in the soil properties that could affect its agricultural use after treatment.

RESUMEN

La contaminación de suelo por derrames de hidrocarburos es común en México. Según la PROFEPA, la Procuraduría Federal de Protección al Ambiente en México, en 2015 más de mil emergencias ambientales fueron causadas por derrames de hidrocarburos. Puebla es uno de los estados más afectados de Mexico por estos derrames. Para evitar las consecuencias negativas de esta contaminación, es necesario implementar tratamientos que disminuyan la concentración del contaminante en el suelo y permitan recuperar su productividad.

Aunque los métodos biológicos han demostrado ser eficaces en el tratamiento del suelo, requieren largos períodos de tiempo para completarse. Se pueden aplicar otras tecnologías efectivas y considerablemente más rápidas para reducir las concentraciones de hidrocarburos a los límites máximos permisibles establecidos en las regulaciones correspondientes. Con este fin, se evaluó un tratamiento de sorción-oxidación para suelo contaminado con hidrocarburos mediante pruebas de sorción en batch utilizando un residuo valorizado de carbón activado (CA) semi-agotado, acopladas con pruebas de oxidación avanzada con peróxido de hidrógeno (H_2O_2) y persulfato de potasio ($K_2S_2O_8$) como oxidantes.

Las muestras de suelo se obtuvieron de una zona agrícola en el municipio de San Martín Texmelucan, Puebla. La caracterización de estas muestras demostró que la textura del suelo es arena francosa, impactada por diésel, y una concentración de hidrocarburos totales de petróleo (HTP) de 55 141 mg/Kg. La degradación y remoción de hidrocarburos del suelo fue determinada por análisis gravimétrico de las concentraciones iniciales y finales de HTP en el suelo.

Aunque ambos tratamientos, sorción y oxidación, lograron buenos rendimientos por sí solos, ninguno de ellos logró disminuir las concentraciones de HTP lo suficiente como para alcanzar el límite máximo permisible de 1 200 mg/Kg. Sin embargo, al acoplar ambos tratamientos en dos pasos, primero sorción y después oxidación, se alcanzó una concentración final de 1 075 mg/Kg. Se observaron importantes cambios en las propiedades del suelo que podrían afectar su uso agrícola después del tratamiento.

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INTRODUCTION

Several years ago, the use of oil became very important in human activities. Given the fact that its usage maintains high levels of risk, the pollution inherent in the use of hydrocarbons emerged with the use of this resource and its products. One of the natural elements affected by these substances is the soil. Contamination of soil due to hydrocarbon spills results in the loss of its fertility and damage to the organisms that depend on it.

Petroleum hydrocarbon spillages are common in Mexico. By the end of 2016, *Petróleos Mexicanos* (Pemex), the main oil and gas state-owned industry of the country, reported 1283.8 hectares of contaminated land by 213 events of hydrocarbon leaks and spillages (Pemex, 2017a). Poor practices in the handling of oil and its derivatives, coupled with the theft of fuels by criminal organizations, positioned Puebla as the fourth state with the greatest number of oil spills in 2014, according to the National Hydrocarbons Commission (CNH, 2014).

Hundreds of clandestine fuel intakes have been detected by Pemex in Puebla in 2017, over nine hundred from January to August (Pemex, 2017b). In September of 2017, farmers from the state of Puebla reported one hundred and twenty thousand hectares of affected land in the area that goes from the municipality of San Martin Texmelucan to the municipality of Esperanza, affecting fifteen thousand agricultural producers, and four hundred and fifty water wells (Cravioto, 2017). To avoid that these contaminated sites continue to generate negative consequences on the environment and human health and development, it is necessary to implement treatments for the soil that allow the degradation or removal of contaminants.

Among the remediation technologies used for hydrocarbon contaminated soils, biological methods stand out. These methods are based on the use of the metabolic functions of living organisms to degrade, transform or remove contaminants. Different types of organisms can be used for this purpose, such as plants, fungi or bacteria. Although these are generally effective treatments, their main disadvantage is the large amount of time they require to develop. Also, their effectiveness depends on whether soil conditions allow the development of organisms, and furthermore, lighter hydrocarbon fractions tend to volatilize during aeration processes before they can be degraded by microorganisms.

Physical methods are another type of treatments that use the physical properties of the contaminants or the contaminated medium to destroy, separate or contain the pollution. Among these physical methods, sorption processes are considered, in which one substance adheres to another one's surface or absorbed by it's structure. For its sorptive properties, activated carbon is commonly used to remove most organic and some inorganic pollutants. This process immobilizes contaminants and prevents their migration through environmental compartments.

Chemical methods, such as advanced oxidation, are also applicable to remediate soils impacted by a wide range of contaminants, including hydrocarbons. This technology can be applied in conjunction with other treatments, it is cost competitive and it is considerably faster than bioremediation since it allows contaminant degradation within days or even hours.

Given the fact that hydrocarbon spills in the state of Puebla have left extensive areas of contaminated soils in agricultural regions, the treatment of these soils and the recovery of their fertility is extremely important to allow farmers to recover their livelihood. Thus, treatment time is a significant factor in the remediation of these areas.

As an alternative to the widely used biological methods for hydrocarbon contaminated soil remediation, a treatment coupling sorption and advanced oxidation processes will be evaluated to lower petroleum hydrocarbon concentrations in a contaminated soil from the state of Puebla. This treatment will couple a sorption process using a valorized semi-wasted activated carbon residue, with an advanced oxidation process applying either a traditionally used oxidant (peroxide) or an emerging one (persulfate).

Even if sorption and advanced oxidation treatments by themselves do not lower the hydrocarbon concentrations to the maximum permissible limits, by coupling both treatments, hydrocarbon removal and degradation should be enough to meet these limits, this should be achieved in less time than with any biological treatment. Also, physical and chemical properties of the soil after treating it, should still favorable for agricultural use.

The sorption treatment was assessed with a semi-wasted activated carbon residue from one single source. Only two oxidants, hydrogen peroxide and potassium persulfate, were tested for the advanced oxidation process. Treatments were carried out in batch tests, not in columns. Also, it should be noted that this treatment was tested on soil from only one site in the state of Puebla, being diesel fuel the spilled product. Complications during the soil sampling were encountered due to insecurity issues in the areas that present hydrocarbon spillages, which are often caused by criminal organizations.

It is expected that this project opens the door to further research in the matter, in order to develop and perfect a field scale soil treatment technology. Such technology should be simple, applicable in a short period of time, and cost competitive with existing technologies. Finally, this research should have an impact in all three dimensions of sustainability: society, economy and environment, by providing an efficient soil treatment that minimizes the environmental effects of hydrocarbon spillages in soils and allows a recovery of the soil's agricultural use.

HYPOTHESIS

A sorption-oxidation treatment for hydrocarbon contaminated soil will reduce the total petroleum hydrocarbon concentration to the maximum permissible limits established in the Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012 *Maximum permisible limits of hydrocarbons in soils, guidelines for the sampling in the characterization and specifications for the remediation,* in less than 120 days.

GENERAL OBJECTIVE

To evaluate a treatment for hydrocarbon contaminated soils through sorption tests with semi-wasted activated carbon, and advanced oxidation tests with hydrogen peroxide (H_2O_2) and potassium persulfate ($K_2S_2O_8$), to reduce in less than 120 days, the concentration of total petroleum hydrocarbons to the maximum permisible limits established in the Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012.

SPECIFIC OBJECTIVES

1. To sample a contaminated site in the state of Puebla, following the *US EPA Standard Operating Procedure 2012*, and the guidelines established in the Official Mexican Standards NOM-021-SEMARNAT-2010 and NOM-138-SEMARNAT/SSA1-2012, to gather contaminated soil samples and carry out their characterization before the sorption and oxidation tests
2. To characterize the soil samples by physical and chemical analysis to qualitatively and quantitatively determine the hydrocarbons present in the site and the initial conditions of the soil, in order to identify the contaminant and define the applicability of the treatment
3. To determine the characteristics of the semi-wasted activated carbon residue by characterization of its structure (surface area and pore volume), to assess its remaining sorption capacity and determine the conditions under which the sorption tests will be carried out
4. To obtain the electron transfer coefficient of the identified hydrocarbons in the soil sample and of the selected oxidants, through computer simulations of their molecules in order to determine which interactions between these compounds are more likely to happen
5. To evaluate the sorption capacity of the semi-wasted activated carbon over time, through batch tests and the analysis of remaining total petroleum hydrocarbons in the soil, to assess the removal of contaminant off the soil and determine the effectiveness of the sorption treatment
6. To evaluate the oxidation of the hydrocarbons in the soil through batch tests of advanced oxidation, plus the analysis of remaining oxidant and total petroleum hydrocarbons in the soil, in order to assess the degradation of the contaminant and determine the effectiveness of the advanced oxidation treatment in the soil
7. To determine the effectiveness of pairing the sorption and oxidation processes previously evaluated in terms of hydrocarbon removal and degradation, using batch tests in one and

two steps, to determine if the coupling of both technologies reduces the concentration of contaminant to the corresponding maximum permissible limits in less than 120 days

8. To assess the final quality of the treated soil through physical and chemical analysis, in order to compare the initial and final state of the soil and determine whether it is possible to continue its agricultural use or suggest land use alternatives

9.

CHAPTER 1. LITERATURE REVIEW

1.1 SOIL CONTAMINATION

1.1.1 Soil and its Importance

Soil is one of the three materials that cover the surface of the earth, apart from water and rock. This material is the result of physical, chemical and biological weathering processes that slowly occur on rock minerals when they are exposed to the surface (Pulford, 2007). The deposition of this unconsolidated material upon the surface of the earth results in the creation of horizontal layers (soil horizons) with significant differences on their properties The arrangement of this layers is known as the soil profile, that goes from the surface to the hard bedrock.

In addition to the weathering processes, the formation of the soil includes the addition of organic matter, which is incorporated by the decomposition of organic residues. This combination of organic and mineral matter, which make about 50% of soil by volume (apart from air and water), is what grants this natural resource its valuable characteristics (Pulford, 2007). Plants, other forms of life, and many ecosystem processes depend on the functions of the soil. Also the process that originates this material is complex and takes long periods of time to occur, therefore, soil is an important natural resource that should be taken care of.

First of all, soil is a major carbon reservoir, which is in constant exchange with the atmosphere, mainly by the uptake and fixation of carbon dioxide (CO_2) by plants. Increasing the carbon content on and in the soil improves some of its chemical and physical properties, for example: nutrient storage and water holding capacity. These properties may enhance other soil functions at the same time, such as agricultural production and biodiversity, thus improving soil quality (Food and Agriculture Organization of the United Nations, 2015).

But the carbon cycle is not the only biogeochemical process in which soil takes part. Soils also have an important function as providers of nutrients to plants, being indirectly vital to humanity. The main nutrients provided by the soil are nitrogen, phosphorous and potassium, known as macronutrients. These elements are so important that they tend to be limiting factors to productivity and are constantly cycling through air, plants, water and of course, soil (FAO, 2015). Some other elements that function as micronutrients, such as calcium, magnesium, sulphur, iron and other metals, are also present in the soil.

Another important service provided by the soil is the purification and storage of water. Soil water stabilizes the land and prevents erosion. The capacity of the soil to retain water is determined by its texture. This water retention has an important role in the development of microorganisms and plants (FAO, 2015). This support of organisms is another important service provided by the complex physical and chemical properties of the soil in terms of biodiversity.

All these essential ecosystem services provided by the soil, usually depend on its quality and its physical, biological and chemical properties. Physical properties of the soil refer to the proportion of sand, silt and clay in a soil (property known as texture) and the arrangement of these particles (structure). The biological properties of the soil are based on the presence of living organisms that break down organic matter, degrade substances, incorporate nutrients into the soil, change its structure, and act harmfully or beneficially to the growth of plants (Stirling *et al.*, 2016).

On the other hand, chemical properties of the soil reflect on a wide range of parameters that change over time. Some of these parameters are: pH, a measure of the concentration of hydrogen ions (H^+) and an indicator of acidity or alkalinity; electrical conductivity (EC) is a measure of the amount of salts in a soil solution, and an indicator of soil salinity; cation exchange capacity (CEC) is a measure of the total exchangeable cations in the soil and its ability to supply nutrients as cations (Stirling *et al.*, 2016). Other chemical properties of the soil are described of course, by the amount of chemical substances that it contains, such as: soil organic matter (SOM), total nitrogen (N), extractable phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), and extractable micronutrients like iron (Fe), copper (Cu), zinc (Zn) and so on.

1.1.2 Soil Contamination by Hydrocarbons

According to the Mexican General Law of Ecological Balance and Environmental Protection (LGEEPA, 2017), a contaminant is all matter or energy in any of their physical states and forms, that when incorporated into the atmosphere, water, soil, flora, fauna or any natural element, alters or modifies its composition and natural condition. Thus, when the composition of the soil changes due to the presence of a substance in greater concentration than its natural state, that soil is contaminated. This results in chemical, physical or biological alterations.

When soil contamination contamination occurs as a result of human activities, it is often referred as pollution (Bini, 2010). Such contamination can be local, when activities or accidents introduce excessive amounts of contaminants directly into the soil, or diffuse when the contaminants are transferred by another media, for example, atmospheric deposition. In many developed countries, the main sources of local soil contamination include waste disposal, industrial activities, transport spills, and military or nuclear operations. On the other hand, in developing countries, some causes of soil contamination are the lack of legal regulations and inadequate waste management (FAO, 2015).

One of the major causers of local soil pollution are industrial activities, among them, the oil industry. Petroleum hydrocarbon contamination results from activities that involve petroleum (crude oil) and its products. Since these substances are often defined as a complex mixture of organic compounds, there are some constituents that are extremely harmful to health and the environment, and some constituents that are not (Speight & Arjoon, 2012).

Petroleum is a complex mixture of substances named hydrocarbons, which are organic compounds mainly formed by carbon and hydrogen atoms, although some compounds may contain a few atoms of sulfur, oxygen, nitrogen or metals. The composition of petroleum actually varies from site to site depending on the place where it was formed. This determines in great extent the concentration of sulfur, nitrogen and metals found in crude oil, as well as the proportions of the different hydrocarbons present in it.

Petroleum occurs underground, when organic matter from remains of plants and animals, is decomposed by the effect of the high temperature and pressure conditions present in the depths of the earth. This precious material is extracted and submitted to a refining process (basically distillation) that separates its components to obtain valuable products that satisfy wide-ranging human needs. These products include fuels (gasoline, kerosene, diesel), solvents, waxes, asphalt, and other carbon sources for the manufacturing of synthetic fibers, rubbers, plastics, fertilizers, and so on. The use of petroleum has been present in humanity since pre-Christian times (Speight, 2006) and today, it is so important that in 2016, the world consumed a total of 4 418.2 million tonnes of oil, remaining as the number one energy source globally (BP plc, 2017).

Hydrocarbons are divided in fractions or ranges, based on their molecular weight, which depends on the number of carbon atoms found in their molecules. The compounds with similar molecular weight usually have similar properties, not only chemical ones, but also toxicological. According to the Official Mexican Standard NOM-138-SEMARNAT/ SSA1-2012, hydrocarbons can be classified in Light Fraction Hydrocarbons (from 5 to 10 carbon atoms), Medium Fraction Hydrocarbons (from 11 to 28 carbon atoms), and Heavy Fraction Hydrocarbons (from 28 to 40 carbon atoms). On the other hand, the classification of Petroleum Hydrocarbons by Ranges, includes Gasoline Range Organics (GRO), Diesel Range Organics (DRO), and Residual Range Organics (RRO), such classification by the Agency for Toxic Substances and Disease Registry (ATSDR, 1999), matches with the classification by fractions, respectively.

However, since all petroleum products contain a wide variety of compounds, it is not convenient to analyze each one of them, instead it is more convenient to measure all hydrocarbons present as Total Petroleum Hydrocarbons (TPH). TPH is the term used to describe the combination of such vast group of chemical substances derived originally from crude oil.

The chemical composition of these complex hydrocarbon mixtures includes different families of compounds: alkanes, branched alkanes, and cycloalkanes (paraffins, iso-paraffins, and naphthenes, in petroleum terms), alkenes (olefins), aromatic constituents that range from benzene to multiple fused rings, and molecules containing not only carbon and hydrogen atoms, like thiol (mercaptan), pyridines, pyrroles, phenols, carboxylic acids, amides. Graphic examples of the structures of these compounds can be found in **Figure 1.1**. For convenience, these hydrocarbon components are divided in three classes: Paraffins, Naphthenes, and Aromatics (Speight, 2006). Olefins are not included because they are rare components of crude oil, however they may be present in fuels as products of thermal reactions.

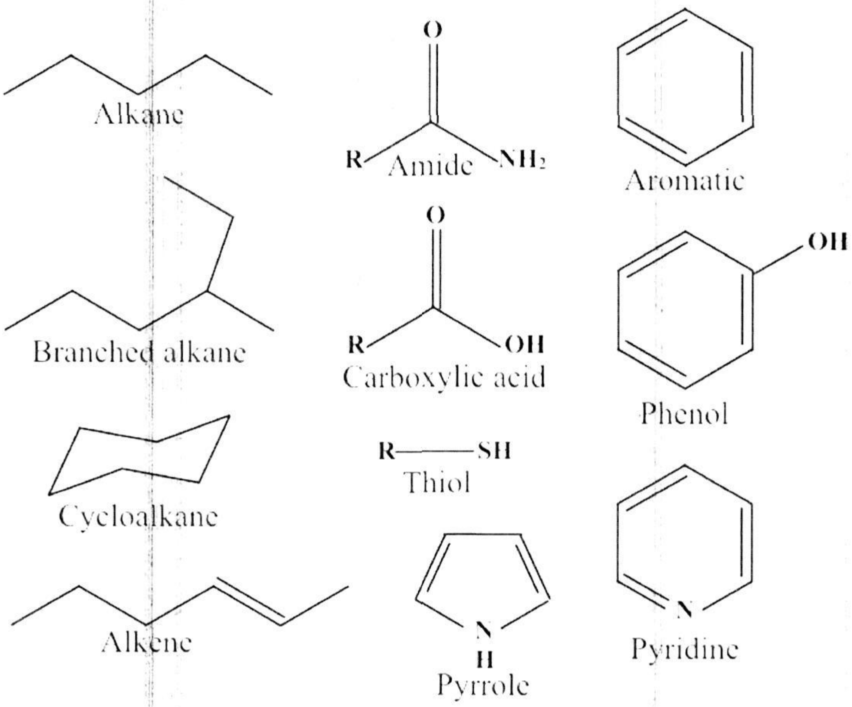

Figure 1.1. Structures of functional groups found in petroleum

The paraffins group (formula C_nH_{n2+2}) includes saturated hydrocarbons with straight or branched chains, they are quite stable and their reactions generally happen by the substitution of their hydrogen atoms by another element or chemical group. The naphthenes group (C_nH_{2n}) contemplates saturated hydrocarbons containing rings and they can only react by the replacement of hydrogen atoms for another element. Finally, aromatics are hydrocarbons containing any amount of aromatic rings (formula C_nH_{2n-6}), these hydrocarbons react via substitution or addition of atoms, also they are susceptible to oxidation, forming organic acids (Speight, 2006; Nelson & Benet, 1958).

When talking about hydrocarbons there are a couple of terms that are quite common: BTEX and PAH. BTEX means Benzene-Toluene-Ethylbenzene-Xylenes, and refers to the analysis of such hazardous compounds to measure gasoline or diesel contamination. Nevertheless modern fuels are better refined and have a higher percentage of straight chain alkanes and not many aromatics, thus BTEX analysis may underestimate the presence of hydrocarbons (Speight, 2006). On the other hand PAH, specifically refers to Polycyclic Aromatic Hydrocarbons, a class of organic compounds known for their toxicity and carcinogenic, teratogenic, and mutagenic effects (Liao *et al.*, 2014; Bispo *et al.*, 1999; Kim *et al.*, 2007).

Unfortunately, the use of petroleum-hydrocarbons often results in serious environmental problems due to their hazardous properties. Petroleum products can be released into the environment by superficial spills or leaks, resulting in soil and water contamination (Yang *et al.*, 2015; Iturbe *et al.*, 2007). These hydrocarbon spills occur frequently in soils and negatively alter their chemical, biological and physical properties (Nwomandah & Mounem, 2013).

Hydrophobic molecules, like hydrocarbons, bind tightly to soil particles (Gong *et al.*, 2007). TPH are sorbed into the soil particles, associating with soil organic matter, so the strength of the hydrocarbon sorption will vary according to the nature of the hydrocarbon and the quantity of organic matter in the soil. When hydrocarbons are discharged into the soil, they will be susceptible to volatilization, reaction, degradation, or leaching and transport to other environmental compartments (Sadler & Connell, 2003).

TPH are considered persistent hazardous contaminants that include some bioaccumulative compounds. They are also toxic and some components, like benzene and PAHs, are recognized as carcinogens (ATSDR, 1999). The toxicity of hydrocarbons in flora and fauna has been demonstrated due to the changes that TPH products produce on the soil. In fact, even toxicological tests can be used as indicators of soil contamination by hydrocarbons (Hentati *et al.*, 2013).

Hydrocarbon spillages have negative impacts in soil, such as destruction of life, loss of fertility and inherent pollution of air and water. Hydrocarbons in soils damage the terrestrial biota, the soil properties, and the plant communities because they inhibit photosynthesis, transpiration and respiration. Since nutrient concentration and availability decreases in contaminated soils, the destruction of bacterial and fungal populations on contaminated soils could be attributed to changes in chemical constituents, nutrients and oxygen supplies (Bello & Inobeme, 2015). The presence of hydrocarbons in the soil creates conditions that make essential nutrients unavailable to plants. Also, infertility due to the destruction of soil microorganisms, and lower rates of germination and plant growth have been demonstrated (Oyem & Oyem, 2013; Adam *et al.*, 2002).

The effects of soil contamination are not entirely environmental issues. Soil contamination also has serious repercussions in economy and society, affecting all three pillars of sustainability. The increase in soil infertility results in the abandonment of degraded agricultural land, because farmers leave to look for other way of living (Bello & Inobeme, 2015). Also, diseases increase in polluted sites, as well as disturbances in communities that feel cheated by oil companies exploiting resources and leaving nothing in return (Oyem & Oyem, 2013).

1.2 SOIL REMEDIATION AND LAND RESTORATION

A contaminated site is defined by the Mexican General Law for the Prevention and Integral Management of Waste (LGPGIR, 2015), as a place, space, soil, water, facility or their combination, that has been contaminated with materials or waste that, because of their quantities and characteristics, they may present a risk for human health, living organisms and the exploitation of resources.

As any risk for the population and for the environment, such condition should be evaluated and corrected until it is no longer a threat. Remediation is precisely the group of activities to which contaminated sites are subjected to eliminate or reduce the contaminants to a safe level for health and environment, or to prevent their dispersion in the environment (LGPGIR, 2015).

It should be noted that remediation is not the same as restoration. Restoration is the group of activities directed to the recovery and reestablishment of the conditions that favor the evolution and continuity of the natural processes (LGEEPA, 2017). This means that a site can be remediated by eliminating the contaminant but this does not necessarily lead to the restitution of the natural conditions of the site.

Remediation technologies involve unitary operations that alter the composition of the contaminant and reduce its toxicity or mobility, through chemical, physical, biological or thermal procedures known as treatments (LGPGIR, 2015). The application of a remediation technology depends on the site characteristics and the physicochemical properties of the contaminant (Volke & Velasco, 2002).

In contaminated sites, the chemical characteristics of the contaminant and the physical characteristics of the receptive media will determine the persistence and concentration of the contaminant, as well as its extension and depth (horizontal and vertical migration), plus the evaporation of volatile compounds. Thus, before applying any remediation technology, a characterization should be carried out, this is the quantitative and qualitative determination of the contaminants present, that originated from hazardous materials or waste, to estimate the magnitude and kind of risks that the contamination entails (LGPGIR, 2015).

The principles behind any treatment are: 1) the destruction or modification of the contaminants (altering the chemical structure of the contaminant), 2) the extraction or separation of the contaminants from the contaminated media according to their physical and chemical properties, and 3) the isolation or immobilization of the contaminant through stabilization, solidification or containment. The application of any remediation technology depends on these principles, the contaminant, the characteristics of the site, and of course the viability of applying such technology (Volke & Velasco, 2002; Federal Remediation Technologies Roundtable FRTR, 2007).

In Mexico, according to the Regulations to the General Law for the Prevention and Integral Management of Waste (RLGPGIR, 2006), the execution of remediation programs in soils can follow any of these three approaches: 1) in the contaminated site (In situ), when the treatment is applied directly in the soil without excavation or removal, 2) at the side of the contaminated site (Ex situ, on-site), when the treatment is applied in an area that is located next to the contaminated site with the previous removal of the soil, which is transferred into a treatment area specially built for this purpose, and 3) out of the contaminated site (Ex situ, off-site), when the soil is removed and transferred to authorized facilities outside of the contaminated site, for treatment.

According to the treatment principle behind the remediation technology, they can be classified in three types: biological treatments (bioremediation), physical/chemical treatments, and thermal treatments (Volke & Velasco, 2002; FRTR, 2007).

1.2.1 Bioremediation

Biological treatments are based on the metabolic functions of living organisms to degrade, transform or remove contaminants. Bioremediation processes are complex and can include reduction-oxidation (redox) reactions, sorption processes, ionic exchange processes, and even some chelation reactions that result in the immobilization of metals. Such processes can be developed by original organisms from the contaminated site, or from other sites (Volke & Velasco, 2002).

All types of biodegradation can be used to remediate soils contaminated with hydrocarbons, specially fuels. In presence of enough oxygen, organisms will convert organic contaminants to carbon dioxide, water and cell mass. In absence of oxygen, the contaminants will turn into methane. However, biodegradation may not be complete and hazardous intermediate products may be produced (FRTR, 2007; Boopathy, 2000). Since the metabolic processes of the organisms are not well understood yet, their by-products cannot be predicted, so toxic and soluble compounds may be produced (Macek *et al.*, 2000).

Bioremediation can be done on site, it is not expensive ($130 to $2 300 USD per cubic meter of soil according to the FRTR, 2007), and has greater public acceptance than physical or chemical methods. Despite such benefits, biological methods present some disadvantages too, like strict government regulations, specially for the use of genetically modified organisms. Also, the development of the organisms depends on many factors that need to be controlled, and some contaminants are not even susceptible to bioremediation (Boopathy, 2000). In the attempt to provide such conditions for the development of the organisms, lighter compounds tend to evaporate during aeration processes before they can even be degraded by the organisms (Khan *et al.*, 2004).

Some biological remediation technologies used for petroleum-hydrocarbon contaminated soil include (FRTR, 2007; Boopathy, 2000; Khan *et al.*, 2004):

- Bioventing: Stimulates the natural in situ biodegradation by injecting air (oxygen) to the soil
- Enhanced bioremediation: The injection of water with nutrients and dissolved oxygen to maximize biodegradation
- Phytoremediation: The use of plants to remove, stabilize and destroy contaminants
- Biopiles: The soil is excavated and arranged in piles. Factors like moisture, pH, temperature, nutrients and oxygen supply, are continuously controlled to enhance biodegradation
- Composting: Soils are excavated and mixed with organic amendments (organic waste). The mixture is oxygenated, and moisture and temperature are controlled
- Landfarming: Contaminated soil is excavated, applied into lined beds, and periodically turned over or tilled to aerate the waste. Moisture, oxygen levels, pH and nutrients need to be controlled too
- Slurry phase biological treatments: An aqueous slurry is created by combining soil with water and other additives. The slurry is mixed to keep solids suspended and microorganisms in contact with the soil contaminants. Upon completion of the process, the slurry is dewatered

Of course, one of the main drawbacks of bioremediation, is that these processes require long periods of time to develop (Volke & Velasco, 2002). These periods of time range from a few months to over a couple of years, depending on the technology applied, as resumed on **Table 1.1**.

Table 1.1 Treatment time of some biological remediation technologies

Treatment	Treatment time	Source
Biopiles	6 months to 2 years	Khan *et al.*, 2004
Phytoremediation	6 months	Macek *et al.*, 2000
Bioslurry systems	1 month to over 6 months	Khan *et al.*, 2004
Bioventing	6 months to 2 years	Khan *et al.*, 2004
Landfarming	15 months	Al-Awadhi *et al.*, 2008
Composting	5 months	Jørgensen *et al.*, 2000

1.2.2 Thermal Treatments

Thermal treatments offer a quick cleanup, but they are the most expensive treatments due to the complex equipments and the high amount of energy required ($44 to $1500 USD per cubic meter, according to the FRTR, 2007). These processes are based on the use of heat to separate (volatilization), burn, decompose, detonate or melt the contaminants Apart from the high costs, these technologies may produce gasses that require further treatment, and solid or liquid waste that need to be treated or confined as hazardous waste (FRTR, 2007; Volke & Velasco, 2002).

The thermal treatments usually applied for soils contaminated with hydrocarbons are (FRTR, 2007):

- Thermal desorption: Soil is heated to volatilize water and the organic contaminants sorbed on the soil (temperatures are usually not high enough to oxidize them, between 90 and 320 °C). A gas or vacuum system carries the volatilized compounds to a gas treatment system. This process does not degrade the contaminant, but merely separates it from the soil.
- Incineration: Soil is exposed to high temperatures (between 870 to 1200 °C) to combust or volatilize the organic contaminants in the soil. Additional fuel is usually necessary to carry out this combustion and the gasses produced may require treatment.

1.2.3 Physical and Chemical Treatments

Physical and chemical treatments use the chemical and physical properties of the contaminants or the contaminated media to destroy, separate or contain the pollution. These technologies are generally cost effective and unlike bioremediation, they can be completed in short periods of time (Volke & Velasco, 2002).

The difference between physical and chemical treatments, is that in physical processes, the chemical properties of the substances are not changed, reason why physical treatments are often used as pretreatments. Physical treatments are usually applied to separate the different phases or substances for further treatment by separate.

A common physical/chemical remediation technology for hydrocarbon-contaminated soils is the one known as SVE, which means Soil Vapor Extraction. This technology is applied for soils contaminated with light hydrocarbons, where vacuum is applied to the soil to favour the flow of air that volatilizes the contaminant from the soil. The gasses need to be recovered or treated (FRTR, 2007).

The remediation technologies mentioned above are traditional technologies, which means that they have been widely used at field scale and their effectiveness has been proven. There are other emerging technologies that are in still in development, and their costs, effectiveness and applicability are still not well defined (Volke & Velasco, 2002). Since contaminated sites remediation presents economic, environmental and technical challenges, innovative solutions are needed to meet cleanup goals while minimizing costs and environmental impacts (Zimmerman *et al.*, 2004)

As alternatives to the existing remediation technologies, current research is investigating other promising technologies like the use of adsorbents, or in situ chemical oxidation (Apul *et al.*, 2016; Hilber & Bucheli, 2010; García-Delgado *et al.* 2015; Liu, *et al.*, 2015; Huling & Pivetz, 2006; Ranc *et al.*, 2016; Chen *et al.*, 2015). The combination of different remediation technologies has been proposed to achieve higher remediation efficiencies (Chen *et al.*, 2015; Gong, 2012; García-Delgado *et al,* 2015; Munakata-Marr et al., 2010). For purposes of this research, two of these novel technologies will be further detailed: sorption and advanced oxidation.

Sorption

The adsorption and absorption processes, collectively referred to as "sorption" (Fang & Chaney, 2016), are included in physical remediation technologies. They are applicable to remove most organic and some inorganic contaminants. These processes are often used for treatment of liquids and gases, although their use for soil treatment has been investigated in recent years. (Meynet *et al.*, 2012)

Absorption is the assimilation of a liquid or a gas into a solid, or a gas into a liquid. On the other hand, adsorption is the adhesion of the molecules of gases, liquids or dissolved substances (adsorbate) to the surface of a solid or liquid particle (adsorbent) (Knödel *et al.*, 2007).

Sorption mechanisms are usually categorized as physical adsorption, based on weak molecular forces; Chemisorption, where a chemical reaction forms bonds between the pollutant and the surface of the solid; And electrostatic sorption, which involves ion adsorption (FRTR, 2007). Several adsorbents are used for decontamination of soil and water. Among them, activated carbon (AC) is one of the best adsorbents for organic compounds due to its hydrophobicity, high specific surface area (800-1200 m2/g), and porous structure (Vasilyeva et al., 2006).

AC is a manufactured, clean type of black carbon with strong sorbing properties. It is produced from coal, peat or other carbonaceous materials, by incomplete combustion followed by activation (Brändli et al., 2008). The carbonization of the material is achieved by heating the carbonaceous material at extremely high temperatures in absence of oxygen. The resulting carbon is activated with acids or oxygen.

AC has a structure similar to graphite. The performance of this material is influenced by its surface area and pore volume (Nunez & Guerreiro, 2011). The pore structure of AC has macropores (> 50 nm), mesopores (2 - 50 nm) and micropores (< 2 nm) (Roussak & Gesser, 2013). Micropores of its structure is where most of the adsorption takes place, specially for small-sized molecules.

The primary source of information on the adsorption process is the adsorption isotherm, it represents the distribution of the adsorbed material between the adsorbed phase and the solution phase at a particular temperature. Isotherms can be used to select the appropriate AC type, to estimate the carbon service life, and to test the remaining sorption capacity (Cecen & Aktas, 2011).

AC has been widely used for many applications in water and wastewater treatment, as well as treatment of gaseous phases (Nunez & Guerreiro, 2011). This material has the capacity to remove a broad range of contaminants, from dyes to hydrocarbons and pesticides (Itodo *et al.*, 2010; Yu *et al.*, 2009; Vasilyeva *et al.*, 2010; Gong *et al.*, 2007). The use of AC for environmental purposes is so important that environmental regulations are boosting up its use and its global market, that is projected to reach 3.0 million metric tons by 2024 (Global Industry Analysis Inc., 2017). In 2015, this market was valued at 4.74 Billion USD and it is projected to reach 8.12 Billion USD by 2021 (Markets and Markets, n.d.).

The adsorptive capacity of carbons gradually deteriorates upon usage. When the carbon is exhausted, it has to be regenerated, reactivated or disposed of. The regeneration of spent adsorbents involves removal of the contaminants from the carbon without destroying the contaminants. Reactivation means destroying the contaminants and reactivating the carbon, usually through thermal processes. If regeneration is not feasible, or the carbon is irreversibly contaminated by the adsorbed substance, the spent carbon is disposed of as hazardous waste. (Cecen & Aktas, 2011)

AC regeneration implies reduced solid waste handling. However, there are some disadvantages of this process associated with air pollution. Moreover, thermal regeneration is energy intensive, that is, it requires large amounts of energy (Cecen &Aktas, 2011). Also, this is a costly process and has encouraged an increasing research concerning low-priced alternatives for regeneration processes. (Ledesma *et al.*, 2015)

When AC is used for soil treatment, it reduces the bioavailability of organic pollutants because of its strong adsorption properties (Hilber & Bucheli, 2010). This material is cost effective, it avoids the migration of pollutants and it is usually more effective than other methods, like phytoremediation. AC has been tested in laboratory and field studies, to remove pesticides, PAH, polychlorinated biphenyls, and nitro compounds (Brändli et al., 2008; Yu *et al.*, 2009; Vasilyeva *et al.*, 2010; Gong *et al.*, 2007; Zimmerman *et al.*, 2004), with removal efficiencies of up to 100% in laboratory studies, and up to 98.1% in field studies (Hilber & Bucheli, 2010).

One of the disadvantages of sorption processes in soils using AC is that when the material is saturated, the wasted AC needs to be disposed of, or the contaminants need to be desorbed. Also, since it is an emerging technology, further studies on the dynamics of the contaminant removal are required, as well as the effects of the material on the living organisms in soil, and its physical alteration.

For soil treatment, activated carbon is added in aqueous suspension in field studies, in which a rapid incorporation of the AC into the soil is reported. On the other hand, in laboratory studies, the soil is mixed with the AC manually or with mixers. It is necessary to balance the advantages and disadvantages of this treatment, and consider its use with other remediation technologies to optimize the treatment according to the demands of each site. (Hilber & Bucheli, 2010)

Despite the advantages of sorption processes with AC as a treatment, the AC to be used is required to have certain characteristics and to be available in sufficient quantities. For this reason, the use of spent or semi-wasted carbon has been investigated (Martínez-Gallegos *et al.*, 2017), which means valorizing the AC residues. Valorization is the principle and group of associated actions with the objective of recovering the remaining value or calorific value of the materials that compose waste (LGPGIR, 2015).

One of the advantages of the use of AC for soil remediation is that it is cost effective compared to other technologies. However, remediation costs tend to increase with the extent of the contaminated area, which requires higher quantities of AC (Hilber & Bucheli, 2010).

According to Patmont *et al.* (2015), the costs of in situ treatment of sediments using AC ranges from \$100 to \$500 USD per cubic meter. Again, site specific conditions can result in varying cost outcomes. In the USA, the price of granular AC was between \$1.65 to \$9.90 USD per Kg, and powdered AC was priced between \$0.80 to \$2.00 USD per Kg (Roussak & Gesser, 2013).

Advanced Oxidation

Chemical oxidation is a physical/chemical treatment that involves reduction-oxidation (redox) reactions that transform toxic or hazardous compounds into stable, less mobile and less toxic or non-hazardous substances (Volke and Velasco, 2002). Oxidation not only decreases the toxicity of contaminants, but also increases their bioavailability (Chen *et al.*, 2015).

Some of the oxidizing agents most commonly used to treat hazardous pollutants in soil are permanganate (MnO_4^-), hydrogen peroxide (H_2O_2, along with iron, known as Fenton oxidation), ozone (O_3) and persulfate ($S_2O_8^{2-}$), the newest oxidant being used for remediation purposes (Huling & Pivetz, 2006; Chen *et al.*, 2015). According to Huling & Pivetz (2006), the amenability of petroleum hydrocarbons, BTEX, benzene and PAHs to oxidation transformations, ranges from good to excellent for persulfate and Fenton's reagent.

Redox reactions are processes in which electrons are exchanged between the reacting chemical species, like atoms, molecules or ions. The oxidant is the substance that is reduced (it gains electrons), whereas the substance that loses electrons is oxidized and called the reductant. These gains and losses of electrons from such reactions can be measured by the electrical potential (either oxidation or reduction potential, depending on the oxidation and reduction half reactions) measured in volts (V) (Crittenden *et al.*, 2012).

Advanced oxidation processes (AOPs) are part of chemical oxidation remediation technologies. AOPs involve the production of free radicals, highly reactive chemical species with a higher reduction potential (tendency to gain electrons) than the oxidant that originated them. Initially AOPs only included the generation of hydroxyl radicals ($OH\cdot$), but the concept has been extended to include oxidative processes with sulfate radicals ($SO_4\cdot^-$) (Deng & Zhao, 2015).

One way to produce hydroxyl radicals ($OH\cdot$) is by combining H_2O_2 and ferrous iron (Fe^{2+}) through the process described by **Equation 1.1**. This combination of reagents is known as the Fenton reagent, that produces $OH\cdot$ radicals with a reduction potential of 2.76 V, meanwhile hydrogen peroxide has a reduction potential of 1.78 V (Bennedsen et al, 2014; Huling & Pivetz, 2006).

$$H_2O_2 + Fe^{2+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Fe^{3+} \qquad \textbf{Equation 1.1}$$

On the other hand, sulfate radicals ($SO_4^{\cdot -}$) can be produced by the activation of $S_2O_8^{2-}$ either with heat, UV light, or transition metals, through the processes described by **Equations 1.2 and 1.3**. Sulfate radicals generated from activated persulfate have a reduction potential of 2.6 V, versus $S_2O_8^{2-}$ itself, which has a reduction potential of 2.01 V (Deng & Zhao, 2015; Tsitonaki et al, 2010).

$$S_2O_8^{2-} \xrightarrow{\text{heat/UV}} 2SO_4^{\cdot -} \qquad \textbf{Equation 1.2}$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + M^{n+1} \qquad \textbf{Equation 1.3}$$

Oxidants have been tested in liquid phase for the removal of hydrocarbons in soils, with favorable results (Apul et al., 2016). When an oxidant is added to contaminated soil and a redox reaction takes place, electrons are transferred from the reductant (the contaminant) to the oxidant. In organic pollutants, these oxidation processes form free radicals that initiate a radical chain oxidation or attack single or resonating π electrons (double or triple bonds). Radicals react with most organic compounds by undergoing addition reactions with double bonds or extracting hydrogen atoms from organic compounds (Crittenden *et al.*, 2012).

Among the AOPs mentioned above, the Fenton oxidation process (H_2O_2/Fe^{2+}) is one of the most effective decontamination methods for organic pollutants. Fenton processes have proven to yield very good results for complete mineralization or destruction of organic compounds. Fenton reaction essentially depends on four factors: temperature, hydrogen peroxide concentration, iron concentration and pH (Abou-Elela *et al.*, 2016; Tsai & Kao, 2009; Kakarla *et al.*, 2002).

Although Fenton's chemistry is more than 100 years old, the strong reactivity of Fenton's reagent with hazardous compounds present in soil and groundwater has been demonstrated, resulting in effective contaminant destruction. A traditional Fenton's reaction involves the catalytic decomposition of hydrogen peroxide to form the hydroxyl radicals. Many common contaminants including petroleum and chlorinated compounds can be oxidized in a matter of hours using an appropriate treatment stoichiometry (Kakarla et al., 2002).

One of the main advantages of the Fenton reagent, is that the free radical produces is a powerful oxidant that will react rapidly with many contaminants. These reactions develop rapidly (in less than 12 hours), and are aided by the presence of intermediate chemical species that also oxidize complex mixtures of organic compounds. However, the characteristics of peroxide can lower the effectiveness of this treatment due to rapid decomposition, acidification, production of gaseous oxygen, and the release of heat (Huling & Pivetz, 2006).

On the other hand, persulfate is one of the most innovative oxidants, highly effective in the treatment of fuel-contaminated soil. Persulfate can remain active in soils and aquifers from weeks to months, it is not influenced by pH, and can oxidize a wide range of pollutants; including aromatic hydrocarbons with low (2-3 rings) and high (4-6 rings) molecular weight. Thus, the application of persulfate can reduce the toxicity of hydrocarbons and limit their effects on the environment (Liao *et al.*, 2014; Huling & Pivetz, 2006; Tsitonaki *et al.*, 2010).

Also, it should be noted that high concentrations of persulfate (over 5%) result in a reduction of remediation time (Chen *et al.*, 2015). Nonetheless, advanced oxidation with persulfate is an emerging technology and further research on its processes and effects is still required.

An important thing to consider in chemical oxidation remediation is the byproducts produced by the chemical reactions. In petroleum-hydrocarbon contaminated soils, oxidation processes convert hydrocarbons into less-complex, water-soluble and biodegradable compounds, susceptible to environmental weathering processes. Some byproducts include aldehydes, carboxylic acids, mineral acids, and of course carbon dioxide (Apul *et al.*, 2016; Crittenden *et al.*, 2012) and water (when the mineralization of the contaminant is complete).

Chemical oxidation is a cost competitive remediation technology. Sodium persulfate costs $2.70 USD per kilogram, and hydrogen peroxide costs $0.57 to $2.00 USD for the same amount (Huling & Pivetz, 2006; Chen *et al.*, 2015). The costs for chemical oxidation remediation in soil, considering excavation (ex-situ) range from $190 to $660 USD per cubic meter (FRTR, 2007).

To summarize, the advantages of oxidation processes over other remediation technologies include: 1) very special soil conditions are not required like in bioremediation, 2) a wide range of contaminants are susceptible to oxidation, 3) oxidants are cost competitive depending on the concentration needed, and of course 4) the redox reactions that occur during these chemical oxidation remediation processes are fast and this reduces remediation time.

Finally, it should be noted that conditions of contaminated soils vary from site to site depending on the characteristics of the soil and the properties of the contaminant. This can hinder the estimation of the required doses of oxidant, which can be estimated by the stoichiometric oxidant demand, that considers the concentrations and composition of the contaminants, plus an experimental design methodology that allows the optimization of laboratory test results (Ranc *et al.*, 2016).

1.3 CONTEXTUAL FRAMEWORK

1.3.1 Petroleum-Hydrocarbon Contaminated Soils in Mexico

About 2 000 million hectares of soil, 15% of the surface of the Earth has been degraded by human activities. In Mexico, 142 million hectares of soil out of the 200 million that cover the country, are in process of degradation, either by water or wind erosion, and chemical or physical degradation (Colegio de Postgraduados, 2013). According to the Mexican Ministry of Environment and Natural Resources (SEMARNAT, 2014), in 2002, 34.04 million hectares of Mexican soil (17.8% of the surface of the country) were affected by chemical degradation processes, which include soil pollution.

Mexico has a very important oil industry. In 2014, oil sales contributed with over 30% to to Federal income (CEFP, 2015). Before the Mexican Energy Reform, Petróleos Mexicanos (Pemex), the state-owned energy company, was in charge of the exploration, production, transformation, storage and distribution of crude oil and its products.

The transport of oil and its products is still a crucial operation for the production-transformation-distribution cycle. Transportation of hydrocarbons, either liquids, gases or mixtures, is performed by pipelines that run throughout the country. It has been reported that more than 30% of the oil pipelines in Mexico have been operating for more than 30 years, although their duration has been estimated in 25 to 30 years (Iturbe et al., 2007).

Petroleum hydrocarbon spillages are common in Mexico. By the end of 2016, Pemex reported 1283.8 hectares of contaminated land by 213 hydrocarbon leaks and spillage, mainly caused by duct damage and criminal activity (Pemex, 2017a). According to the National Hydrocarbons Commission, from 2000 to 2014, Puebla was in the fourth place of the Mexican States with most oil spills, with 6.93 thousand barrels of oil spilled (CNH, 2014). In this region, spills that affect human life, crops, irrigation systems, soils, animals and the environment in general, are detected each year. (Cavazos-Arroyo *et al.*, 2014)

Fuel theft in Mexico increased hydrocarbon spills in pipelines by 466% during the first four years of the administration of Enrique Peña Nieto in comparison to the previous administration. In these first four years, the Federal Office of Environmental Protection in Mexico (PROFEPA) detected 4 290 hydrocarbon leaks (Hernández, 2017). This criminal activity is a worsening crisis that makes the federal government loose more than a Billion USD a year, with the theft of over 1.47 million gallons of fuel a day. Mexico's largest criminal organizations are involved in this activity, using bribery and violence to co-opt government people, Pemex workers, and members of the population by offering criminal employment with high wages (Semple, 2017).

In Puebla, this criminal activity is concentrated in a cluster of rural municipalities located in the center of the state, known as the *Triángulo Rojo (*Red Triangle), an area where pipelines transport oil products from the state of Veracruz, in the Gulf of Mexico to Mexico

City, the capital of the country (Semple, 2017). This activity represents further risks for the population, like the events occurred in 2010 in the municipality of San Martín Texmelucan, where an explosion caused by a clandestine intake killed 30 people and injured 12. At 5:50 hours a clandestine intake got out of control and a diesel leak from the pipeline caught fire, affecting over a hundred homes.

Over 7 000 clandestine fuel intakes have been detected throughout Mexico by Pemex in in 2017, from January to September. More than a thousand of these intakes correspond to the state of Puebla, only outnumbered by Guanajuato with 1 400 intakes in the same period (Pemex, 2017b). In September of 2017, farmers from Puebla reported 120 thousand hectares of affected land in the area that goes from the municipality of San Martin Texmelucan to the municipality of Esperanza, affecting 15 000 agricultural producers, and 450 water wells (Cravioto, 2017).

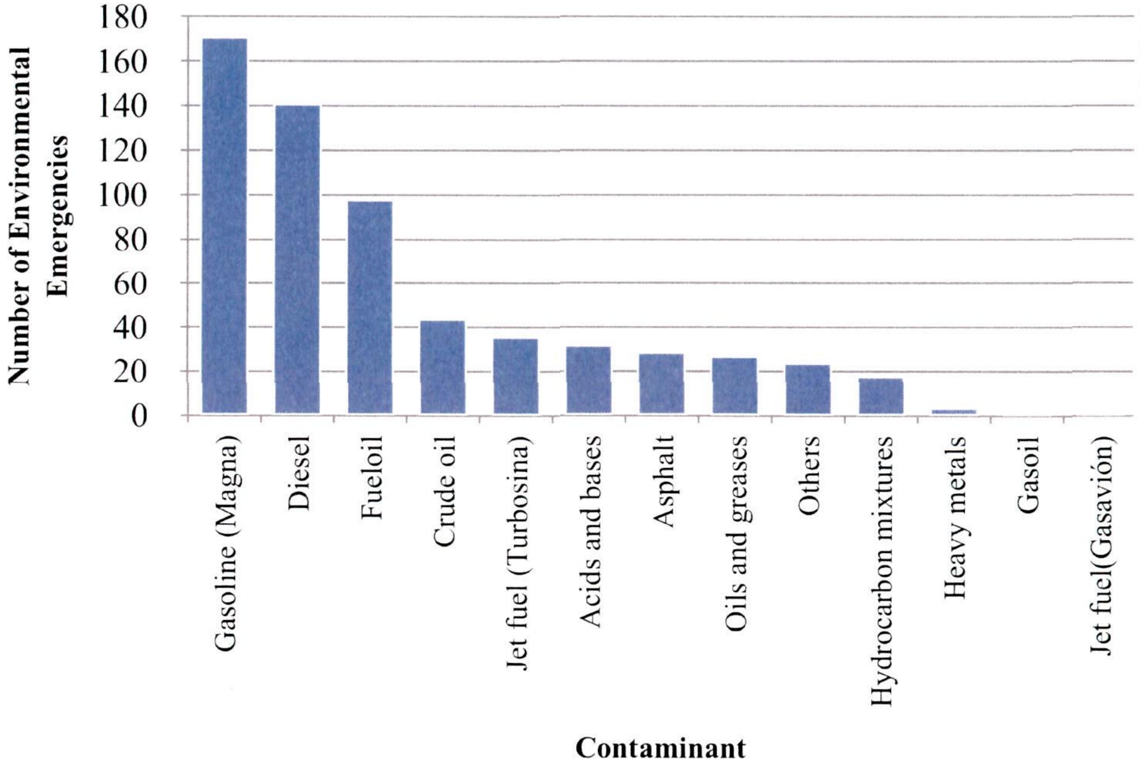

Figure 1.2. Contaminants involved in environmental emergencies in Mexico, from 2008 to 2013. Data obtained from SEMARNAT (2014)

From 2008 to 2013, the most involved contaminants in environmental emergencies were hydrocarbons: gasoline with 171 emergencies (27.3%), diesel with 141 (22.5%), fueloil with 98 (15.6%) and jet fuel with 36 (5.7%) (SEMARNAT, 2014). This information is represented in **Figure 1.2**.

Regarding remediation, Pemex hires companies specialized in bioremediation to remediate the soils. The company compensates the farmers and the leakages are stopped. Unfortunately, hydrocarbon spills and the deterioration of agricultural soils only draw the attention of the authorities when there are human losses involved, otherwise farmers and affected soils are ignored. The environmental effects of hydrocarbon spills (gasoline, diesel or crude oil) coincide with the damages that the farmers themselves describe in their crops (Cavazos-Arroyo *et al.*, 2014).

1.3.2 Mexican Regulations on Soil Contamination and Remediation

Mexican environmental regulations consider contaminated soils as hazardous waste, as stated in Fraction XXXII of Article 5 of the LGPGIR mentioned above. According to this fraction, hazardous waste considers residues that posses any of the characteristics of corrosiveness, reactivity, explosiveness, toxicity, flammability, or that contain infectious agents, as well as containers, packages and soils that have been contaminated (LGPGIR, 2015).

The same LGPGIR establishes that Federal government, along with the governments of the states and the municipalities are obliged to collaborate in the prevention of site contamination and their remediation. This Mexican law classifies contaminated sites in two categories, depending on the type and causes of the contamination: 1) Environmental emergencies, when the contamination originates from an unexpected circumstance or event that suddenly occurs and results in the uncontrolled liberation, fire or explosion of hazardous substances that affect human health or the environment immediately; 2) Environmental liability, when a site is contaminated by the release of hazardous materials that were not remediated promptly to avoid the dispersion of contaminants, but that require remediation (LGPGIR, 2015).

According to the Article 134 of the Mexican environmental law LGEEPA (2017), the required actions to recover the previous conditions of contaminated soils must be applied in order to use these remediated soils for any activity dictated by the urban development programs. The LGPGIR (2015), specifies that the people responsible for the contamination of a site and its effects, are obliged to carry out the remediation of the site, following the pertinent regulations. When the site is abandoned, or its owner is unknown, the government can develop the remediation program.

SEMARNAT, the Mexican Ministry of Environment and Natural Resources, along with the SSA, the Mexican Ministry of Health, issued an Official Mexican Standard in 2012 specifically meant for remediation of hydrocarbon-contaminated soils. This Official Mexican Standard identified as NOM-138/SEMARNAT/SSA1-2012 is compulsory, and establishes the maximum permisible limits of hydrocarbons in soils, the sampling guidelines in the characterization and the specifications for the remediation.

According to this NOM-138/SEMARNAT/SSA1-2012, every soil that presents higher hydrocarbon concentrations than the ones established as the maximum permissible limits in this regulation, needs to be remediated. This remediation should be carried out according to a remediation proposal previously approved by SEMARNAT. The maximum permissible limits established in this Standard are reproduced in **Table 1.2**.

Table 1.2 Maximum permissible limits of hydrocarbon fractions in soil

Hydrocarbon fraction	Maximum permissible limit (mg/Kg dry base), according to the predominant land use		
	Agriculture, forestry, conservation	**Residential, recreational**	**Industrial, comercial**
Light	200	200	500
Medium	1200	1200	5000
Heavy	3000	3000	6000

1.3.3 Site of Study

For purposes of this research, samples of contaminated soil were obtained from a contaminated site in the state of Puebla, Mexico, a place with precedents of fuel theft in the area and soil contamination due to hydrocarbon spillages. The place selected was the municipality of San Martín Texmelucan de Labastida **Figure 1.3**, commonly known as simply Texmelucan.

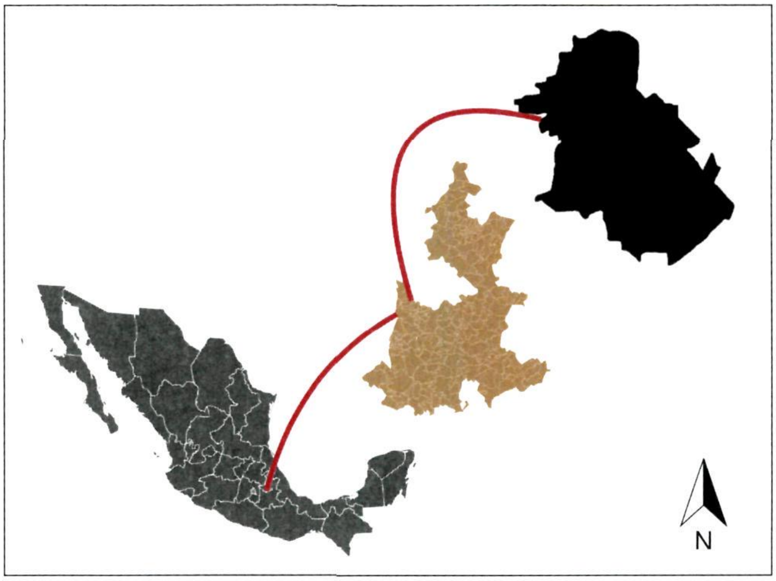

Figure 1.3. Municipality of San Martín Texmelucan de Labastida in Puebla, Mexico

Texmelucan is located 32 kilometers to the northwest of Puebla de Zaragoza, the capital of the state of Puebla, and 75 kilometers to the east of Mexico City, the capital of the country. The municipality is limited by the geographical coordinates: to the north 19° 21", to the south 19° 12" latitude N; 98° 22" to the east and to the west, 98° 29" longitude west. Texmelucan is located in the valley of Puebla at an average altitude of 2 280 meters. San Martín Texmelucan adjoins with the municipality of San Matías Tlalancaleca and the state of Tlaxcala to the north; to the south, with the municipality of Huejotzingo, Puebla; to the east again with the state of Tlaxcala; and to the west with the municipality of San Salvador el Verde, Puebla (Secretaría de Cultura y Turismo del Estado de Puebla, n.d.).

According to the Committee of Statistical and Geographical Information of the State of Puebla (CEIGEP, n.d.), San Martín Texmelucan has a population of over 152 thousand people in an extension of 89.5 Km^2, which represents about 0.26% of the extension of the state of Puebla. The climate of this area is sub-humid temperate with rains in summer, from May to October, with an average precipitation of 804.5 mm each year and an average temperature of 17.7 °C (INEGI,1994).

The valley of Puebla, that includes the municipality of Texmelucan, is located in the hydrological region of the Balsas river, in its subregion of High Balsas. The Balsas river flows into the Pacific Ocean, through the state of Michoacán in the west coast of Mexico. The subregion of High Balsas contemplates the Atoyac river watershed (INEGI, n.d.), this river is precisely the main river of the city of San Martín Texmelucan. This river is constituted by several currents that descend from the Iztaccíhuatl volcano, located between the state of Puebla and the State of Mexico, nonetheless the river is facing severe contamination problems due to the industrialization of the area.

In 2010, over 58% of the population of Texmelucan lived in poverty. By 2015, over 95% of the population had water, electricity and sewer services (CEIGEP, n.d.). In most of its territory agriculture is practiced, dedicated to the production of corn, legumes and fruit; although this activity has been decreasing (INAFED, 2010). The value of the agricultural production in 2014 was of 65.85 millions of Mexican pesos (MXN), which represents 0.5% of the agricultural production of the state of Puebla (CEIGEP, n.d.).

On the other hand, the industrial activity in Texmelucan has been growing in the last decades, and it has been characterized by the manufacture of chemical products, metal, paper, and of course automotive and petrochemical industries (Méndez-Espinoza et al., 2013). Also, Texmelucan is widely known for its textile market that opens every Tuesday, the biggest market in Latin America.

The original flora of the region is typical to the temperate weather, including pines and oaks species. The fauna includes, among others, coyotes, rabbits, snakes, rats, squirrels, mice, eagles, owls and other migratory birds. Texmelucan has deposits of sand and gravel. The types of soil of this region are Cambisol (young soils with presence of rocks, calcium carbonate, iron and magnesium), Phaeozems (dark top layer, rich in organic matter and nutrients), Lithosols (very low depth, with presence of rocks), Fluvisols (located near rivers, contain stones and gravels carried by water), Gleysols (soils with accumulation of water and salts). (INAFED, 2010)

As mentioned above, San Martín Texmelucan has been part of the fuel theft scenario. Proof of this was the accident occurred on December 19, 2010, that terribly affected the municipality (Semple, 2017).

Unfortunately, the criminal activity in the area is not ceasing, and on the contrary, it has been increasing. Fuel theft has been causing hydrocarbon spillages all over the region and causing the social, economical and environmental problems mentioned above. In **Figure 1.4**, the red spot marks the sampling site assigned by the municipal authorities for this research. The dotted line that crosses the sampling site in the figure, is identified in the map as one of the Pemex's pipelines that cross the state of Puebla and particularly the municipality of San Martín Texmelucan.

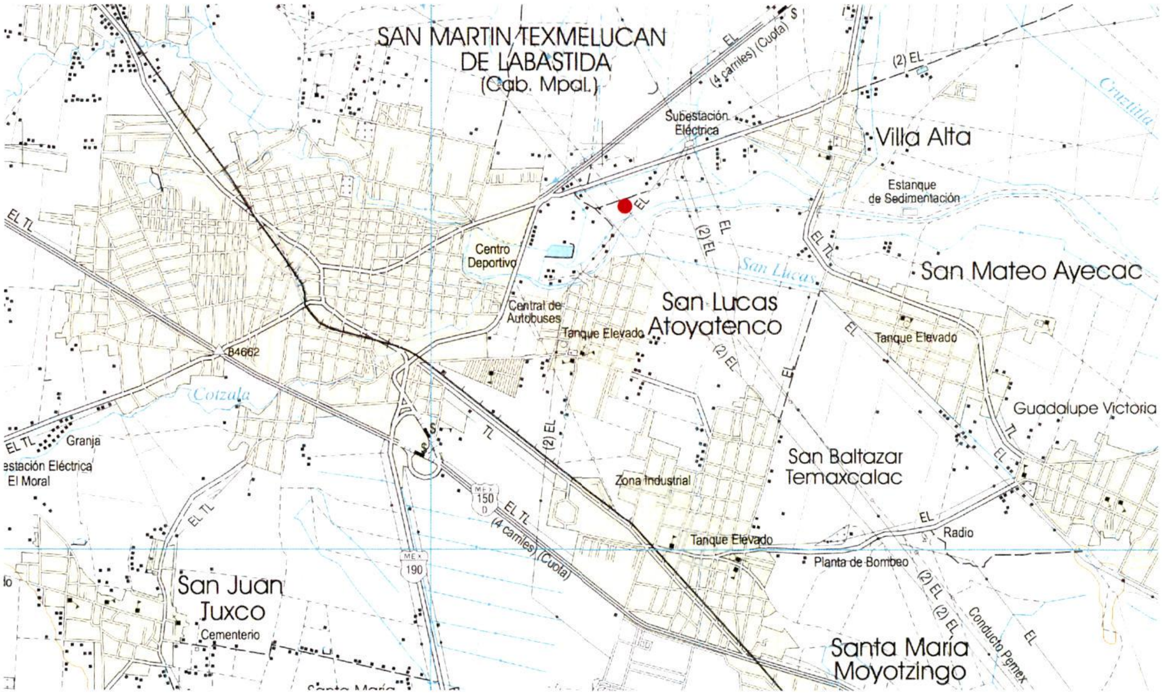

Figure 1.4. Enlargement of Topographic Map 1:50 000 San Martín Texmelucan E14B32. Reprinted from San Martín Texmelucan E14B32 by INEGI, 1996. Retrieved from: http://internet.contenidos.inegi.org.mx/contenidos/productos/prod_serv/contenidos/espanol/bvinegi/productos/geografia/imagen_cartografica/1_50_000/702825634711.PDF

CHAPTER 2. MATERIALS AND METHODS

The methodology outline of this research is represented in **Figure 2.1**. Materials and methods employed in each stage and analysis will be further detailed in this chapter.

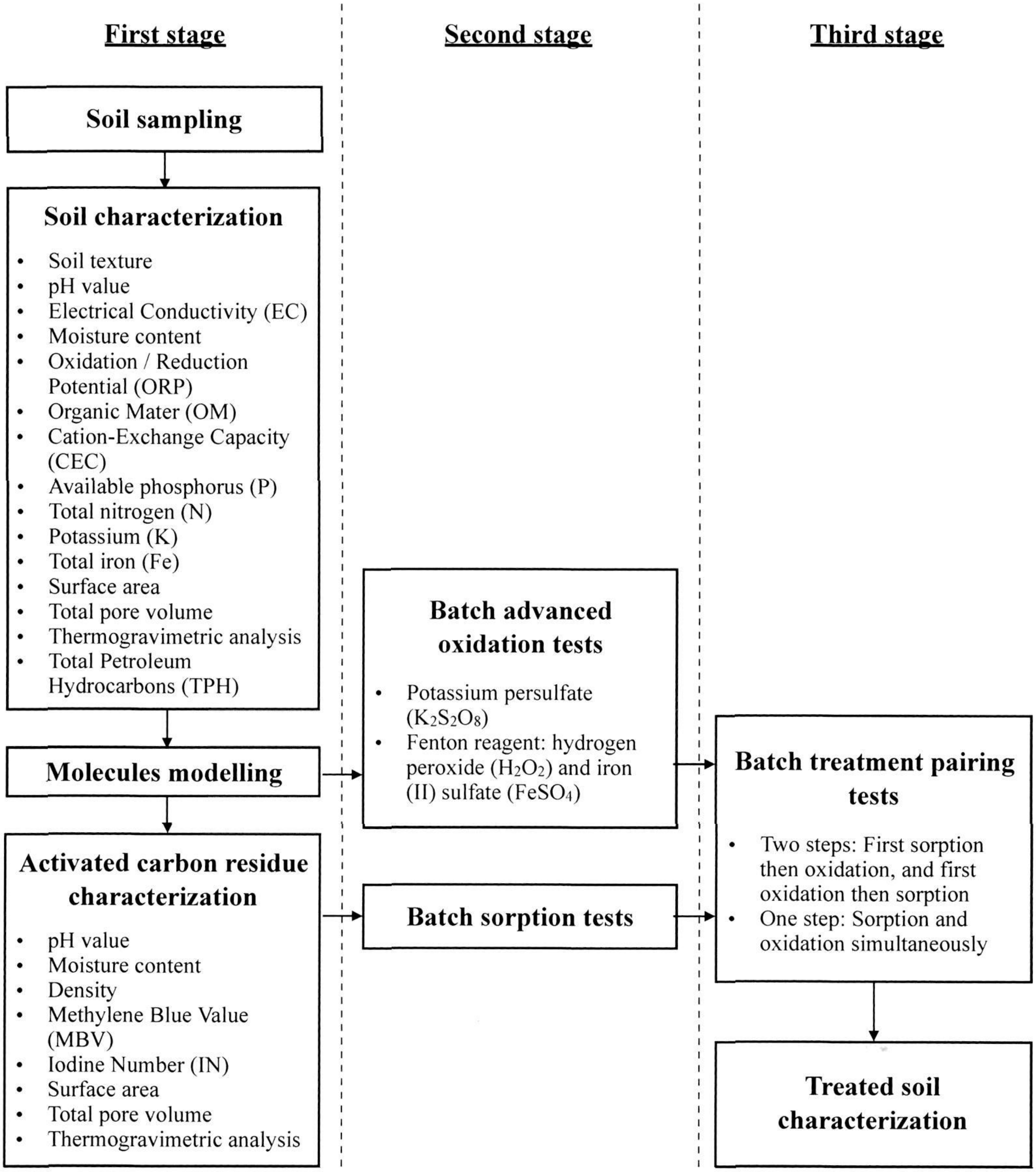

Figure 2.1. Methodology outline

2.1 SOIL SAMPLING

2.1.1 Sampling

The objective of this procedure was to obtain a representative sample of contaminated soil to develop the experimentation, as well as an uncontaminated soil sample to compare the properties of the original soil with the properties of the soil after the spillage and after applying the sorption-oxidation treatment.

The sampling was planned following the Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012, that establishes the maximum permisible limits of hydrocarbons in soils, the sampling guidelines in the characterization and the specifications for the remediation. In section 7.1 of this standard, the contents of the sampling plan are specified. The next section, 7.2, establishes the guidelines for sampling, such as the sampling method and the number of sampling points required. The chain of custody requirements are specified in section 7.4 of the same document. The sampling plan designed for this research, the chain of custody and the samples record sheet are detailed in Appendix A.

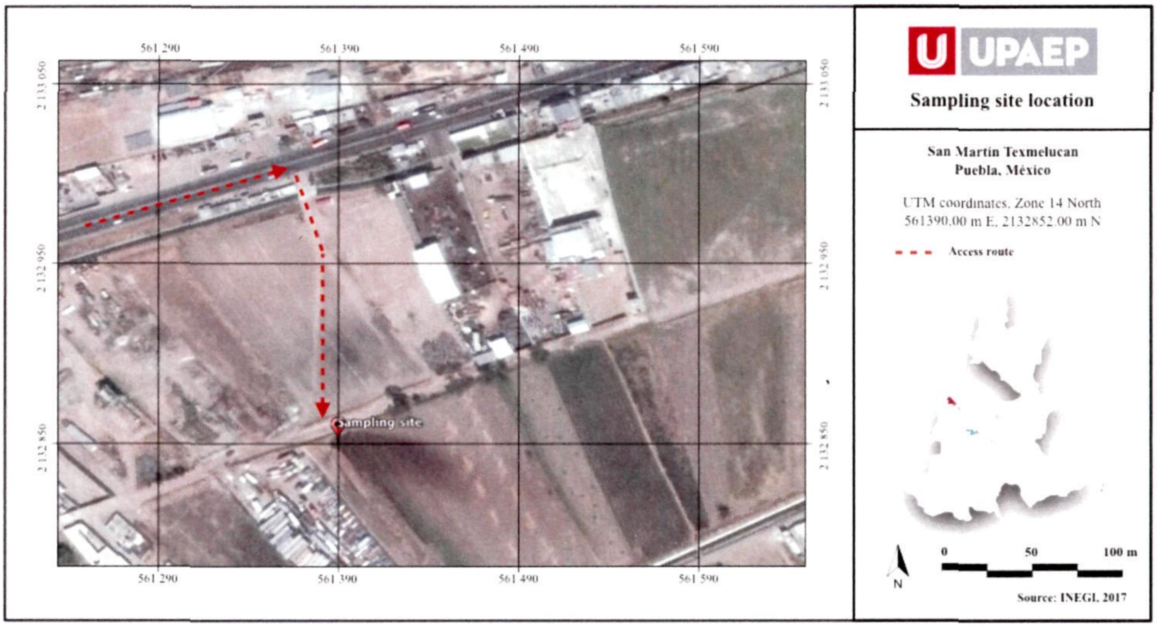

Figure 2.2. Location of the sampling site and access route

Sampling was carried out in the municipality of San Martín Texmelucan, in the State of Puebla, Mexico. The contaminated site is located in the UTM coordinates: 561390 , 2132852, in UTM Zone 14 North (**Figure 2.2**). Due to the complicated security situation in the area, before initiating the sampling activities, a formal petition was submitted to the municipal government of San Martín Texmelucan to ask for their permission to access the site. A copy of this document is attached in Appendix A. With the support of the government, the sampling was carried out on April 27th 2017 at 09:30 hrs., aided by *Protección Civil,* the Fire Department, and Pemex's physical security personnel.

Upon arrival, the extension of the contaminated area was estimated to be below 0.1 hectares. According to the NOM-138-SEMARNAT/SSA1-2012, when the contaminated soil covers an area of up to 0.1 hectares, a minimum of 4 sampling points is required. Thus, sampling of the contaminated site was designed with 5 sampling points in a systematic polar grid arrangement with a central sampling spot and four equidistant points towards north, south, east and west, at a distance of 2.3 meters from the central sample (due to the contaminated area observed). Details on these sampling points can be found in **Table 2.1**. A diagram of the distribution of the samples is shown in **Figure 2.3**.

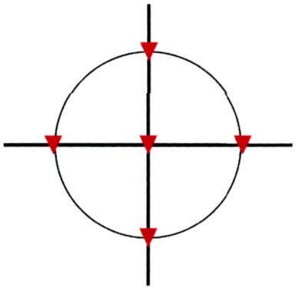

Figure 2.3. Systematic polar grid arrangement of the sampling points

Given the agricultural approach of this research, all samples were taken at a depth of 30 cm, the suggested depth to evaluate farming soils by section 6 of the Official Mexican Standard NOM-021-RECNAT-2000, which establishes the specifications of fertility, salinity and classification of the soils, studies, sampling and analysis. The US EPA Standard Operating Procedure 2012 (SOP 2012) on soil sampling, states that collection of samples at a depth of 12 inches (30 cm) can be accomplished with simple tools, such as shovels, in most soil types.

Table 2.1. Identification of soil samples taken

Sample No.	Soil type	Sample identification by sample code	Type of sample	UTM coordinates (UTM Zone: 14 N) X	Y
1	Uncontaminated	SS-01-U	Single sample	561392.4	2132860.9
2	Contaminated	SC-01-C	Subsample	561390.0	2132852.0
3	Contaminated	SC-02-S	Subsample	561390.0	2132849.7
4	Contaminated	SC-03-E	Subsample	561392.3	2132852.0
5	Contaminated	SC-04-N	Subsample	561390.0	2132854.3
6	Contaminated	SC-05-W	Subsample	561387.7	2132852.0

The procedure to collect the samples started by marking the sampling points with wooden stakes. Then, as established by the SOP 2012, the surface material, such as roots, rocks and vegetation, was removed. Using a shovel, a V shaped hole was dug, with a 30 cm depth at the deepest point of the V. The required soil sample was then extracted by extracting a 5 cm slice of soil from both inclined walls of the V shaped hole. These portions were transferred into a plastic bag, individually labelled for each sampling point. The sample size of each sample was somewhere between 3.5 to 5 Kg, which was estimated to be sufficient to carry out the desired analysis.

An additional single sample of uncontaminated soil was taken following the same procedure in a spot where no contamination was evident by the smell and color of the soil, according to the Munsell soil color chart. Such change in the color of the soil can be appreciated in **Figure 2.4**. All equipment was cleaned between sampling points to avoid sample contamination.

Figure 2.4. View of the contaminated site

Figure 2.5. Sampling procedure. A) Marking of the sampling points. B) Extraction of the sample

2.1.2 Samples preparation

All collected soil samples were taken to the biotechnology and environment research laboratory facilities of the Universidad Popular Autónoma del Estado de Puebla, located in 11 poniente street, No. 2316, Barrio Santiago, Puebla de Zaragoza, Puebla, México. Once there, each sample was pulverized with a hammer to break lumps and passed through a 2 mm mesh size sieve.

Before carrying out any soil analysis or experimentation, the five subsamples of contaminated soil were homogenized into a single contaminated soil sample through the quartering method. To do this, an equal amount of 3.5 Kg of each subsample was spread on a flat surface and divided in four equal portions. Two opposite portions of each subsample were separated and mixed, the rest of the soil was discarded. After applying this method, a final single sample of 8 Kg of contaminated soil was obtained.

Both final soil samples, contaminated and uncontaminated, were stored at room temperature in a well ventilated spot. Both samples were stored separately in sacks, inside hermetic and opaque plastic containers to protect them from light, and humidity.

2.2 SOIL CHARACTERIZATION

2.2.1 Soil texture

Soil texture was determined through the hydrometer method, appropriate for soils with less than 5% of organic matter (Simon Fraser University, 2012). The hydrometer method is based on the relationship between particle size and sedimentation rate. This principle, known as the Stokes' law, allows the assessment of particle sizes according to their settling velocity in an aqueous solution (Beretta *et al.*, 2014).

A sample of 50 g of air-dry non-contaminated soil was weighed and transferred into a metal cup where 5 mL of sodium hexametaphosphate [$(NaPO_3)_6$, Meyer] 1N, and 100 mL of osmotized water were added. All water used throughout this research was osmotized water (water purified by reverse osmosis). This water was Type 3 Laboratory Water, purified with a Millipore RiOs-DI 3 UV Water Purification System.

The contents of the cup were mixed with an Oster mixer (model 2523) for 15 minutes and then completely transferred to a graduated 1 L cylinder. The cylinder was filled to the 1 L mark with more water. Contents were shaken vigorously and a Bouyoucos hydrometer was immediately placed into the cylinder.

The first reading was taken in the hydrometer 40 seconds after shaking the cylinder, the second reading was taken 2 hours after shaking. Temperature was taken with a thermometer at both moments to correct both readings according to the temperature of the mixture at that moment. For every Celsius degree above 19.5 °C, 0.36 was added to the original reading, and for every Celsius degree below 19.5 °C, 0.36 was subtracted from the original reading.

Sand, slit and clay percentages were calculated with **Equations 2.1, 2.2,** and **2.3**.

$$Sand\ \% = \frac{sample\ weight\ (g) - 1st\ corrected\ reading}{sample\ weight\ (g)} \times 100$$ **Equation 2.1**

$$Clay\ \% = \frac{2nd\ corrected\ reading}{sample\ weight\ (g)} \times 100$$ **Equation 2.2**

$$Slit\ \% = 100 - (sand\ \% + clay\ \%)$$ **Equation 2.3**

After calculating these values, they were used to classify the sample into a textural class, using the soil textural triangle displayed in **Figure 2.6**. Each axis of the triangle represents one of the soil separates determined. The calculated percentages are located in their corresponding axis and then diagonal lines inside the triangle are followed towards the opposite axis. The point where the tree lines intersect corresponds to the textural class of the soil.

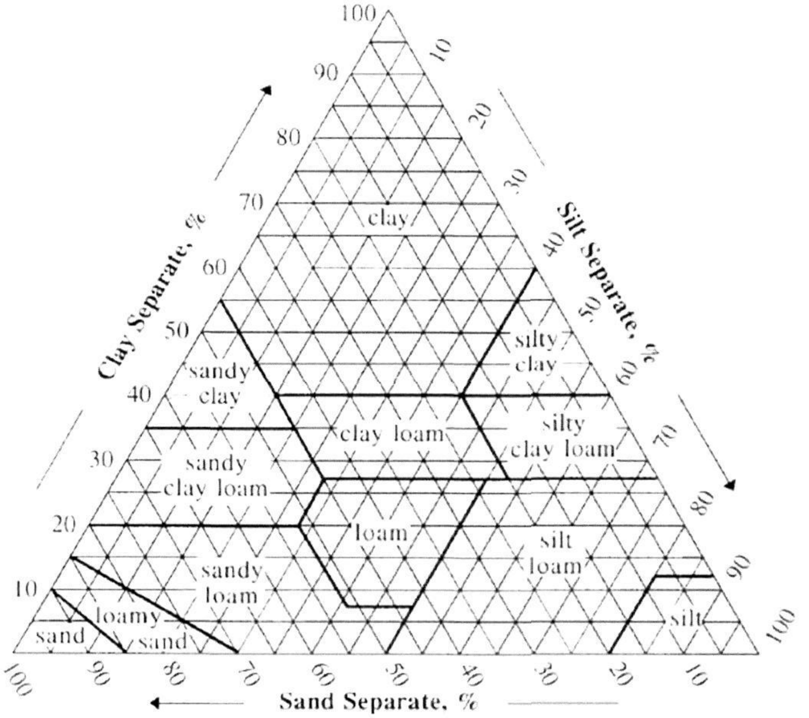

Figure 2.6. Soil Textural Triangle. Reprinted from *Soil Texture Calculator*, by United States Department of Agriculture, n.d. Retrieved from https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_054167.

2.2.2 pH value

Soil pH was determined through the electrometric method described by Fernández-Linares *et al.* (2006). This method is based on the quantification of the potential of an electrode sensitive to H^+ ions. For soils, this parameter is determined through a soil-water mixture, thus the obtained pH value depends on the soil:water ratio. (Fernández-Linares *et al.*, 2006)

As mentioned above, pH value was obtained through a water solution with a soil:water ratio of 1:10. 1 g of both soil samples (contaminated soil and non-contaminated soil) was placed in a beaker and 10 mL of osmotized water were added. The mixture was stirred for 10 minutes using a magnetic stir bar. Then, the mixture was set aside to settle for 10 minutes more.

After this time, pH value was measured with a Termo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter, using a Thermo Scientific Orion 9107BNMD electrode, previously calibrated with J.T. Baker Buffer solutions pH 4.00, 7.00 and 10.00, following the instructions of the apparatus.

Both pH values were then compared with the values established in section 7.1.2 of the NOM-021-RECNAT-2000, to determine the soil classification according to the pH value obtained.

2.2.3 Electrical Conductivity (EC)

Electrical conductivity was determined with a solution of soil in osmotized water. Like pH, EC depends on the soil:water ratio, because EC is directly proportional to the quantity of salts in the soil, which are soluble in water. EC of the soil was determined using a soil:water ratio of 1:5 for all samples as suggested by the New South Wales Office of Environment and Heritage (n.d.). 10 g of each sample were placed in a beaker and 50 mL of osmotized water were added. The mixture was stirred for 10 minutes using a magnetic stir bar and set aside to settle for 24 hours.

EC value was measured with a Thermo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter equipped with a Thermo Scientific Orion 013010MD Conductivity Cell, previously calibrated with Hanna Instruments conductivity standard solutions of 84.1 and 1413 μS/cm at 25 °C, following the instructions of the apparatus. The temperature of soil solutions was measured and registered to correct conductivity readings to the equivalent value at 25 °C.

Both EC values were compared with the values established in section 7.2.5 of the NOM-021-RECNAT-2000, to indirectly determine the salinity of the soil.

2.2.4 Moisture content

Moisture content of the soil was determined with a gravimetric method based on the weight difference of the same sample, before and after drying it in the oven until constant weight. The method used to determine this characteristic of the soil was adapted from the Official Mexican Standard NOM-021-RECNAT-2000, section 7.1.5.

1 g of soil was accurately weighed in a porcelain capsule, that had been previously set at constant weight. These samples were dried in the oven at 105 °C ± 5 °C. After 24 hours, capsules were taken out of the oven and set to cool in a desiccator.

Once cool, the capsules were weighed and set in the oven for another hour, then cooled again and weighed until constant weight.

Soil moisture content was calculated with **Equation 2.4**.

$$Moisture\ \% = \frac{capsule\ with\ moist\ sample\ (g) - capsule\ with\ dry\ sample\ (g)}{capsule\ with\ moist\ sample\ (g) - capsule\ at\ constant\ weight(g)} \times 100 \qquad \textbf{Equation 2.4}$$

2.2.5 Oxidation / Reduction Potential (ORP)

Soil oxidation / reduction potential (redox potential) was determined following the method recommended by Fernández-Linares *et al.* (2006) for samples in laboratories. The determination of this parameter is based on the measurement of the electric potential differences (the electromotive force), produced by oxidation or reduction reactions, that involve the movement of electrons, and changes in electric charges.

A Thermo Scientific Orion 9179BNMD low maintenance ORP electrode, previously calibrated with a Thermo Scientific Orion ORP Standard, was directly introduced into the soil and the oxidation reduction potential was measured in millivolts (mV) at 25 °C, using a Thermo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter. When using this method, thorough cleaning of the electrode with water is necessary after each reading.

2.2.6 Organic Matter (OM)

Soil organic matter was determined through the Walkley & Black method (AS-07) specified in the section 7.1.7 of the NOM-021-RECNAT-2000. This method is based on the determination of residual potassium dichromate(VI) ($K_2Cr_2O_7$), after the organic carbon of the soil is oxidized with this substance and concentrated sulfuric acid (H_2SO_4).

1 g of each soil sample, previously air-dried, was weighed and transferred into a 500 mL Erlenmeyer flask. 10 mL of $K_2Cr_2O_7$ (99.0%, Karal) 1 N were added and stirred gently. Carefully 20 mL of concentrated H_2SO_4 (95.0-98.0%, Meyer) were added under a fume hood and vigorously stirred. Then, the flask was set to stand for 30 minutes on a wooden surface to avoid heat loss.

After 30 minutes, osmotized water was added to approximately 200 mL along with 5 mL of concentrated phosphoric acid (H_3PO_4, 85.1%, J.T. Baker), contents were mixed again, and 10 drops of previously prepared 1,10-Phenanthroline ($C_{12}H_8N_2 \cdot H_2O$, Omnichem) indicator were added. Finally, the mixture was titrated with iron(II) sulfate ($FeSO_4$, 99.0%, Karal) in a 1 N solution.

The percentage of organic matter content was calculated using **Equations 2.5** and **2.6.**

$$Organic\ C\ \% = \frac{mL\ used\ to\ valorize\ blank - mL\ used\ to\ valorize\ sample}{sample\ weight\ (g)} \times FeSO_4\ (N) \times 0.39 \qquad \textbf{Equation 2.5}$$

$$OM\ \% = Organic\ C\ \% \times 1.724 \qquad \textbf{Equation 2.6}$$

Organic matter percentages obtained were compared with the values in section 7.1.7 of the NOM-021-RECNAT-2000, to assess the level of organic matter in the soil.

2.2.7 Cation-Exchange Capacity (CEC)

Cation-Exchange Capacity was determined through the ammonium acetate ($NH_4CH_3CO_2$) method by titration. This method involves saturation of the soil with $NH_4CH_3CO_2$, to extract the soil exchangeable cations, which are replaced with ammonium from the acetate solution. The excess of ammonium is washed with ethanol and then cations are exchanged again with a sodium chloride solution. The washed away ammonium is quantified by titration. (McKean, 1993)

A 1 N $NH_4CH_3CO_2$ solution was prepared by dissolving 28.5 mL of acetic acid (CH_3COOH, 99.7%, J.T. Baker) and 34 mL of ammonium hydroxide (NH_4OH, 28.0-30.0%, Meyer) in 350 mL of water. pH of the solution was adjusted to 7 with CH_3COOH and NH_4OH, and the volume was brought to 500 mL.

5 g of soil were placed in an Erlenmeyer flask, and 30 mL of ammonium acetate 1 N (pH 7) were added. The mixture was stirred for 10 minutes, then set aside to settle for 5 minutes more and finally the liquid was vacuum filtered and collected. This process was repeated with two more portions of 1 N ammonium acetate. The collected filtrate volume was completed to 100 mL and stored for further analysis of potassium by Atomic Emission Spectroscopy.

The soil remaining in the Erlenmeyer flask was completely transferred to the filter and washed with five portions of 10 mL of ethanol (CH_3CH_2OH, 99.5%, RBM), this filtrate was discarded. Then, the soil was washed again with five portions of 10 mL of 10% sodium chloride (NaCl, 99.9%, Productos Químicos Monterrey) solution. The filtrate was collected and 10 mL of formaldehyde (HCHO, 38.6%, Meyer) were added along with 3 drops of 1% phenolphthalein ($C_{20}H_{14}O_4$, Sigma) indicator. This solution was titrated with 0.1 N sodium hydroxide (NaOH, >97.0%, Karal) until a permanent soft pink color was reached.

CEC was calculated in cmol(+)/Kg following the **Equation 2.7**.

$$CEC = mL\ of\ NaOH\ used \times NaOH\ N \times \frac{100}{sample\ weight\ (g)} \qquad \textbf{Equation 2.7}$$

2.2.8 Available phosphorus (P)

Available phosphorus was determined through the Bray & Kurtz method specified in section 7.1.11 of NOM-021-RECNAT-2000. This method is used for soils with a pH lower than 7.5. The soil phosphorus is extracted with a combination of hydrochloric acid (HCl) and ammonium fluoride (NH_4F). The extracted phosphorus is determined colorimetrically by measuring the absorbance of Molybdenum blue at 882 nanometers in a spectrophotometer.

Extracting solution was prepared with NH_4F (98%, Meyer) to a concentration of 0.03 N and HCl (36.8%, J.T. Baker) 0.025 N.

100 mL of reducing solution were prepared with 10 mL of antimony potassium tartrate ($K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$, 99%, Productos Químicos Monterrey) 0.5% (w/v) solution, 45 mL of 14 N H_2SO_4, 2 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}$, 84.44%, J.T. Baker), and 0.5 g of

L-Ascorbic acid ($HC_6H_7O_6$, 99.9%, EMD Millipore), the volume was brought to 100 mL with water.

1 g of dry soil was placed in a 50 mL polyethylene centrifugue tube with 25 mL of extracting solution and mixed for 5 minutes. Then, the contents were filtered by gravity and a 2 mL aliquot of the filtrate was placed into a 50 mL volumetric flask.

Approximately 20 mL of osmotized water were added to the flask, and 5 mL of reducing solution. Contents were shaken and the volume was completed to 50 mL with water. The flask was set to stand for 30 minutes and then the absorbance was measured at 882 nm in a VELAB UV/Vis Spectrophotometer, model VE-5100UV.

A standard phosphorus solution was prepared with dry potassium phosphate monobasic (KH_2PO_4, 99.3%, J.T. Baker) with an initial concentration of 200 mg/L. A calibration curve for 0, 0.1, 0.2, 0.3, 0.4, 0.5 mg/L of phosphorus was prepared by diluting the standard phosphorus solution. 2 mL of extracting solution and 5 mL of reducing solution were added to each dilution. Each solution was brought to a volume of 50 mL with water and 30 minutes later, absorbance was measured at 882 nm. This calibration curve can be found in Appendix B.

Available phosphorus in the soil was calculated in mg/Kg, following **Equation 2.8**.

$$P = CC \times \frac{colorimetric\ solution\ volume\ (mL)}{aliquot\ volume\ (mL)} \times \frac{extracting\ solution\ volume\ (mL)}{sample\ weight\ (g)} \qquad \textbf{Equation 2.8}$$

Where CC is the concentration of phosphorus calculated by plotting the calibration curve and interpolating the absorbance values of the analyzed soil samples with a linear regression fitting.

Available phosphorus concentrations obtained were compared with the values in section 7.1.11 of the NOM-021-RECNAT-2000, to classify the level of phosphorus in the soil.

2.2.9 Total nitrogen (N)

To determine total nitrogen, a macro-Kheldahl equipment was used, such equipment is displayed in **Figure 2.7**. The Kjeldahl method starts with the digestion of the soil sample with heat, concentrated H_2SO_4 and a mixture of salts that accelerate the oxidation of organic matter and the conversion of nitrogen to ammonium cation (NH_4^+). Then, these cations are exposed to NaOH to form ammonium hydroxide (NH_4OH), that is decomposed to ammonia (NH_3) and water by heat. Ammonia is distilled and collected in a boric acid (H_3BO_3, 100%, J.T. Baker) solution. The amount of NH_3 that reacted with the solution is quantified by titration with H_2SO_4.

Figure 2.7. Macro-Kjeldahl equipment

The method described by Fernández-Linares *et al.* (2006) was scaled to fit the macro-Kjeldahl equipment. 1 g of soil was placed in a Kjeldahl flask with 2 g of catalysts mixture: potassium sulphate (KSO_4, 99%, Meyer) and copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$, 98.5%, Merck) in a 10:1 proportion. 30 mL of concentrated H_2SO_4 were added to the solid mixture and heated a medium temperature for digestion in the Kjeldahl equipment, until the liquid turned clear and the soil residue acquired a black color (approximately 4 hours).

The products in the flask were allowed to cool and then 90 mL of previously prepared 10 N NaOH were added to the flask, along with approximately 150 mL of water. This mixture was placed in the distillation section of the Kjeldahl equipment. Before starting the distillation process, a 500 mL Erlenmeyer flask was placed in the outlet of the equipment, containing 50 mL of 2% (w/v) H_3BO_3 solution and five drops of indicators mixture (0.0099 g of bromocresol green, 0.0066 g of methyl red in 10 mL of ethanol.).

When the liquid in the Erlenmeyer flask acquired an aquamarine blue and the volume reached the 100 mL mark, it was titrated with a normalized 0.02 N H_2SO_4 solution, until the mixture returned to its original pink color before distillation.

A blank was prepared by repeating the whole procedure without adding soil. The total nitrogen content was calculated with the following **Equation 2.9**.

$$N\% = \frac{(mL\ used\ to\ valorize\ sample - mL\ used\ to\ valorize\ blank) \times H_2SO_4(N)}{sample\ weight\ (g)} \times 1.4 \qquad \textbf{Equation 2.9}$$

Total nitrogen concentrations obtained were compared with the values in section 7.3.17 of the NOM-021-RECNAT-2000, to classify the level of nitrogen in the soil.

2.2.10 Potassium (K)

The potassium extract obtained from 5 g of soil with 1 N ammonium acetate during the Cation-Exchange Capacity determination, was analyzed by Flame Emission Atomic Spectroscopy. No dilution was required to analyze these samples.

Emission is opposite to absorption. The sample is atomized into a high temperature flame to excite the atoms, that emit radiation at specific wavelengths. The intensity of this radiation is measured. (McKlean, 1993)

A potassium calibration curve was prepared by diluting a 1000 ppm PerkinElmer Potassium (K) Pure Grade Atomic Spectroscopy Calibration Standard, with nitric acid (HNO_3, 69.0 - 70.0%, J.T. Baker) in a 2% (w/v) solution. The non-linear through zero calibration curve was automatically constructed by the equipment with concentrations of 0, 250, 500, 700 and 1000 ppm of potassium. This calibration curve can be found in Appendix B.

A PerkinElmer AAnalyst 200 Atomic Absorption Spectrophotometer equipment was used to analyze all samples.

2.2.11 Total iron (Fe)

Total iron was determined with a PerkinElmer AAnalyst 200 Atomic Absorption Spectrophotometer. Atomic Absorption Spectroscopy is based on the principle that atoms absorb light at certain wavelengths. A specific lamp for the element to analyze emits an spectrum line characteristic of the element. The sample is atomized into a flame and the atoms absorb the energy of the line. The intensity of this absorption is measured by the equipment.

Iron was extracted from the soil samples with a mixture of concentrated acids. 1 g of soil was placed into a beaker, where 10 mL of HNO_3 and 30 mL of HCl were added. The mixture was covered with a watch glass, and placed on a stirring hot plate, where it was stirred and heated at 70 °C, until color changed to a bright yellow (approximately 10 minutes). The liquid was filtered twice by gravity and transferred into a 100 mL volumetric flask containing about 30 mL of water. The volume was brought to 100 mL with water.

An aliquot of 5 mL was transferred into a 50 mL flask and volume was completed with 2% (w/v) HNO_3. These samples were analyzed in the Atomic Absorption Spectrophotometer and iron content was calculated by plotting the calibration curve and interpolating the absorbance values of the analyzed soil samples with a linear regression fitting, considering dilutions.

An iron calibration curve was prepared by diluting a 1000 ppm PerkinElmer Iron (Fe) Pure Grade Atomic Spectroscopy Calibration Standard, with 2% (w/v) HNO_3 solution. The linear through zero calibration curve was automatically constructed by the equipment with concentrations of 0, 0.1, 0.5, 2.5, 5 and 10 ppm of iron. This calibration curve can be found in Appendix B.

2.2.12 Surface area and total pore volume

Surface area and total pore volume of the soil was measured using the BET method, which directly measures surface area and pore size distribution. The Brunauer-Emmett-Teller (BET) method is based on the adsorption of nitrogen on the surface of the sample. The gas particles form a monolayer on the surface of the material, and considering the dimensions of the nitrogen molecule, the surface area can be calculated knowing the amount of adsorbed gas.

The amount of gas adsorbed is calculated from the adsorption isotherm, plotted at 77 K, the boiling point of nitrogen.

Nitrogen adsorption tests were carried out at 77 K, using a BELSORP-max equipment. The 0.3225 g soil sample was pretreated at 80 °C for 21 hours in a BELPREP-vacIII equipment before the adsorption test.

2.2.13 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) is based on the continuous registry of the loss of weight in a given sample, as a function of the temperature. The sample is heated at a given speed and the weight-loss of the sample, due to the different losses of the components of the sample, is registered. Following this principle, this analysis is helpful to characterize the components of the sample.

The analysis of a contaminated soil sample was carried out in an air atmosphere, using a Linseis STA PT1600 TG equipment. The temperature increase velocity was 5 °C/min, in a range from 15 to 1000 °C.

2.2.14 Total Petroleum Hydrocarbons (TPH)

Initial Total Petroleum Hydrocarbons (TPH) concentration in the sampled soil was determined gravimetrically though the method detailed by Fernández-Linares *et al.* (2006). This method starts with the extraction of TPH from soil by contact with a solvent. The solvent is separated from the soil by centrifugation. Then, the solvent is then evaporated, and the extracted hydrocarbons remaining on the flask are quantified by weight.

Gravimetric determination of TPH offers a quantification method that does not require sophisticated equipment, and it is a simple, not expensive and fast procedure. However, this method is not suitable for low hydrocarbon concentrations. It is also not recommended for light hydrocarbons ($<C_{15}$) or gasoline range hydrocarbons that volatilize below 85 °C. Detection limits for TPHs of 50 mg/Kg in soils have been reported. Also, depending on the selected solvent for extraction, the method may have serious health and safety concerns that

should be taken into account by following the safety procedures established in safety data sheets. (Nwomandah & Mounem, 2013)

1 g of dry soil was accurately weighed and transferred into a 15 mL centrifuge tube, along with 3 g of previously dried (4 hours at 120 °C) sodium sulfate anhydrous (Na_2SO_4, 99.0%, Merck). This solid mixture was mixed with vortex mixer until it acquired an homogeneous appearance.

5 mL of the solvent, 2-propanone ($(CH_3)_2CO$, 99.5%, RBM), were added to the centrifugue tube and mixed again with vortex mixer for 45 seconds. The tubes were centrifuged at 5 000 rpm for 10 minutes using a HERMLE Labnet Z 326 centrifuge. The supernatant was carefully extracted with a pipette and placed into a round bottom flask at constant weight.

The process was repeated twice from the solvent addition on the solid residue until approximately 15 mL of supernatant were recovered in the flask at constant weight.

Solvent was evaporated using a Hahn Shin Scientific HS-2001NS rotary evaporator at 45 °C and 30 rpm, until no solvent was visible and only hydrocarbons remained in the flask (approximately 3 to 4 minutes). Then, the flask was removed from the water bath and set aside to dry and cool for approximately 1 hour. The flask was weighed and TPH concentration was calculated with **Equation 2.10**.

$$TPH(mg/Kg) = [flask\ with\ extract\ (g) - flask\ at\ constant\ weight\ (g)] \times \frac{1000}{sample\ weight\ (g) \times [1 - (Moisture\ \%/100)]}$$

Equation 2.10

In order to obtain further information on the hydrocarbons in the soil, a soil sample was submitted to an accredited laboratory (Intema S.A. de C.V.) for Gas Chromatography-Flame Ionization Detection (GC-FID) analysis. GC-FID is used for quantitative and qualitative determination by introducing the previously extracted hydrocarbons into a capillary column. As the temperature gradually raises, TPH are separated according to their boiling points. These separated compounds are ionized by a flame at the end of the column causing electric conductivity in the gas, which is measured by an electrode (Nwomandah & Mounem, 2013). TPH are considered the sum of the area under the curves in the resulting chromatogram.

2.3 MOLECULES MODELLING

2.3.1 Molecule construction

Computational quantum chemistry methods were applied to run simulations of the molecules interacting in the redox reactions of the advanced oxidation treatment. These simulations were carried out to predict the flow of electrons during these reactions and thus, determine which interactions are more likely to occur. The software used to do this was *HyperChem(TM) 8.0*, following the methods described by González-Pérez *et al.* (2014).

Since the contaminant in the soil is a complex mixture of many organic compounds, and considering that hydrocarbons with similar structures exhibit similar properties, representative compounds of the diesel-range hydrocarbons were used to run these simulations. Such representative hydrocarbons were selected from the compounds identified in the GC-FID analysis carried out during the soil characterization, and from the diesel composition described by Chevron Corporation (2007). The hydrocarbon molecules constructed were: n-decane ($CH_3(CH_2)_8CH_3$), n-dodecane ($CH_3(CH_2)_{10}CH_3$), n-tetradecane ($CH_3(CH_2)_{12}CH_3$), n-eicosane ($CH_3(CH_2)_{18}CH_3$), benzene (C_6H_6), 1,3,5-trimethylbenzene (C_9H_{12}), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$). On the other hand, the oxidant molecules constructed were: hydroxyl radical ($\cdot OH$), hydrogen peroxide (H_2O_2), sulfate radical ($\cdot SO_4^-$), and persulfate ($S_2O_8^{2-}$).

A molecule of each selected compound was built on the program with the SE-PM3 (Semi-empirical parametric method 3), and its geometry was optimized with Polak-Ribiere algorithm. The molecular orbitals of the molecule were shown following the route: *Compute* → *Orbitals*. The energy values in eV were obtained for the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), these values were copied in a spreadsheet. Then the Electrostatic Potential (EP) was plotted following the sequence: *Compute* → *Plot Molecular Properties* → *Molecular Property: Electrostatic Potential*. Once plotted, the maximum (E+) and minimum (E-) EP values shown in the scale were copied in the spreadsheet file. The specific parameters selected for each molecule can be found in Appendix C. This procedure was repeated for each molecule in individual files.

2.3.2 Electron Transfer Coefficient calculation

A spreadsheet file containing the information of each modelled molecule was generated following the methods described by González-Pérez *et al.* (2014). Each hydrocarbon molecule was paired with each oxidant molecule in rows, and their HOMO, LUMO, E+, E- values were arranged, according to the interaction between them, for example: for n-decane as reductor and hydrogen peroxide as oxidant, the HOMO and E- values of the n-decane were paired with the LUMO and E+ values of the hydrogen peroxide.

Then, the Band Gap (BG), the Electrostatic Potential (EP) and the Electron Transfer Coefficient (ETC) of the interaction were calculated for each row using **Equations 2.11, 2.12,** and **2.13**, respectively.

$$BG = |HOMO - LUMO| \qquad \textbf{Equation 2.11}$$

$$EP = |E+ \ - \ E-| \qquad \textbf{Equation 2.12}$$

$$ETC = \frac{BG}{EP} \qquad \textbf{Equation 2.13}$$

The ETC values obtained for each interaction were compared to describe the electron transfer and determine which reactions are more likely to happen based on their electron flow. According to González-Pérez *et al.* (2014), electrons can jump a BG where the ETC has lower values, thus the substance is more likely to be stable. On the other hand, when the ETC is higher, the probability of a chemical reaction is high.

2.4 VALORIZED ACTIVATED CARBON CHARACTERIZATION

The Activated Carbon (AC) used throughout this research was from a single source: a 10-inch impregnated AC cartridge (JMXKITR02, Merck) which had been previously used for tap water pretreatment for the Millipore RiOs-DI 3 UV Water Purification System in the laboratory. The laboratory protocol requires the replacement of this filter every 6 months. Thus, this AC filter had been in use in the water treatment system for 6 months before it was taken for this research purposes.

Since the AC filter had completed its primary function in the water treatment system, it was now considered a residue that was valorized and given a second use as the AC source for this project. This was selected as the AC source for the sorption tests due to the environmental and economical advantages of valorizing the residual sorption capacity of this semi-wasted AC residue.

Given that the AC to be employed for the sorption tests was not new, it had to be submitted to characterization analysis to determine its residual sorption capacity. Before performing such analysis, the impregnated AC filter residue to valorize was taken out of its plastic cover and the AC cylinder was pulverized using a hammer and a mortar before performing these analysis (**Figure 2.8**). The coarsely pulverized AC was air dried for 24 hours before its use. AC was characterized as coarse powder. No specific particle size was selected until sorption treatment tests with soil started.

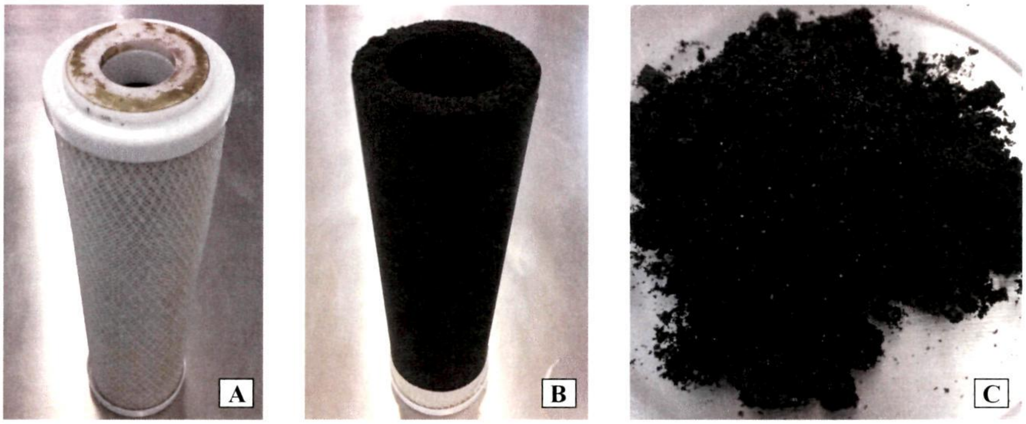

Figure 2.8. Procedure of valorization of the AC residue. A) Packed AC cartridge residue. B) Unpacked AC cartridge. C) Coarsely pulverized AC

All AC characterization tests followed the methods described by the European Council of Chemical Manufacturers' Federations, in their document *Test Methods For Activated Carbon* (1986). Most of the methods described, follow procedures by the American Society for Testing and Materials (ASTM) and the American Water Works Association (AWWA).

2.4.1 pH value

AC may carry chemical species on its surface that may change the pH of liquids that enter in contact with the material. To determine these pH alterations and indirectly determine the presence of such chemical species on the AC surface, its pH value is measured in a water. solution.

4 g of non-dried AC were weighed and placed into a 250 mL beaker. 100 mL osmotized water (previously boiled to remove carbon dioxide, CO_2) were added into the beaker, which was covered with watch glass and set on a hot plate to boil for 5 minutes.

After 5 minutes of boiling, heat was turned off and a thermometer was used to measure the temperature. AC was allowed to settle and supernatant was decanted before temperature reached 60 °C. This liquid was set aside to cool until it reached room temperature (approximately 20 °C).

pH value of the AC corresponds to the pH measured in the decanted supernatant. pH was measured with a Termo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter, using a Thermo Scientific Orion 9107BNMD electrode, previously calibrated with J.T. Baker Buffer solutions pH 4.00, 7.00 and 10.00.

2.4.2 Moisture content

Moisture content of the AC was determined gravimetrically through a similar methodology used to determine moisture in the soil. This procedure is also used to dry AC samples for other tests.

1 g of air-dry AC was accurately weighed in a porcelain capsule at constant weight. This capsule was placed in the oven at 150 °C for 3 hours, then set to cool in a disicator and weighed. The moisture content of the AC sample was calculated following **Equation 2.4**.

2.4.3 Density

The AC density is the mass of a certain volume of an AC sample including the pores and the spaces between particles. It depends on the shape, size and density of the AC particles.

A 10 mL graduated cylinder was filled up to the 10 mL mark with a previously dried AC sample (at 150 °C for 3 hours). Once full, the base of the cylinder was hit against a flat surface repeatedly for 5 minutes to settle the contents. The volume was read and this procedure was repeated to settle the AC until volume variation was less than 0.2 mL.

Finally, the contents of the cylinder were weighed with an analytic balance and density was calculated using **Equation 2.14**.

$$Density = 1000\frac{AC\ sample\ weight\ (g)}{volume\ of\ the\ sample\ (mL)} \qquad \textbf{Equation 2.14}$$

2.4.4 Methylene Blue Value (MBV)

The methylene blue number is the maximum amount of dye adsorbed per gram of AC. This determination can shed some light on the textural properties of activated carbons, because the dimensions of the methylene blue molecules allow them to be mainly adsorbed in mesopores, and a small portion in large micropores. (Nunes & Guerreiro, 2011)

A methylene blue ($C_{16}H_{18}ClN_3S \cdot 2H_2O$, 82%, Merck) solution was prepared with 300 mg of pure dry powdered methylene blue (MB), which were dissolved in osmotized water to a volume of 250 mL in a volumetric flask. This solution was allowed to stand overnight before performing the MBV test. Before its use, an aliquot of 0.5 mL of this MB test solution was diluted to 100 mL with a 0.25% (v/v) acetic acid solution. This diluted solution was analyzed in a spectrophotometer at 620 nm, using 1 cm disposable cuvettes, the absorbance value must be 0.840.

AC used had been previously pulverized, dried in the oven at 150 °C for 3 hours and set in a disicator to cool.

First MBV test was performed by placing a sample of exactly 0.1 g of powdered AC in a 25 mL Erlenmeyer flask and adding 50 μL of MB test solution. The contents of the flask were shaken until discolor of the solution occurred within 5 minutes.

Second MBV test was performed with an accurately weighed 0.5 g sample of AC in a 25 mL Erlenmeyer flask. 250 μL of MB test solution were added and contents were shaken until discolor of the solution occurred within 5 minutes.

The MBV of the AC corresponds to the mass of MB present in the volume of MB test solution discolored. MBV is reported in mg of adsorbed MB per gram of AC.

2.4.5 Iodine Number (IN)

Iodine number is a relative indicator of porosity in AC, in much the same way that methylene blue value is. The iodine molecules have smaller dimensions than the molecules of methylene blue, meaning they can be adsorbed in micropores (Nunes & Guerreiro, 2011). Iodine number (IN) is determined through the ASTM D4607-94 Method. The amount of iodine absorbed in milligrams per gram of carbon, corresponds to IN of the analyzed AC.

AC used for this test had been previously pulverized, dried in the oven at 150 °C for 3 hours, and set in a disicator to cool.

An approximately 0.100 N sodium thiosulfate solution was prepared dissolving 24.820 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 99.5-101%, Meyer) and 0.1 g of sodium carbonate (Na_2CO_3, 99.5%, Merck) in water. The volume of the solution was completed to 1 L and stored in an amber bottle. The solution was allowed to stand 4 days before standardizing it using potassium iodate (KIO_3, 99.7%, J.T. Baker).

A Iodine solution approximately 0.10 N was prepared with 12.7 g of iodine (I) and 19.1 g of potassium iodide (KI, >99.0%, Meyer). The volume was brought to 1 L with water and the solution was stored in an amber bottle. This solution was standardized with the previously standardized sodium thiosulfate solution.

First IN test was performed using an AC sample of 2 g. For the second test, a sample of 3 g was used. Each sample was accurately weighed and transferred into a 250 mL Erlenmeyer flask. 10 mL of 5% (w/v) HCl solution were added into each flask, which were gently swirled to completely wet the carbon samples with the solution.

The flasks were placed on a hot plate and contents were boiled for exactly 30 seconds. Then, flasks were set aside to cool at room temperature. Once cool, 100 mL of approximately 0.10 N Iodine solution were added into each flask. Both flasks were immediately covered with a stopper and shaken vigorously for 30 seconds.

The contents of the flasks were filtered by gravity with filter paper. The first 30 mL of filtrate were discarded. The rest of the filtrate volume was collected in a clean beaker and stirred before pipetting 50 mL of this liquid into a clean 250 mL Erlenmeyer flask. These aliquots were titrated using the standardized sodium thiosulfate solution until yellow color almost vanished. Then, 1 mL of starch indicator solution was added and titration was continued until color disappeared completely. The IN of AC was calculated considering the sodium thiosulfate solution volume used, following **Equation 2.15**.

$$IN = Correction\ factor\,\frac{(12693 \times Iodine\ N) - (126.93 \times thiosulfate\ N) \times Dilution\ Factor \times mL\ of\ thiosulfate\ used}{AC\ sample\ weight\ (g)}$$

Equation 2.15

The dilution factor is calculated using **Equation 2.16**.

$$Dilution\ Factor = \frac{mL\ of\ iodine\ added \times mL\ of\ 5\%HCl\ used}{mL\ of\ filtrate\ used}$$

Equation 2.16

Correction factor used can be found in the table reproduced in *Test Methods For Activated Carbon* (CEFIC, 1986). This correction factor depends on the residual normality of the filtrate, which can be calculated with **Equation 2.17**. The IN test must be repeated with a bigger AC sample if residual N is higher than 0.0334, or a smaller amount of AC if it is below 0.008.

$$Residual\ N = thiosulfate\ N \times \frac{mL\ of\ thiosulfate\ used}{50}$$

Equation 2.17

2.4.6 Surface area and total pore volume

Surface area and total pore volume of the valorized AC was also determined using the BET method. The AC sample of 0.0636 g was outgassed at 150 ºC for 19 hours in a BELPREP-vacIII equipment before adsorption measurements. Nitrogen adsorption tests were carried out at 77 K, using a BELSORP-max equipment.

2.4.7 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on an AC sample, which was placed into a Linseis STA PT1600 TG equipment, with a temperature increase velocity of 5 ºC/min, in a range from 15 to 1000 ºC. The sample was heated using an air atmosphere.

2.5 ADVANCED OXIDATION TESTS

2.5.1 Design of experiments

Oxidation tests were designed following a general full factorial design of experiments, with the objective of studying the effect of several factors on an output variable. The three considered factors were: oxidant, oxidant concentration, and reaction time. The output variable was the concentration of hydrocarbons in the soil.

Each factor contemplates different levels. The first factor, "oxidant", has two levels: potassium persulfate ($K_2S_2O_8$), and hydrogen peroxide (H_2O_2). The second factor, "oxidant concentration" has three levels: 0%, 1.5%, 3.0% for H_2O_2, and 0%, 5%, 10% para $K_2S_2O_8$. Finally, the factor "reaction time" has five levels: 0.5, 1, 2, 6, and 24 hours. For oxidation tests with $K_2S_2O_8$) a sixth level of 48 hours was added in this last factor, in order to achieve complete consumption of the oxidant.

The design of experiments (DOE) was performed in the software *Minitab 18* (2017). The sequence employed was: *Statistics → DOE → Factorial → Create Factorial Design → General full Factorial Design.* The number of factors and output variable were entered, named, and the number of levels for each factor was added. The software automatically generates columns for each factor and output variable. A summary of this design can be found in **Table 2.2.** The analysis of variance (ANOVA) was performed using the same software after carrying out the treatments in the laboratory.

Table 2.2. Advanced Oxidation Design of Experiments Summary

Oxidant	Oxidant concentration (% w/v)	Time (hours)					
H_2O_2	Low: 0	**0.5**	1	2	6	24	
	Medium: 1.5	0.5	1	2	6	24	
	High: 3	0.5	1	2	6	24	
$K_2S_2O_8$	Low: 0	**0.5**	1	2	6	24	48
	Medium: 5	**0.5**	1	2	6	24	48
	High: 10	**0.5**	1	2	6	24	48

All advanced oxidation experiments were carried out in batch reactors, based on the methods described by Liao *et al.* (2014). The soil:oxidant-solution ratio was maintained at 1:1.5 throughout all the treatments, which were carried out in triplicates.

2.5.2 TPH degradation tests with hydrogen peroxide

The hydrogen peroxide solutions for soil treatments were prepared parting from a stock hydrogen peroxide solution (H_2O_2, 30%, Sigma-Aldrich). The stock solution was diluted to get concentrations of 3% and 6% (w/v), by diluting 10 mL and 20 mL in water and bringing the volume of the solutions to 100 mL with osmotized water.

Iron (II) (Fe^{2+}) catalyst solutions were prepared in concentrations of 0.3% and 0.6% (w/v) using iron (II) sulfate ($FeSO_4$, 99.0%, Karal). Solutions were prepared by dissolving 1.4935 g and 2.9871 g of $FeSO_4$ in water. The volume of the solutions was brought to 100 mL with more water.

Reactors were prepared by placing 5.00 g of accurately weighed contaminated soil in a 15 mL test tube. 3.75 mL of 3%, or 6% H_2O_2 solution were added and mixed with a vortex mixer. Immediately, 3.75 mL of 0.3%, or 0.6% Fe^{2+} solution were added respectively, and mixed to catalyze the reactions. For controls (0% H_2O_2 and 0% $FeSO_4$), only 7.5 mL of osmotized water were used. This procedure was repeated for each concentration and designated time point established in **Table 2.2**, in triplicates. The test tubes were not closed with caps to avoid damage because of pressure built during reactions. These reactors are depicted in **Figure 2.9**.

All reactors were maintained at room temperature and at the given time points, samples were collected. Five drops of concentrated H_2SO_4 were added and mixed with vortex mixer. The soil fraction in the tubes was allowed to settle for at least 2 hours inside a refrigerator. Supernatant was extracted with a pipette and transferred to clean test tubes with caps.

The treated soil was carefully removed from the tubes and air-dried for 24 hours before TPH analysis with the gravimetric method described above in section 2.2.14. On the other hand, the supernatants were submitted to residual oxidant analysis through the methods described below in section 2.5.4.

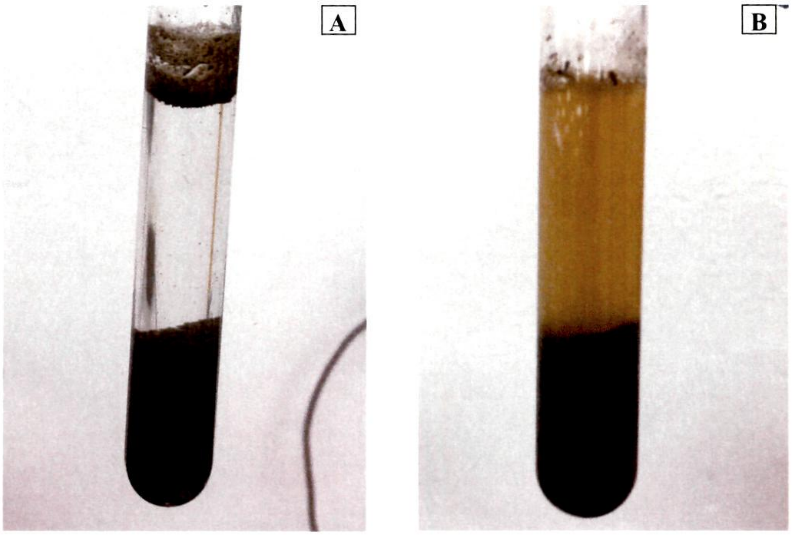

Figure 2.9. Advanced oxidation tests. A) Control treatment. B) 24 hours treatment.

Before treating the soil with hydrogen peroxide catalyzed with iron (II) (Fe^{2+}), a preliminary test was held to determine the best oxidant:catalyst ratio. To do this, 25 mL of 3% and 6% (w/v) H_2O_2 solutions were placed in 6 Erlenmeyer flasks, 3 for each concentration. 25 mL of previously prepared 0%, 0.3%, 0.6% or 1.2% (w/v) Fe^{2+} solutions were immediately added to the flasks. The resulting reactions had oxidant:catalyst ratios of 1:0, 5:1, and 10:1.

An aliquot of 25 μL of the reacting liquid was immediately extracted from each flask and the concentration of oxidant was analyzed following the methods described below in section 2.5.4. The best oxidant:catalyst ratio resulted to be 10:1 for both H_2O_2 concentrations, such ratio was used to carry out the Fenton oxidation treatments detailed above.

2.5.3 TPH degradation tests with potassium persulfate

Potassium persulfate ($K_2S_2O_8$, 99.0%, Karal) solutions were prepared with concentrations of 5% and 10% (w/v), by dissolving 10 g and 20 g of $K_2S_2O_8$ in water, respectively, and bringing the volume of the solutions to 200 mL with osmotized water. For controls (0% $K_2S_2O_8$), only osmotized water was used. All solutions, including the control one, were activated at 50 °C by heating the solution in a beaker covered with watch glass, on a hot plate.

For each treatment, reactors were prepared following these steps: 5.00 g of contaminated soil were accurately weighed and transferred into a 15 mL test tube. 7.5 mL of 0%, 5%, or 10% $K_2S_2O_8$ solution were added and mixed with a vortex mixer until the contents of the test tubes acquired an homogeneous aspect. This procedure was repeated for each concentration and designated time point established in **Table 2.2**, in triplicates. The test tubes were closed with caps and maintained at 50 °C ± 5 °C inside an oven.

At the given time points, samples were collected and placed in a cool water bath. Five drops of concentrated H_2SO_4 were added and mixed with vortex mixer to stop the reactions. The soil fraction in the tubes was allowed to settle for at least 2 hours inside a refrigerator. Supernatant was extracted with a pipette and transferred to clean test tubes with caps.

Treated soil was removed from the tubes and air-dried for 24 hours before TPH extraction and analysis through the methods described above in section 2.2.14. Supernatants were submitted to residual oxidant analysis using the spectrophotometric method described below in section 2.5.4.

2.5.4 Residual Oxidant Analysis

Residual oxidant analysis was performed on the supernatant of each advanced oxidation experiment to evaluate oxidant consumption, using the spectrophotometric method for peroxygens analysis developed by Bennedsen *et al.* (2014). This method is based on the spectrophotometric measurement of the absorbance at 352 nm, of the iodine produced by the reaction of the oxidant species with iodide (**Equations 2.18** and **2.19**).

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad \textbf{Equation 2.18}$$

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-} \qquad \textbf{Equation 2.19}$$

KI solution was prepared by dissolving 16 g of KI and 0.8 g of sodium bicarbonate ($NaHCO_3$, 100%, Meyer) in osmotized water and bringing the volume to 200 mL. This solution was prepared fresh every day.

25, 50, or 100 µL of supernatant was diluted 200, 100, or 50 times respectively, using osmotized water, in order to fit the absorbance range of the calibration curve. An aliquot of 25, 50, or 100 μL of these dilutions was transferred into a 10 mL test tube, where 4.975, 4.950, or 4.900 mL of KI solution were added respectively. Test tubes were mixed with a vortex mixer and stored in the dark for 20 minutes. After this time, absorbance was read in a VELAB UV/Vis Spectrophotometer (model VE-5100UV) at 352 nm, using 1 cm disposable cuvettes.

A calibration curve was plotted with concentrations of oxidant of 0.037, 0.030, 0.022, 0.015, 0.007, 0.004, and 0.000 mM, considering the dilution of the KI solution addition. Since the handling of $K_2S_2O_8$ is easier due to its solid state, a 1% (w/v) stock solution was prepared with $K_2S_2O_8$ by dissolving 0.5 g in water and bringing the volume to 50 mL. This stock solution was further diluted with water to get the required concentrations for the calibration curve, considering the further addition of the KI solution. An aliquot of 50 μL of these solutions was transferred into a 10 mL test tube, where 4.950 mL of KI solution were added. Absorbance was read 20 minutes later at 352 nm. Such calibration curve can be found in Appendix B.

Percentage of residual oxidant in the supernatant was calculated with **Equation 2.20**. Where CC is the concentration of oxidant in the calibration curve in mM, calculated by plotting the calibration curve and interpolating the absorbance values of the analyzed supernatants with a linear regression fitting.

$$\%Residual\ oxidant = \frac{CC\ (mM) \times dilution\ factor \times molecular\ weight \times 0.01}{original\ concentration\ of\ oxidant\ solution\ (\%)} \qquad \textbf{Equation 2.20}$$

2.6 SORPTION TESTS

The valorized semi-wasted AC that was characterized throughout section 2.4, was air dried for 24 hours and pulverized using a hammer and a mortar. This pulverized AC was sieved through a standard sieve No. 200 (74 μm mesh-size), to obtain fine-powdered AC. All AC used for all sorption treatments had this particle size of <74 μm.

All sorption tests were performed by mechanically mixing the contaminated soil with the powdered AC. This mixing should lead to a homogenous distribution of the AC in the soil matrix (Hilber & Bucheli, 2010). In order to simplify the analysis of remaining TPH in the soil fraction, the soil has to be separated from the AC once the material has sorbed the hydrocarbons from the soil. To ease this separation, all contaminated soil used for sorption tests was also sieved through the 74 μm mesh before the experiments. The coarse fraction (sand) was recovered and used to run the experiments. The fine fraction (slit and clay) was discarded.

2.6.1 Preliminary tests

Preliminary sorption tests were carried out by mixing contaminated soil with varying concentrations of AC, 0%, 5%, and 15% (w/w). These mixtures were prepared by accurately weighing 5, 4.75, and 4.25 g of contaminated soil and adding powdered AC until the total mass of the mixture was 5 g. These mixtures were placed in 30 mL glass vials, mixed with a vortex mixer, sealed with wax paper, and left undisturbed in the dark at room temperature for 15 and 30 days.

All tests were carried out in triplicates. After the designated time points of 15 and 30 days, samples were taken out of each flask and sieved to recover the soil fraction, which was analyzed for TPH concentration following the methods described in section 2.2.14.

2.6.2 Time optimization

After finding no significant difference between 5% and 15% AC treatments, the 5% concentration was selected to carry out the rest of the sorption tests, in order to optimize the use of the AC.

Since the concentration of remaining TPH in the soil after 15 and 30 days was similar, the time factor was optimized by repeating the 5% AC treatment for 5 days and analyzing the TPH concentration in the soil fraction every 24 hours. This was achieved by placing 0.5 g of AC and 9.5 g of contaminated soil in Erlenmeyer flasks, to get an AC concentration of 5% (w/w). The flasks were sealed with wax paper and placed in a shaking incubator (Benchmark Incu-Shaker 10L) at 30 °C ± 0.1 °C and 250 rpm for 5 days. Every 24 hours, 2 g of the mixture were extracted from the flasks, the soil from these samples was separated from the AC by sieving them with the 74 μm sieve. The AC fraction was discarded and TPH in the soil were extracted and analyzed through the methods described in section 2.2.14.

When the TPH removal in the soil remained constant for the first 5 days, also corresponding to the response obtained in the preliminary tests for 15 and 30 days, the experiment was repeated to further optimize the treatment time.

1 g of AC and 19 g of contaminated soil were accurately weighed in Erlenmeyer flasks, to get an AC concentration of 5% (w/w). Again, the flasks were sealed with wax paper and placed in the shaking incubator at 30 °C ± 0.1 °C and 250 rpm for 150 minutes. At designated time points of 5, 10, 15, 30, 45, 60, 90, 120, and 150 minutes, 2 g of the mixture were extracted from the flasks. The soil from these aliquots was separated from the AC by sieving them with the 74 μm sieve. The AC fraction was discarded and TPH in the soil were extracted and analyzed by the methods described in section 2.2.14. The remaining TPH concentration in the soil was plotted to find the time point where the stabilization of TPH removal by the AC is reached.

2.7 TREATMENT PAIRING

2.7.1 Statistical analysis of sorption and oxidation tests

Before coupling sorption and oxidation treatments, the best sorption and oxidation treatments in terms of TPH removal and degradation, were chosen after performing statistical analysis on the obtained data from the sorption and oxidation tests. The best sorption treatment and the best oxidation treatment according to this statistical analysis, were then paired in two-step and one-step arrangements.

Four statistical analysis of the obtained data were carried out using the software *Minitab 18* (2017). All analysis of variance (ANOVA) were performed after carrying out the treatments in the laboratory. The four analysis performed were:

- Statistical significance of the factor effects in advanced oxidation treatments
- Comparisons between advanced oxidation treatments
- Comparisons between sorption treatments with 0%, 5%, and 15% (w/w) AC
- Comparisons between sorption treatment with 5% (w/w) AC and all advanced oxidation treatments

An ANOVA was carried out to determine the statistical importance of the factor effects on the TPH degradation during the advanced oxidation tests. This ANOVA was carried out by entering the data of the TPH remaining in the soil for each treatment in the original DOE generated in section 2.5.1. The results were analyzed to determine which factors have a significant influence in the TPH degradation. The sequence employed to do this was: *Statistics → DOE → Factorial → Analyze Factorial Design*. The column containing the TPH data was selected as the response, and all factors with their interactions were selected to be analyzed.

The rest of the statistical analysis were carried out by comparing the means of the TPH degradation in all sorption and oxidation treatments. To do this, a one-way ANOVA was performed by entering the data in two columns (the treatment identification in one column, and the remaining TPH in another column). The sequence used to do this was *Statistics →*

ANOVA → One way. Then, the columns containing the data were selected and the desired mean comparisons were selected. The methods selected were Fisher, Dunnet, and Tukey.

After comparing the results, the treatments selected for the treatment coupling were: the advanced oxidation treatment with 10% (w/v) $K_2S_2O_8$ for 48 hours, and the sorption treatment with 5% (w/w) AC for 90 minutes.

2.7.2 Two-step pairing

The two-step pairing was implemented in two arrangements: first oxidation then sorption (oxidation-sorption), and first sorption then oxidation (sorption-oxidation).

Before starting the treatment pairing, the oxidant solution was prepared and activated. 200 mL of 10% (w/v) $K_2S_2O_8$ solution were prepared by dissolving 20 g of $K_2S_2O_8$ in water, and bringing the volume of the solution to 200 mL with osmotized water. This solution was activated by heating it at 50 °C in a beaker covered with watch glass, on a hot plate.

The oxidation-sorption treatment started by treating the soil with the oxidation treatment first. 10 g of contaminated soil were placed in a 125 mL Erlenmeyer flask and 15 mL of 10% $K_2S_2O_8$ solution were added (**Figure 2.10**). This procedure was repeated in triplicates. The flasks were sealed with plastic wrap and maintained at 50 °C ± 0.1 °C and 250 rpm for 48 hours in a shaking incubator (Benchmark Incu-Shaker 10L). 48 hours later, the liquid was decanted and the soil was air-dried for 24 hours.

Figure 2.10. Treatment pairing carried out in Erlenmeyer flasks

The sorption treatment was subsequently applied, by sieving the previously treated soil through a 74 μm mesh. The coarse fraction was recovered and 8.5 g of this fraction were placed in a clean Erlenmeyer flask, where 0.4474 g of powdered AC (previously air-dried and sieved through the same 74 μm mesh) were added, to reach a concentration of 5% (w/w) of AC. These flasks were maintained at 30 °C ± 0.1 °C and 250 rpm for 90 minutes in the shaking incubator. After this time, the mixture was sieved again. The AC was discarded and the soil was recovered to carry out the TPH extraction and analysis through the methods described above in section 2.2.14.

On the other hand, the sorption-oxidation treatment started with the sorption treatment, again in triplicates. A portion of contaminated soil was sieved through a 74 μm mesh. Portions of 9.5 g of the coarse fraction were placed in 125 mL Erlenmeyer flasks, where 0.5 g of powdered AC (previously air-dried and sieved through the same 74 μm mesh) were added, to achieve an AC concentration of 5% (w/w). These flasks were maintained at 30 °C ± 0.1 °C and 250 rpm for 90 minutes in the shaking incubator.

90 minutes later, the mixture was sieved again. The AC was discarded and the soil was recovered and transferred to clean Erlenmeyer flasks to carry out the advanced oxidation process. 14.25 mL of activated 10% $K_2S_2O_8$ solution were added into each flask. The flasks were sealed with plastic wrap and maintained at 50 °C ± 0.1 °C and 250 rpm for 48 hours in the shaking incubator. 48 hours later, the liquid was decanted and the soil was air-dried for 24 hours. Then, the soil was submitted to TPH extraction and analysis.

2.7.3 One-step pairing

The one-step pairing (simultaneous) was implemented by simultaneously adding the oxidant solution and the AC to the soil.

A portion of contaminated soil was sieved through a 74 μm mesh. Portions of 9.5 g of the coarse fraction were placed in 125 mL Erlenmeyer flasks, where 0.5 g of previously air-dried and sieved powdered AC were added, to get an AC concentration of 5% (w/w). 15 mL of activated 10% $K_2S_2O_8$ solution were added into each flask, that were also sealed with plastic wrap. These flasks were placed in the shaking incubator and maintained at 50 °C ± 0.1 °C and

250 rpm for 48 hours. After this time, the supernatant was decanted and the solid mixture was air-dried for 24 hours. Once dry, the AC was separated from the soil by sieving it with the 74 µm mesh. The AC was discarded and the soil was submitted to TPH extraction and analysis.

2.8 TREATED SOIL CHARACTERIZATION

After determining which paired treatment achieved the lowest TPH concentration, the soil that resulted from such treatment was characterized. To avoid the effects of any residual oxidant present in the soil, before carrying out the characterization analysis, the soil was washed with three 25 mL portions of osmotized water at 50 °C and vacuum filtered, to dissolve any residual $K_2S_2O_8$. Then, the soil was air-dried again for 24 hours at room temperature. The final soil quality of the treated soil was assessed by repeating the initial physical, chemical and physical-chemical tests applied to the contaminated and uncontaminated samples.

pH, electrical conductivity and oxidation/reduction potential were determined again following the methods described in the soil characterization section, using the same Thermo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter equipment.

Moisture content and TPH final concentration were analyzed gravimetrically again. Organic matter content was determined through the Walkley & Black method. Cation-Exchange Capacity through the ammonium acetate method by titration.

Finally, total nitrogen was determined once more through the Kjeldahl method, phosphorus was determined colorimetrically through the Bray & Kurtz extraction, and potassium and iron content was determined using a PerkinElmer AAnalyst 200 Atomic Absorption Spectrophotometer.

CHAPTER 3. RESULTS AND DISCUSSION

3.1 SOIL SAMPLING OBSERVATIONS

The soil sampling was successfully carried out in San Martín Texmelucan, Puebla, Mexico. The type of soil of the site was characterized as Cambisol, which as mentioned in previous chapters, corresponds to young soils, with coarse particles, like sand and gravel in the subsurface, and may present accumulations of calcium carbonate, iron and magnesium.

Even when hydrocarbon spillages are common in Puebla, the increase in fuel theft by criminal organizations in the area challenged the obtention of the soil samples for security reasons. For this same reason, despite the assistance of the municipality authorities, the sampling activities had to be developed as quickly as possible.

The violence issues in the area made impossible the analysis of the soil profile and the assessment of the vertical migration of the contaminant. Apart from the agricultural approach of this research, the need to extract the samples hurriedly was another reason to take the samples at a depth of 30 cm. Besides, this depth is suggested by NOM-021-RECNAT-2000 for the characterization of soils, because the root area of plans reaches this depth of 30 cm.

As observed in Figures 2.4 and 2.5, the color of the soil was different in some areas of the sampling site. These changes in the color of the soil, along with the strong fuel smell easily perceived, made the extent of the contamination evident. The color of the soil in the contaminated areas (light reddish brown) was darker than the uncontaminated ones (reddish gray), it had the appearance of being wet. No vegetation covered the contaminated areas, but some remains of plants were observed; such remains exhibited yellowing.

According to information provided by the personnel of *Protección Civil* who assisted the sampling, the spilled product was diesel and the spillage had happened about a month before the sampling was carried out. Pemex's physical security personnel confirmed that the product transported in the pipelines of that area is diesel. The presence of this substance was further confirmed with the GC-FID analysis.

3.2 SOIL CHARACTERIZATION RESULTS

3.2.1 Soil texture

The particle-size distribution of the soil determined through the hydrometer method delivered a high percentage of sand: 86.04%, this corresponds to particles between 0.05 to 2mm of diameter. The percentages of silt was 8.00%, which includes particles between 0.002 mm to 0.05 mm of diameter. Finally, the percentage of clay was 5.96%, with a particle-size of less than 0.002 mm. When plotting these values in the soil textural triangle, a loamy sand textural class was obtained.

The permeability of a soil increases with increasing particle size (Beard & Weyl, 1973). Permeability indicates the capacity of a material to let a fluid flow through it without altering its internal structure. The analyzed soil contains a high percentage of sand and low percentages of silt and clay, since it is a soil with high particle sizes, its permeability is higher. Therefore, when a fluid, like the diesel that contaminated the site, is spilled over this type of soil, its vertical migration will be high (Oyem & Oyem, 2013). This does not necessarily means that the contaminant reached excessively long depths, there could be layers of clay or presence of rocks beneath the surface that could have stopped the mobility of the contaminant.

Soil texture is an important characteristic because it also influences its nutrient and water-holding capacities, its porosity and aeration. These characteristic influence the development of organisms in and on the soil. Soils with high percentages of sand present little resistance to root growth, low water and nutrient-holding capacity, leaching of nutrients, and los organic matter content (Stirling *et al.*, 2016).

3.2.2 pH Value

Another parameter analyzed was pH. Soil is a highly buffered system, meaning its pH does not change easily. According to the NOM-021-RECNAT-2000, pH indicates the alkalinity or acidity of a soil. Following this principle, a soil can be classified as shown in **Table 3.1**. The pH values obtained from the characterization of the soil samples were 6.6 for uncontaminated soil and 6.9 for contaminated soil. Both pH values are in the range of 6.6 to 7.3, therefore the soil can be classified as neutral.

Table 3.1 Soil classification based on its pH value

Classification	pH
Highly acid	< 5.0
Moderately acid	5.1 - 6.5
Neutral	6.6 - 7.3
Moderately alkaline	7.4 - 8.5
Highly alkaline	> 8.5

The optimal soil pH for microbial activity and crop development is close to neutral. When soil is highly acidic, major nutrients have a low availability. On the other hand, when the soil is extremely alkaline (high pH values), there are trace element deficiencies like iron, manganese, copper and zinc. Both extreme conditions result in low crop performances (Stirling *et al.*, 2016). Specifically, acid soils restrict microbial activity and may cause aluminium toxicity and yellowing of leaves, alkaline soils may be sodic (Stirling *et al.*, 2016; Oyem & Oyem, 2013).

3.2.3 Electrical conductivity (EC)

Electrical conductivity (EC) is related to the type of ions in the soil and their concentrations. The determination of the EC is an indirect way of measuring the salinity of soils (Fernández-Linares *et al.*, 2006). Values above 1 dS/m indicate that crops sensitive to salts are likely to be affected. More salt-tolerant crops can cope with EC values of up to 5 dS/ m (Stirling *et al.*, 2016). The classification of soil salinity, based on its EC is reproduced in **Table 3.2**, obtained from the NOM-021-RECNAT-2000.

The EC values obtained for the soil samples are: 0.203 dS/m at 25 °C for uncontaminated soil, and 0.159 dS/m at 25 °C for contaminated soil. According to **Table 3.2**, such values indicate low salinity and no important effects of it.

Table 3.2 Soil classification based on its EC value

Classification	EC (dS/m)
Insignificant salinity effects	< 1.0
Lightly saline	1.1 - 2.0
Moderately saline	2.1 - 4.0
Saline soil	4.1 - 8.0
Highly saline	8.1 - 16.0
Very highly saline	> 16.0

3.2.4 Moisture content

Water is an essential component for the processes that develop in the soil, for example, it dissolves nutrients and makes them available for plants and microorganisms. But sometimes high contents of water can be harmful. In this sense, water regulates physical, chemical and biological activity in the soil (Fernández-Linares *et al.*, 2006). Water enters the soil and moves down the soil profile, filling the soil pores. As mentioned above, clay soils with small pores will have reduced infiltration compared with sandy soils (Stirling *et al.*, 2016).

Water moves through the soil matrix by gravity or by capillary action (due to hydrogen bonding and magnetic attraction). Water around soil particles is controlled by adhesive and cohesive forces. Cohesive and capillary forces move water against gravity to favor its availability for plants (Oyem & Oyem, 2013). The moisture content of the contaminated soil was 3.09%, and for the uncontaminated soil was 1.11%. These values were used throughout the whole research to perform moisture corrections in other analysis.

3.2.5 Oxidation / Reduction Potential

Regarding soil redox potential, in this case referred to as oxidation potential, it is defined as a quantitative measurement of the oxidation energy, or the tendency of electrons to escape a redox system. It should be noted that it is not possible to reach reproducibility of this measurement in complex systems like soils and sediments (Fernández-Linares *et al.*, 2006).

According to Oyem & Oyem (2013), oil spillages increase the redox properties of a soil, in contrast to non-affected soil.

The oxidation potential measured for the uncontaminated soil sample was 320 mV (0.320 V) at 25 °C. According to Fernández-Linares *et al.* (2006), a value over 300 mV, indicates that aerobic respiration and denitrification by microorganisms is occurring in the soil, this is an indicator of the presence of organisms in the soil, confirming that this sample hadn't suffered contamination by hydrocarbons. On the other hand, the contaminated soil had an oxidation potential of 288 mV (0.288 V) at 25 °C. This value could indicate reduction of Mn^{+4} or Fe^{+3} (Fernández-Linares *et al.*, 2006).

The electrode potential for an overall redox reaction (E^0_{Rxn}) can be determined by adding the reduction (E^0_{red}) and oxidation (E^0_{ox}) potentials together, following **Equation 3.1**, because the numbers of electrons transferred in the reaction are identical for both, reduction and oxidation (Crittenden *et al.*, 2012).

$$E^0_{Rxn} = E^0_{red} + E^0_{ox} \quad \textbf{Equation 3.1}$$

Considering the soil E^0_{ox} and taking into account that oxidants selected for this research have a E^0_{red} of 1.78 V for H_2O_2, 2.76 V for $OH\cdot$, 2.01 V for $S_2O_8^{2-}$, and 2.60 V for $SO_4^{\cdot-}$, as given by the half reactions represented in **Equations 3.2**, to **3.5** (Huling & Pivetz, 2006), E^0_{Rxn} values were calculated and are shown in **Table 3.3**.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad 1.78\ V \quad \textbf{Equation 3.2}$$

$$2\cdot OH + 2H^+ + 2e^- \rightarrow 2H_2O \quad 2.76\ V \quad \textbf{Equation 3.3}$$

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \quad 2.01\ V \quad \textbf{Equation 3.4}$$

$$SO_4^{\cdot-} + e^- \rightarrow SO_4^{2-} \quad 2.60\ V \quad \textbf{Equation 3.5}$$

Positive values of E^0_{Rxn} can be considered a general indication that a reaction will proceed as written (Crittenden *et al.*, 2012), and high E^0_{Rxn} values suggest that the reaction is very likely to occur spontaneously. Also, the higher the E^0_{red} value, the easier it is for the oxidant to accept electrons. Taking this into account, the positive results in **Table 3.3** indicate that redox reactions involving the soil matrix and the oxidants will in fact proceed towards the oxidation of the hydrocarbons in the soil. Thus, the contaminant will loose electrons that will be transferred to the oxidant species, generating sulfates (SO_4^{2-}) and water (H_2O). Also, the hydrocarbons will have changes in their bonds, due to the interactions with their π electrons (Crittenden *et al.*, 2012). Eventually, if the mineralization of the contaminant is complete, the products of the oxidation of hydrocarbons will be carbon dioxide (CO_2) and water (H_2O)

Also, higher E^0_{Rxn} values for sulfate and hydroxyl radicals resulting from AOPs, proves that these are better oxidants than their predecessors and redox reactions will occur easily, as it has been widely reported (Bennedsen et al, 2014; Deng & Zhao, 2015; Huling & Pivetz, 2006; Tsitonaki et al, 2010).

Table 3.3 Calculation of E^0_{Rxn} values

Oxidant / Soil	Oxidant E^0_{red} (V)	Soil E^0_{ox} (V)	Reaction E^0_{Rxn} (V)
H_2O_2 / uncontaminated	1.78	0.320	2.100
$\cdot OH$ / uncontaminated	2.76	0.320	3.080
$S_2O_8^{2-}$ / uncontaminated	2.01	0.320	2.330
$SO_4^{\cdot -}$ / uncontaminated	2.60	0.320	2.920
H_2O_2 / contaminated	1.78	0.288	2.068
$\cdot OH$ / contaminated	2.76	0.288	3.048
$S_2O_8^{2-}$ / contaminated	2.01	0.288	2.298
$SO_4^{\cdot -}$ / contaminated	2.60	0.288	2.888

3.2.6 Organic matter (OM)

The amount of organic matter (OM) varies with soil type and climate. Soil OM represents a small fraction of the soils, but it influences many processes that occur in the soil, for example, agricultural production. Soil OM can be bound to soil particles and it is generally composed of living and dead components, like leaf litter, crop residues, roots, animal waste and microorganisms. The presence of OM improves aeration and diffusion of nutrients, water-holding capacity. OM also increases the activity and diversity of soil fauna and improves the soil buffering capacity, meaning it basically regulates pH (Stirling *et al.*, 2016).

Organic Carbon is the carbon component of OM that comprehends about 58% of the mass of OM The Organic Carbon (OC) content of the uncontaminated soil sample was 1.62%, therefore following **Equation 2.6** its OM content was 2.78%. The contaminated soil had an OC content of 2.60% and an OM content of 4.48%, of course this 1.70% increase in the OM content is related to the presence of the hydrocarbons (Fernández-Linares *et al.*, 2006). This does not necessarily mean that this is the TPH concentration in the soil, since the presence of plant tissue or other organisms in the uncontaminated soil could be rising this OM value, and viceversa, the lack of this OM sources in the contaminated soil could be lowering the OM value.

Table 3.4 presents the classification of the organic matter in non-volcanic soils, given by the NOM-021-RECNAT-2000. According to this table, the uncontaminated soil has a medium OM content, whereas the hydrocarbon contamination elevated the OM content from medium to high.

Table 3.4 OM content classification for non-volcanic soils

Class	OM content (%)
Very low	< 0.5
Low	0.6 - 1.5
Medium	1.6 - 3.5
High	3.6 - 6.0
Very high	> 6.0

3.2.7 Cation-Exchange Capacity (CEC)

According to the NOM-021-RECNAT-2000, Cation-Exchange Capacity (CEC) is the sum of exchangeable cations (positively charged ion) adsorbed in the particles of a soil, expresses in cmol(+), meaning centimoles of monovalent cations, per Kg of soil. The most common cations in soil are: calcium, magnesium, sodium, potassium, ammonium and hydrogen. Basically CEC indicates the ability of a soil to hold these as nutrients and supply them to organisms. CEC is influenced by soil texture, OM, pH and the minerals present in the soil (Stirling *et al.*, 2016). CEC can help to infer the grade of weathering of soils, as shown in **Table 3.5** (NOM-021-RECNAT-2000; Fernández-Linares *et al.*, 2006). Soils with CEC below 4 cmol(+)/Kg) have a very limited ability to hold nutrient cations, that leach when water flows through the soil profile (Stirling *et al.*, 2016).

CEC calculated for the uncontaminated soil was 14.24 cmol(+)/Kg, and for the contaminated sample was 15.69 cmol(+)/Kg. According to **Table 3.5,** the grade of weathering of the soil is from low to medium. CEC is strongly related to clays, but in soils with low clay contents, OM is responsible for most of the CEC (Stirling *et al.*, 2016), so it is logical that in the sampled soil, the higher the OM content, the higher the CEC.

Table 3.5 Grade of weathering of soils, according to their CEC

Grade of weathering	CEC cmol(+)/Kg
Very Low	< 5
Low	5 - 15
Medium	15 - 25
High	25 - 40
Very high	> 40

3.2.8 Macronutrients: Available Phosphorus (P), Total Nitrogen (N), Potassium (K)

Phosphorus (P) itself is not found in nature because it is easily oxidized, nonetheless there are many organic compounds and minerals that contain P. In the soil, P can be either organic or inorganic, depending on the nature of the compounds. Usually inorganic compounds containing P are more abundant.

Anyhow, P is a macronutrient for plants and soil microorganisms, along with nitrogen (N) and potassium (K) (Fernández-Linares *et al.*, 2006; Stirling *et al.*, 2016). The availability of nutrients is affected by pH. Calcium, potassium, magnesium and sodium are alkaline elements, which are lost with increasing acidity. On the other hand, phosphorous is more available in acidic soil conditions (Oyem & Oyem, 2013). **Table 3.6** shows the classification of soils, depending on the concentration of the mentioned macronutrients (NOM-021-

RECNAT-2000), which is an indicator of the soil quality and fertility. Since OM is a source of these macronutrients, this resource can be added to soils to improve their quality (Stirling *et al.*, 2016).

Although sandy loam soils present low nutrient retention, low phosphorus fixation, and excessive leaching of nitrates, potassium and sulfate (Stirling *et al.*, 2016), the concentration of available P found in the soil samples classified as high according to **Table 3.6**. In the uncontaminated soil, available P concentration was 164.3 mg/Kg, and in the contaminated soil, such concentration was 74.4 mg/Kg. In some cases hydrocarbon spills can diminish the available P concentration (Bello & Inobeme, 2015), thus it can be inferred that the contamination event lowered such concentration by over 50%. The lightly acid pH of the soil samples could be the reason why the available phosphorus is still high (Oyem & Oyem, 2013).

Soil N undergoes continuous transformations from mineral forms (like ammonium and nitrates) to organic ones (like proteins or amino acids). Plants and microorganisms transform mineral N forms to organic forms, which can be decomposed and mineralized again (Stirling *et al.*, 2016). These transformations are the reason why total N analysis in soils only gives partial information on the amount of available N for organisms. Also, some hydrocarbon molecules contain nitrogen atoms (Speight, 2006), that change the total N concentration in contaminated soils. Generally a carbon : nitrogen (C:N) ratio of 10:1 is equilibrated enough for the development of organisms (Fernández-Linares *et al.*, 2006), although this ratio can change from organism to organism.

Total N concentrations obtained in the soil samples were 0.13% for uncontaminated soil and 0.06% for contaminated soil. According to **Table 3.6**, N content before the hydrocarbon spill was medium and dropped to low after the contamination. Taking into account the previously mentioned OC content samples, the C:N ratio of the uncontaminated soil is approximately at 13:1, and for the contaminated soil it is around 43:1. The C:N ratio was near the required 10:1 ratio, making the soil good for the development of plants and organisms, however, the hydrocarbon contamination increased the C concentration and lowered the N concentration, deteriorating the quality of the soil. According to Oyem & Oyem (2013), a C:N ratio below 10:1 is problematic for soil fertility.

Potassium (K) is one of the dominant cations in most soils, except in sodic and acid soils, which favor its displacement by other cations. The critical deficiency concentration for exchangeable potassium is between 0.2 and 0.5 cmol(+)/Kg. The amount of K found in the uncontaminated soil was 2.02 cmol(+)/Kg, and 1.64 cmol(+)/Kg in the contaminated soil. Both values are high, still the hydrocarbon contamination diminished the amount of K in the soil, an effect of hydrocarbon spillages as described by (Bello & Inobeme, 2015).

Table 3.6 P, N and K content classification for non-volcanic, and acid to neutral soils

Class	P (mg/Kg)	N (%)	K (cmol(+)/Kg)
Very Low	-	< 0.05	< 0.2
Low	< 15	0.05 - 0.10	0.2 -0.3
Medium	15 - 30	0.10 - 0.15	0.3 - 0.6
High	> 30	0.15 -0.25	> 0.6
Very High	-	< 0.25	-

3.2.9 Total iron (Fe)

Iron (Fe) is the third greatest metal in soils, its concentration in soil can range between one and several hundred g/Kg (Fan *et al.*, 2016). Iron is present in the biosphere in wide variety of chemical compounds, specifically in many minerals, like magnetite (Fe_3O_4), goethite ($FeO(OH)$) or hematite (Fe_2O_3) (Fernández-Linares *et al.*, 2006).

The concentration of total extracted Fe in the soil was 3.1 g/Kg for uncontaminated soil and 2.5 g/Kg for contaminated soil. As a micronutrient, the required iron concentration should be above 4.5 mg/Kg (NOM-021-RECNAT-2000), therefore, the amount of iron in the soil is adequate as a micronutrient, however its concentration also dropped after the hydrocarbon spillage. Taking into account the information mentioned above by Fan *et al.* (2016), the iron content in the soil is low but not insignificant.

3.2.10 Surface area and total pore volume

Surface area is the area of the solid particles in a given quantity of soil or porous media. Pore volume or pore space is the portion of soil bulk volume occupied by soil pores (Kirkham, 2014). The surface area of the soil, obtained through the BET method, was 2.2306 m^2/g. The total pore volume was 0.0052 cm^3/g, with an average pore diameter of 9.2957 nm. The measurement of these parameters is important in soil contamination scenarios because they have a great influence on the movement and sorption of the contaminant in the soil (Kirkham, 2014).

Because the surface area to volume ratio decreases as particle size becomes larger, sand particles have a smaller surface area than clay particles, which also have charged surfaces and promote chemical interactions on their surface (Stirling *et al.*, 2016), thus, sandy soils will not adsorb as much contaminant as clay soils. However, this property of sandy soils also leads to poor nutrient and water-holding capacity. Also, it should be considered that organic matter in soils boosts surface area (Knödel *et al.*, 2007), therefore retention capacity of water, nutrients or contaminants improves in soils with high contents of OM. Naturally, the studied soil had a medium content of OM, which could influence the adsorption of hydrocarbons onto the soil particles, despite the loamy sand texture.

With an average pore diameter of 9.3 nm, the studied soil can be considered a mesoporous media. The obtained pore volume and pore diameters, indicate that coarse particles like sand, allow air and other fluids to move easily through the soil (Stirling *et al.*, 2016). This could result adverse in a contaminated soil, because it may favor the migration of the contaminant to other environmental compartments through leaching or volatilization.

Gas adsorption is used for measuring surface area and pore sizes of porous materials. This is done by measuring the volume of gas adsorbed and desorbed at constant temperature, varying the pressure, to generate the adsorption and desorption isotherms. Both isotherms determined for a sample of soil are presented in **Figure 3.1**. The y axis of the plot represents que quantity of gas absorbed per gram of sample at standard temperature and pressure conditions; the x axis represents the relative pressure. The S shape of the curves is typical of the BET model.

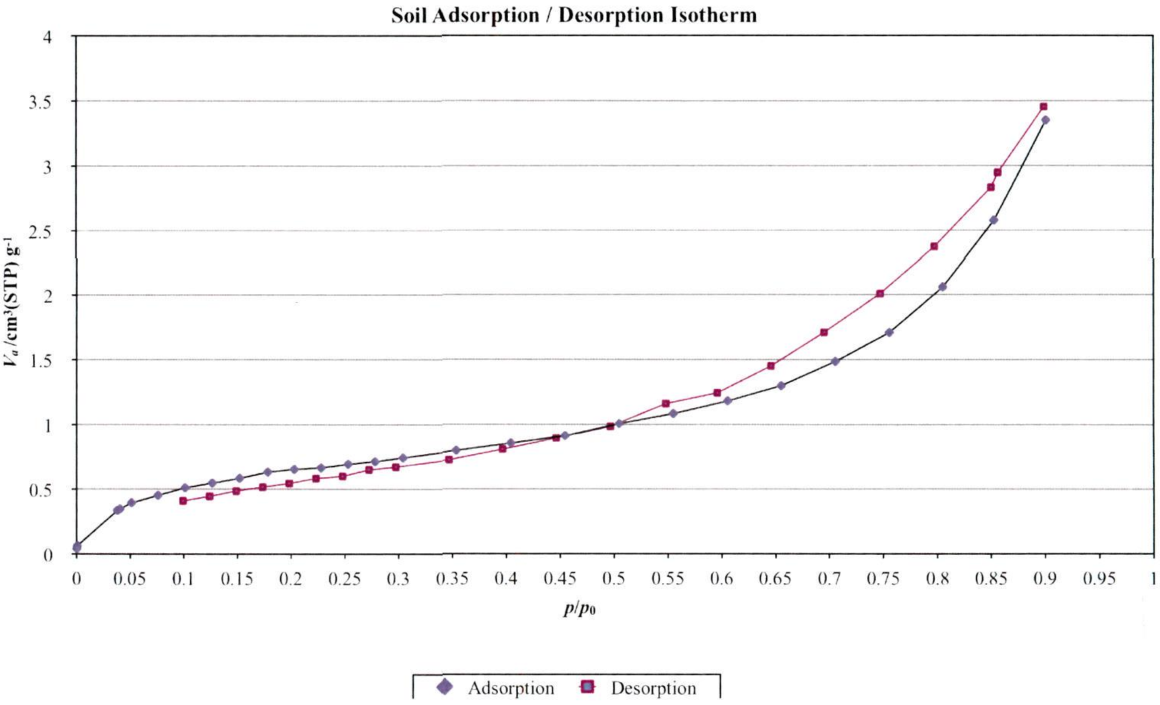

Figure 3.1 Adsorption and desorption isotherm of the soil sample

3.2.11 Thermogravimetric analysis (TGA)

TGA is useful in soil science to estimate the contents of organic carbon and inorganic carbon in soil samples. Inorganic carbon is identified with thermal mass losses at 500 to 800 °C, while organic carbon is fairly related to losses between 180 and 450 °C (Kristl *et al.*, 2016). The mass losses below 100 °C mainly indicate water volatilization; from 200 to 280 °C they are mainly due to decomposition of organic matter, mainly carboxylic and phenolic groups, and hydrocarbon compounds; from 270 to 370 °C the mass loss is related to carbon oxidation of the organic matter ($R\text{-}CH + O_2 \rightarrow CO_2 + H_2O$); finally, from 380 to 530 °C, the mass loss is mainly due to dehydroxilation of metallic hydroxides (Miyazawa *et al.*, 2000).

Figure 3.2. shows the TGA performed on a contaminated soil sample. As mentioned above, up to 100 °C the soil looses about 3 to 5% of its weight, corresponding to the moisture

content of the contaminated soil sample. The weight loss does not stop there, it continues from 100 to 250 °C, this weight loss most likely corresponds to the diesel identified as the soil contaminant. According to Garavaglia (2014), diesel fuel consumes completely in a TGA at 252.8 °C, such weight loss is appreciated in a TGA curve associated with a soil contaminated with such substance, still, most of the first major weight losses is related to water loss than to hydrocarbons loss.

From 300 to 600 °C, no significant weight loss is observed, probably caused by the absence of any other OM that decomposes at those temperatures (Miyazawa *et al.,* 2000). The second major weight loss that starts right after the 600 °C and continues until the 1000 °C, is related to the loss of inorganic matter, like the inorganic carbon mentioned above (Kristl *et al.,* 2016; Garavaglia, 2014). Over 430 °C, inorganic sources start to contribute to mass losses with diminishing contributions related to organic matter, except for more recalcitrant organic matter (Pallasser et al., 2013). These results show that the studied soil is a mineral soil with low amounts of organic matter

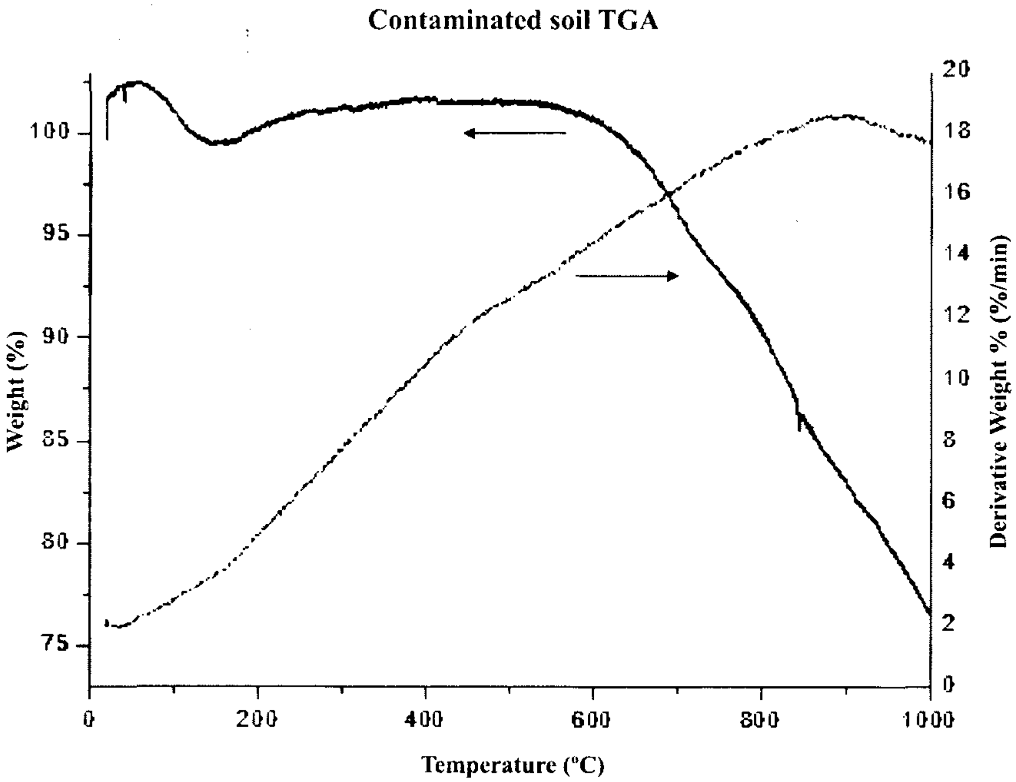

Figure 3.2 Contaminated soil TGA

3.2.12 Total Petroleum Hydrocarbons (TPH)

Although according to Speight (2006), the term Hydrocarbons refers to molecules strictly containing only atoms of hydrogen and carbon, NOM-138-SEMARNAT/SSA1-2012 uses this term to refer to organic compounds constituted mainly by hydrogen and carbon atoms, therefore, this term is used throughout Mexican regulations referring to compounds contained in petroleum and its products. The term hydrocarbons is used throughout this research in the sense that NOM-138-SEMARNAT/SSA1-2012 uses it.

The Gas Chromatography-Flame Ionization Detection (GC-FID) analysis results for Medium Fraction Hydrocarbons, provided by an accredited laboratory are shown in **Table 3.7.** These results were obtained following EPA Method 8015D/GC/FID. The chromatogram corresponding to the soil sample is shown in **Figure 3.3**. Diesel Range Organics (DRO), or Medium Fraction Hydrocarbons (MFH) correspond to all the signals that start at minute 24, and end between minutes 32 and 33 (Sadler & Connell, 2003). In **Figure 3.3** it is evident that lighter hydrocarbons (signals before minute 24) are not as abundant as MFH, confirming that in fact, the contaminant present in the soil is diesel and not gasoline.

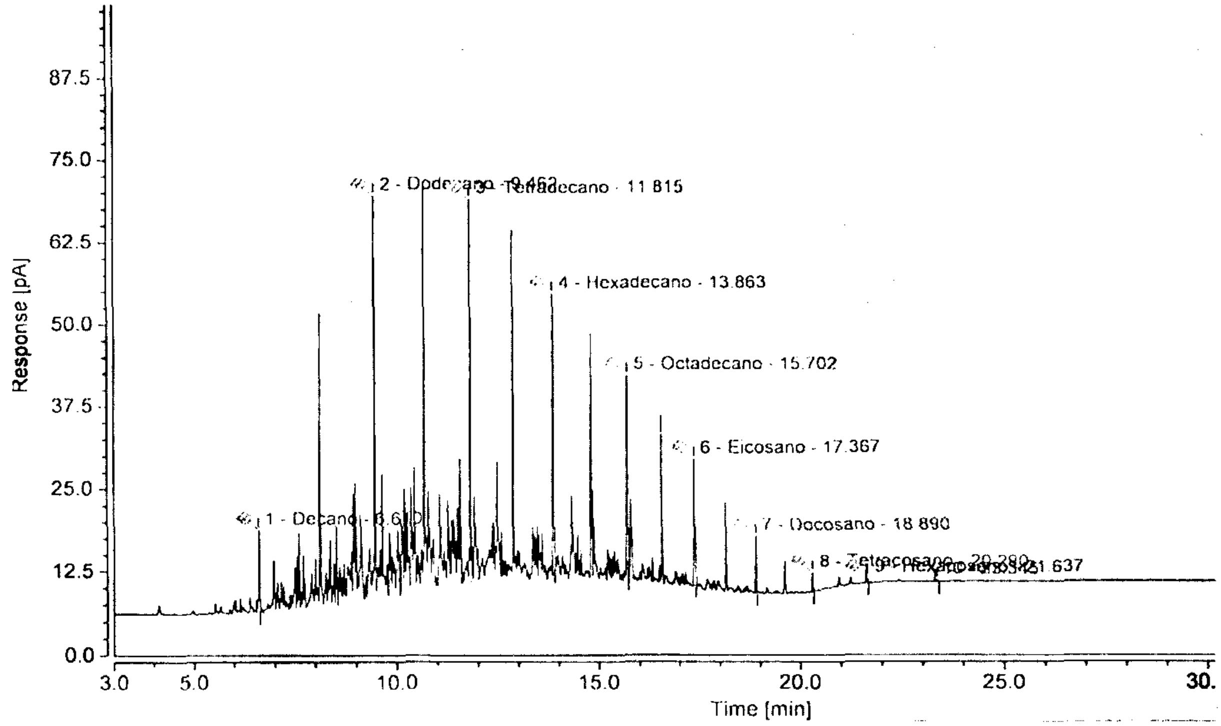

Figure 3.3 Contaminated soil GC-FID Chromatogram

Table 3.7 Diesel Range Organics (DRO) / Medium Fraction Hydrocarbons

Medium Fraction Hydrocarbons	Analytic Result (mg/Kg)
Decane	110.006
Dodecane	466.217
Tetradecane	545.433
Hexadecane	514.893
Octadecane	432.039
Eicosane	350.653
Docosane	204.867
Tetracosane	88.882
Hexacosane	30.964
Octacosane	< 1.500

Initial TPH concentration was determined gravimetrically in the contaminated soil sample. The determination was repeated several times to accurately determine the initial TPH concentration, which resulted in 55 141 mg of TPH per Kg of soil (55 141 mg/Kg). TPH were extracted using 2-propanone, commonly known as acetone. This solvent was selected to avoid high costs of dichloromethane (CH_2Cl_2). Also, to avoid the toxicity of CH_2Cl_2, methanol (CH_3OH), or hexane (C_6H_{14}), for health and safety reasons and of course, to avoid their generation as waste solvents.

The concentration of TPH in the contaminated soil is quite high, for every Kg of soil, there are over 55 g of diesel sorbed on the soil particles. Such value is nearly 46 times the maximum permissible limit established in NOM-138-SEMARNAT/SSA1-2012, for agricultural and residential soils. Other authors on remediation research report initial TPH concentrations of 4 000 mg/Kg (Chen *et al.*, 2015), 10 000 mg/Kg (Tsai & Kao, 2009; Liang & Guo, 2012), 16 808 mg/Kg (Iturbe *et al.*, 2007), from 220 to 18 500 mg/Kg (Wu *et al.*, 2015), 32 100 mg/Kg (Hernández-Espriú *et al.*, 2013), 38 300 mg/Kg (Gong, 2012), 40 867 mg/Kg (McAlexander *et al.*, 2015), and from 12 830 to 94 200 mg/Kg (Apul *et al.*, 2016).

Table 3.8 Soil characterization summary

Parameter (unit)	Uncontaminated soil	Contaminated soil
Texture	Loamy sand	-
pH	6.6	**6.9**
EC (dS/m) at 25 °C	0.203	0.159
Moisture content (%)	1.11	3.09
Oxidation potential (mV)	320	**288**
OM (%)	2.78	4.48
CEC (cmol(+)/Kg)	14.24	15.69
Available P (mg/Kg)	164.3	74.4
Total N (%)	0.13	0.06
K (cmol(+)/Kg)	2.02	1.64
Total Fe (mg/Kg)	3134	2499
Surface area (m^2/g)	2.2306	-
Total pore volume (cm^3/g)	0.0052	-
Average pore diameter (nm)	9.2957	-
TPH (mg/Kg)	-	55141

3.3 MOLECULES MODELLING RESULTS

All simulated reductant - oxidant interactions can be found in Appendix D. The energy values obtained for the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) for each modelled molecule, are listed in **Table 3.9**, as well as the positive (E+) and negative (E-) electrostatic potential values.

The molecular EP is the potential energy of interaction of a positive charge near a molecule that will interact with it, depending on the electron density throughout the molecule (Gupta, 2016). The positive charge will be attracted to the negative parts of the molecule, while in the positive parts of the molecule, there will be repulsion.

The theory of the molecular orbitals considers that when individual atoms combine to form a molecule, their atomic orbitals combine to form molecular orbitals with complex shapes in which electrons are not confined to determinate bonds in a molecule, but they move throughout the whole molecule. The HOMO is the orbital that, in accordance with the building-up principle (Aufbau principle), is the last one occupied by electrons. On the contrary, the LUMO is the next orbital that does not have any electrons (Atkins *et al.*, 2008).

HOMO and LUMO, are the two molecular orbitals that play an essential role in a wide range of reactions of saturated and unsaturated compounds. It was discovered that the electron delocalization between the HOMO and LUMO is generally the principal factor determining the ease of a chemical reaction (Fukui, 1982). When two molecules approach and their molecular orbitals overlap, a reaction will proceed.

Table 3.9 Obtained parameters from modelled hydrocarbon molecules and oxidant chemical species

Component	HOMO	LUMO	E-	E+
n-decane	-11.275	3.185	0.018	0.099
n-dodecane	-11.265	3.137	0.017	0.093
n-tetradecane	-11.267	3.105	0.016	0.094
n-eicosane	-11.266	3.050	0.017	0.095
benzene	-9.751	0.396	-0.005	0.109
1,3,5-trimethylbenzene	-9.273	0.432	-0.011	0.114
naphthalene	-8.837	-0.406	-0.005	0.111
anthracene	-8.249	-0.968	-0.003	0.112

Table 3.9 (Continuation)

Oxidant	Orbital	HOMO	LUMO	E-	E+
$OH\cdot$	Alpha	-13.186	4.239	-0.089	0.179
	Beta	-12.542	-0.760	-0.089	0.179
H_2O_2		-11.601	1.580	-0.081	0.179
$SO_4^{\cdot -}$	Alpha	-6.205	6.603	-0.368	0.091
	Beta	-6.178	3.470	-0.368	0.091
$S_2O_8^{2-}$		-3.121	7.948	-0.464	-0.023

The results of the reductant - oxidant interactions between hydrocarbons as reductant species and free radicals as oxidant species are represented in **Table 3.10**. Since all aromatic and all aliphatic hydrocarbon molecules simulated exhibit similar HOMO, LUMO, E- and E+ values, only one representative compound of each group of hydrocarbons is presented in **Table 3.10**, the interactions with all simulated molecules can be found in Appendix D.

Table 3.10 Reductant - oxidant interactions between hydrocarbons (aromatic & aliphatic) and free radicals

Reductant	Oxidant	HOMO	LUMO	BG	E-	E+	EP	ETC
benzene	**$OH\cdot$**	-9.751	4.239	13.990	-0.005	0.179	0.184	76.033
benzene	**$OH\cdot$**	-9.751	-0.760	8.991	-0.005	0.179	0.184	48.864
benzene	**$SO_4^{\cdot -}$**	-9.751	6.603	16.354	-0.005	0.091	0.096	170.354
benzene	**$SO_4^{\cdot -}$**	-9.751	3.470	13.221	-0.005	0.091	0.096	137.719
n-decane	**$OH\cdot$**	-11.275	4.239	15.514	0.018	0.179	0.161	96.361
n-decane	**$OH\cdot$**	-11.275	-0.760	10.515	0.018	0.179	0.161	65.311
n-decane	**$SO_4^{\cdot -}$**	-11.275	6.603	17.878	0.018	0.091	0.073	244.906
n-decane	**$SO_4^{\cdot -}$**	-11.275	3.470	14.745	0.018	0.091	0.073	201.988

According to González-Pérez *et al.* (2014), when the Electron Transfer Coefficient (ETC) is higher, the probability of a chemical reaction is high. Taking this into account, lower oxidation rates are expected for aromatic hydrocarbons. This assumption is logic due to the stability of aromatic rings. In fact, the simpler the hydrocarbon molecule, the higher the probability of it being oxidized, so it is likely that linear molecules with less carbon atoms will be oxidized before ramified molecules with high molecular weight.

Also, higher oxidation rates are expected with sulfate radicals generated from the activation of persulfate. Even when persulfate interactions with hydrocarbons showed higher

ETC values, it has been highly documented already that the activation of oxidants is more efficient in the degradation of contaminants (Bennedsen *et al,* 2014; Deng & Zhao, 2015; Huling & Pivetz, 2006; Tsitonaki *et al,* 2010). This is evident because hydroxyl radical interactions showed higher ETC values than hydrogen peroxide itself.

3.4 VALORIZED ACTIVATED CARBON CHARACTERIZATION RESULTS

As previously mentioned, the Activated Carbon (AC) source for this project was an AC cartridge that had been previously used for municipal water treatment. This type of AC that has been used but not completely spent is referred to as semi-wasted AC by Martínez-Gallegos et al. (2017). This research valorizes this residue of semi-wasted AC to make good use of it for soil treatment purposes. Since this acquired AC was not new, its characteristics had to be analyzed again.

Regarding pH value of AC, when a fluid is put in contact with AC, chemical reactions may take place between the material, its other constituents, and the fluid. these chemical changes may alter the pH of the AC or the pH o the AC may influence these reactions (ASTM, 2017). pH of new AC should be neutral, when it is activated, AC should be washed until it reaches a pH value ranging from 6 to 8 (Ahmedna *et al,* 2000; Itodo *et al.*, 2010; Jadhav & Mohanraj, 2016; Ospina-Guarín *et al.*, 2014). The oxidation of the material produces hydroxyl, carbonyl and carboxyl groups that make the AC acid and basic at the same time (Luna *et al.*, 2007). The pH of the valorized semi-wasted AC was 7.1, still in the neutral range for new AC.

One of the components that AC looses during its thermal activation is moisture (Itodo *et al.*, 2010). Actually, AC can be considered hydrophobic because of its low affinity to water, which is an important property during its usage for sorption processes in presence of water; however, the presence of chemical species adsorbed into the surface of the AC may make its surface more hydrophilic (Luna *et al.*, 2007). In fact, moisture content is a required analysis for all AC manufacture. Moisture content of AC as packed is usually less than 5%. The moisture content of the analyzed AC was 3.93%.

Bulk density is the mass of a unit volume of the AC sample in air, including the whole pore system. This parameter becomes useful when estimating the amount of AC required for a certain system. Powdered AC usually have a bulk density between 0.25-0.75 g/cm^3, and granular AC usually have bulk densities around 0.40-0.50 g/cm^3 (Marsh & Rodríguez-

Reinoso, 2006). The bulk density of the valorized AC was 0.3860 g/cm^3, such value is in the range of a powdered AC.

Adsorption tests with methylene blue and iodine, provide information on the structure of AC. According to their molecular sizes, methylene blue is adsorbed in mesopores and iodine is adsorbed in micropores. The methylene blue value (MBV) is the amount of dye adsorbed on 1 g of AC. Similarly the iodine number (IN) is the amount of iodine adsorbed per gram of AC (Nunes & Guerreiro, 2011).

MBV usually ranges from 11 to 28 mg of methylene blue per gram of AC, and IN goes from 500 to 1200 mg of iodine per gram of AC (Itodo *et al.*, 2010). MBV of the semi-wasted AC was 9.6 mg/g, meaning that a 0.1 g AC sample adsorbed 0.800 mL of methylene blue solution (250 mL with 300 mg of dye), and a 0.5 g AC sample adsorbed 4 mL of such solution. On the other hand, obtained IN was 244.182 mg/g, the residual normality of the decolorized iodine solution was 0.0292, a value between 0.008 and 0.0334, so the analysis did not have to be repeated (CEFIC, 1986).

Both values, MBV and IN, are outside of their usual range, which is logical since the AC is not new and it was expected that its sorption capacity had diminished due to its previous use. Since the MBV is closer to the reference range than the IN, it can be inferred that the analyzed AC has a mesoporous structure. Since sorbents with high IN performs better in the removal of small sized contaminants (Itodo *et al.*, 2010), and high MBV indicate better performance with big sized molecules, the studied AC has the capacity to remove contaminants with big molecular sizes, like hydrocarbons.

As mentioned above, surface area is the area of the solid particles in a given quantity of porous media, and pore volume is the portion of AC volume occupied by pores (Kirkham, 2014). The surface area of the analyzed semi-wasted AC, obtained through the BET method, was 387.34 m^2/g. The total pore volume was 0.2521 cm^3/g, with an average pore diameter of 2.6035 nm. Comparing these values with the values mentioned above for the soil characterization, proves that in fact AC is a highly porous media with high surface area. With an average pore diameter of 2.6 nm, this AC can be considered a mesoporous media, confirming the information obtained with the MBV and the IN analysis, previously discussed.

In the study carried out by Nunes & Guerreiro (2011), they analyzed the surface area and total pore volume of several AC samples through the BET method. According to their findings, the surface area of the samples varied from 199 to 2015 m^2/g. and the pore volume from 0.09 to 1.11 cm^3/g. The semi-wasted AC characterization gave surface area and pore volume values that still enter in the ranges obtained by Nunes & Guerreiro (2011), therefore, even though the AC had been previously used, it still has an acceptable sorption capacity, taking into account the MBV, IN and surface area obtained.

Adsorption and desorption isotherms of the analysis can be found in **Figure 3.**. Again, the y axis is que quantity of gas absorbed per gram of sample at standard temperature and pressure conditions, and the x axis represents the relative pressure.

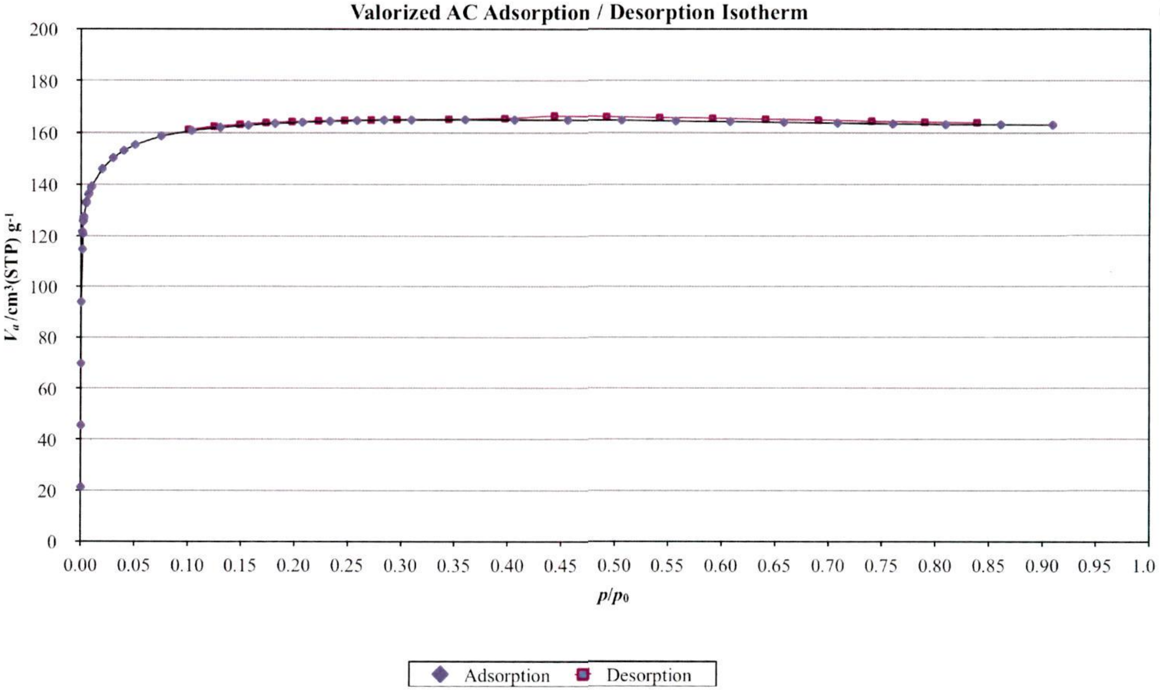

Figure 3.4 Adsorption and desorption isotherm of the valorized semi-wasted AC sample

TGA was also performed on the AC sample. In activated carbons characterization, TGA is used to track the carbonization behavior (Jadhav & Mohanraj, 2016), as well as the determination of the AC contents based on the weight losses with a temperature increase.

Figure 3.5. shows the TGA performed on the AC soil sample. As mentioned above, the first major weight loss, from 0 to 100 °C, is attributed to water vaporization, during this stage, the AC lost over 10% of its weight, showing a high moisture content. It should be noted that the previously reported moisture value of 3.93% corresponds to previously air-dried AC. The weight loss continues until approximately 600 °C, this second major weight loss can be attributed to the loss of organic and inorganic materials adsorbed to the surface of the AC during its previous use. The curve exhibits a similar shape to the ones presented by (Jadhav & Mohanraj (2016).

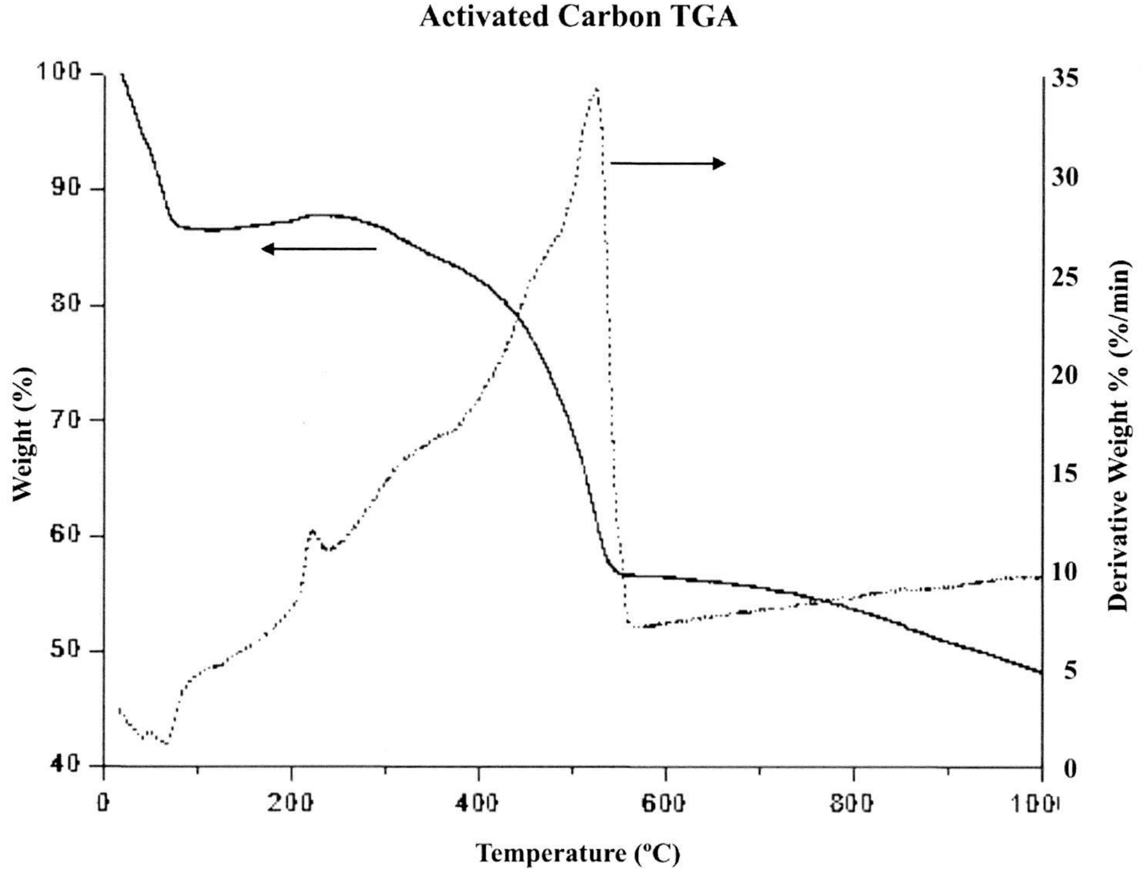

Figure 3.5 TGA of the valorized semi-wasted AC sample

Table 3.11 AC characterization summary

Parameter (unit)	Semi-wasted AC
pH	7.1
Moisture content (%)	3.93
Density (g/cm^3)	0.386
Methylene Blue Value (mg/g)	9.6
Iodine Number (mg/g)	244.182
Surface area (m^2/g)	387.34
Total pore volume (cm^3/g)	0.2521
Average pore diameter (nm)	2.6035

3.5 ADVANCED OXIDATION TESTS

Previous research indicate that the factors that influence AOPs for the degradation of contaminants in soils include: temperature, pH, time, oxidant concentration, catalyst concentration, type of soil, and the characteristics and amount of contaminant present (Apul *et al.*, 2016; Chen *et al.*, 2016; Kakarla *et al.*, 2002; Liao *et al.*, 2014; Tsai & Kao, 2009; Tsitonaki *et al.*, 2010). To shorten the number of treatments, pH, type of soil, and contaminant were not taken into account, since these factors would depend on the soil obtained from the sampling site. Specifically, pH was measured but not controlled during any reaction in an attempt to simplify the processes and work with the natural soil conditions.

The temperature of the persulfate treatments was set at 50 °C, since according to Tsitonaki *et al.*, (2010), temperature is the best way of activating persulfate to date, plus 50 °C is high enough to activate the persulfate. The Fenton-driven treatments were set at room temperature since Fenton reaction is exothermic, meaning it produces heat.

To shorten even more the experimental design, the best oxidant:catalyst ratio for the Fenton treatments was set in a previous test, which was performed before starting the treatments with soil. The best oxidant:catalyst ratio for the Fenton treatments was determined to be 10:1. As appreciated in **Table 3.12**, higher concentrations of oxidant were found in 10:1 reactions than in 5:1. The 1:0 ratios were merely performed as controls, they were not considered as candidates for soil treatments since it has been widely documented that adding an iron catalyst will produce ·OH, improving oxidation processes (Huling & Pivetz, 2006; Kakarla et al., 2002; Tsai & Kao, 2009).

Table 3.12 Best oxidant:catalyst ratio screening results

Oxidant:Catalyst ratio	Oxidant concentration for 1.5% H_2O_2	Oxidant concentration for 3.0% H_2O_2	pH of the liquid after reaction
1:0	1.50%	3.08%	6.2
5:1	1.25%	3.07%	2.1
10:1	1.42%	3.14%	2.2

Controls were equivalent to the concentration of H_2O_2 prepared. The concentration of oxidant decreased rapidly with 5:1 ratio, as a consequence of the iron catalyst addition, which evidently started consuming oxidant, since an orange color appeared immediately indicating the oxidation of iron. Another effect of these Fenton reactions was the acidification of the mixtures. The initial pH of the prepared H_2O_2 solutions was 6.2, which dropped to 2.1 - 2.2 after the reaction stopped. This effect is typical of Fenton-driven processes (Huling & Pivetz, 2006).

Once the oxidant:catalyst ratio to be used was obtained, the Fenton treatments on soil were applied. **Figure 3.6**, shows the results on the oxidation experiment with 1.5% hydrogen peroxide (H_2O_2). As observed, total consumption of the oxidant occurred after 24 hours, when oxidant was no longer detectable through the spectrophotometric method, achieving a hydrocarbon degradation of 33.12%, and a final TPH concentration in the soil of 36 876 mg/ Kg, as observed in **Figure 3.7**. The TPH degradation of this treatment is not enough to reach the maximum permisible limit established in NOM-138-SEMARNAT/SSA1-2012.

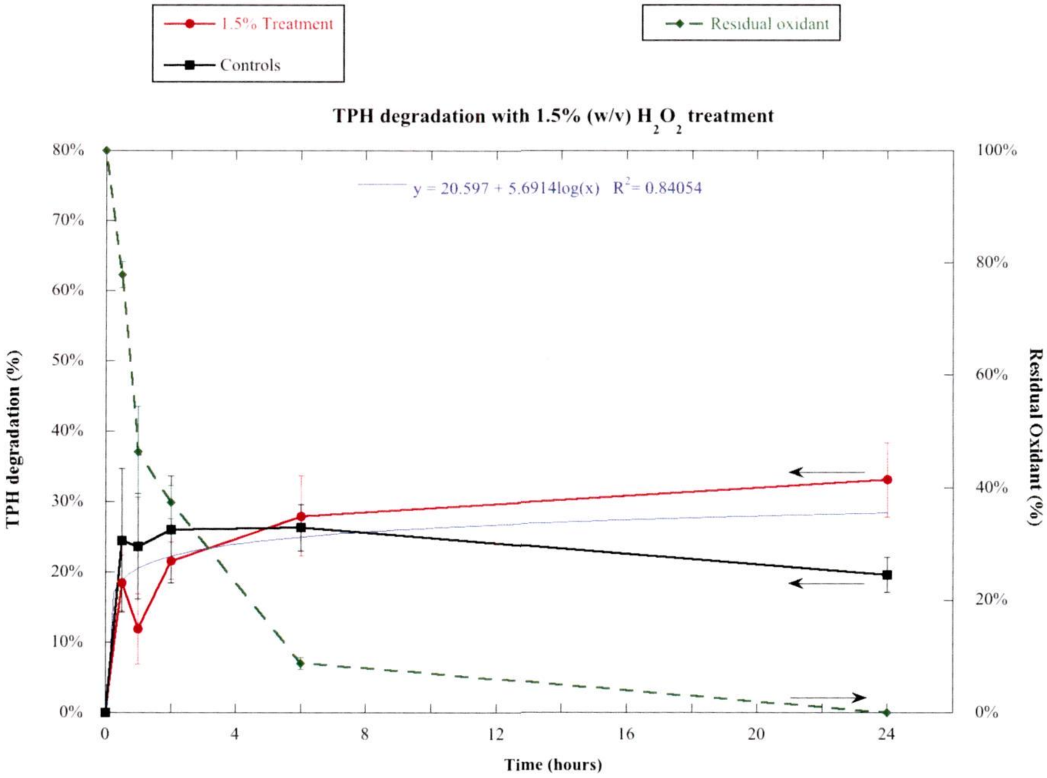

Figure 3.6 TPH degradation with 1.5% H_2O_2 treatment. Green dotted line reads on the secondary Y axis

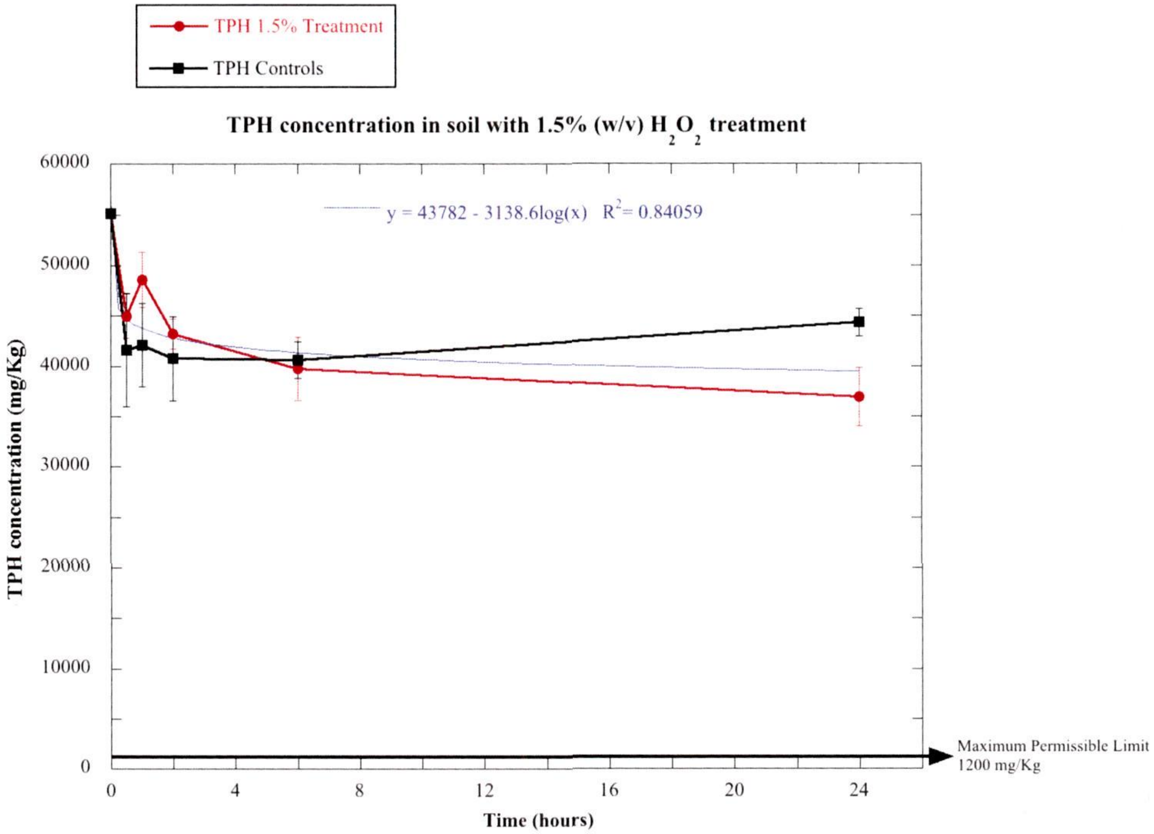

Figure 3.7 Changes of the TPH concentration in soil with 1.5% H_2O_2 treatment

The treatment with 3% H_2O_2, had a removal efficiency of 64.67% and a final concentration of TPH of 19 483 mg/Kg. This can be observed in **Figures 3.8** and **3.9**. Also, the full oxidant consumption was achieved faster, with a complete consumption after the first 6 hours, when oxidant was no longer detected. Actually, in **Figure 3.9** it can be observed that the TPH concentration in the soil started stabilizing from the second and sixth hour, coinciding with the complete consumption of the oxidant.

Apart from these results, a few observations were noted while performing these experiments. First of all, reactions proceeded as literature describes typical Fenton reactions: exothermic, violent at high concentrations (tubes were not stoppered to avoid damage), and gas-producing. Also, lower permeability of the oxidant solution was observed after the first two hours, due to the gas production that formed air-filled cavities between the soil particles decreasing their contact with the oxidant.

Additionally, the supernatant of the reactors, which was recovered for oxidant analysis was heavily acidified, with a final pH of 0.2. These supernatants acquired colors that ranged from yellow to orange, due to the oxidation of iron which was dissolved under the acidic conditions, such color can be observed in **Figure 2.9**. Furthermore, in the treatments corresponding to the first time points (0.5, 1, and 2 hours) a little bit of iridescence could be observed on the surface of the liquid, indicating that some of the diesel sorbed in the soil was transferred to the liquid, which can be confirmed by observing the control results presented in **Figures 3.6, 3.7, 3.8** and **3.9**.

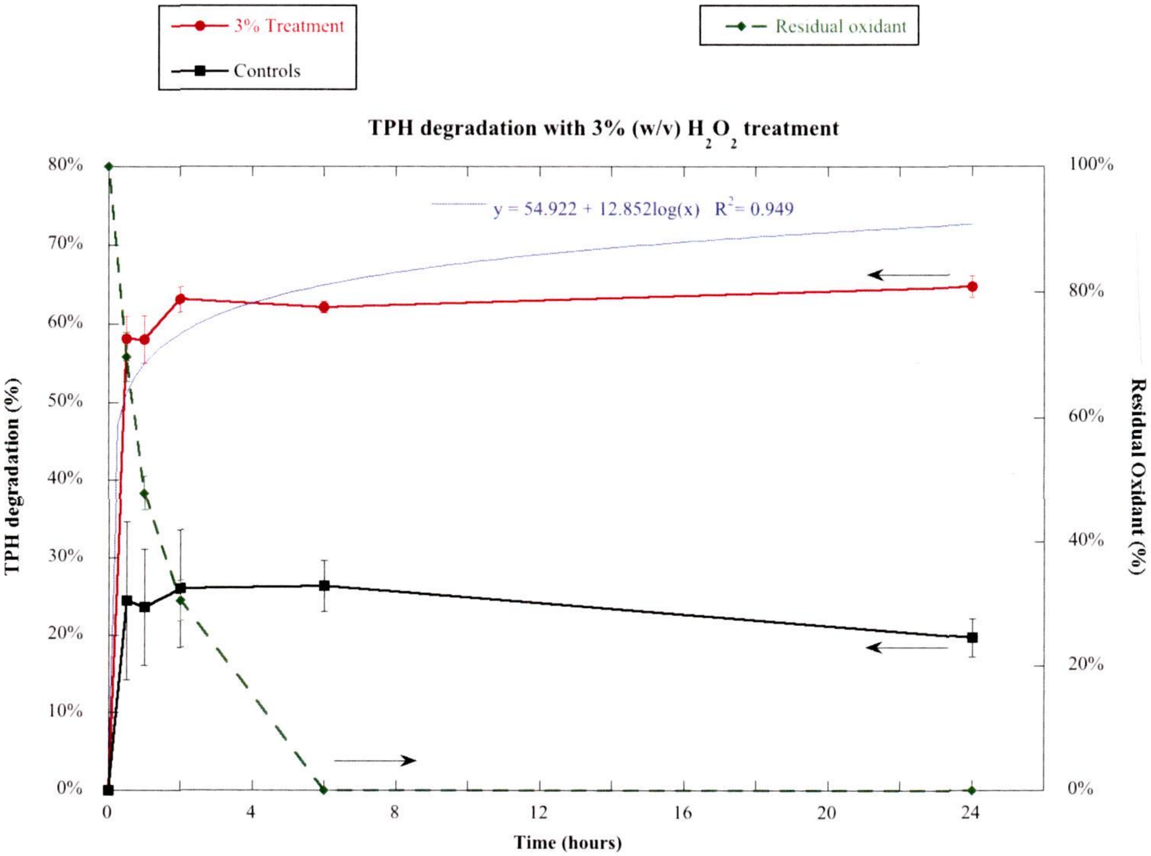

Figure 3.8 TPH degradation with 3% H_2O_2 treatment. Green dotted line reads on the secondary Y axis

H_2O_2 treatments were fast in terms of oxidant consumption, but several disadvantages of these treatments were encountered. Most of these disadvantages are related to the characteristics of the process. For example, the production of heat, which according to Huling & Pivetz (2006) temperature can go higher than 200 °C. This is a disadvantage since this can damage treatment systems and infrastructure, besides, this could increase the volatilization of the contaminants, resulting in their introduction into the atmosphere.

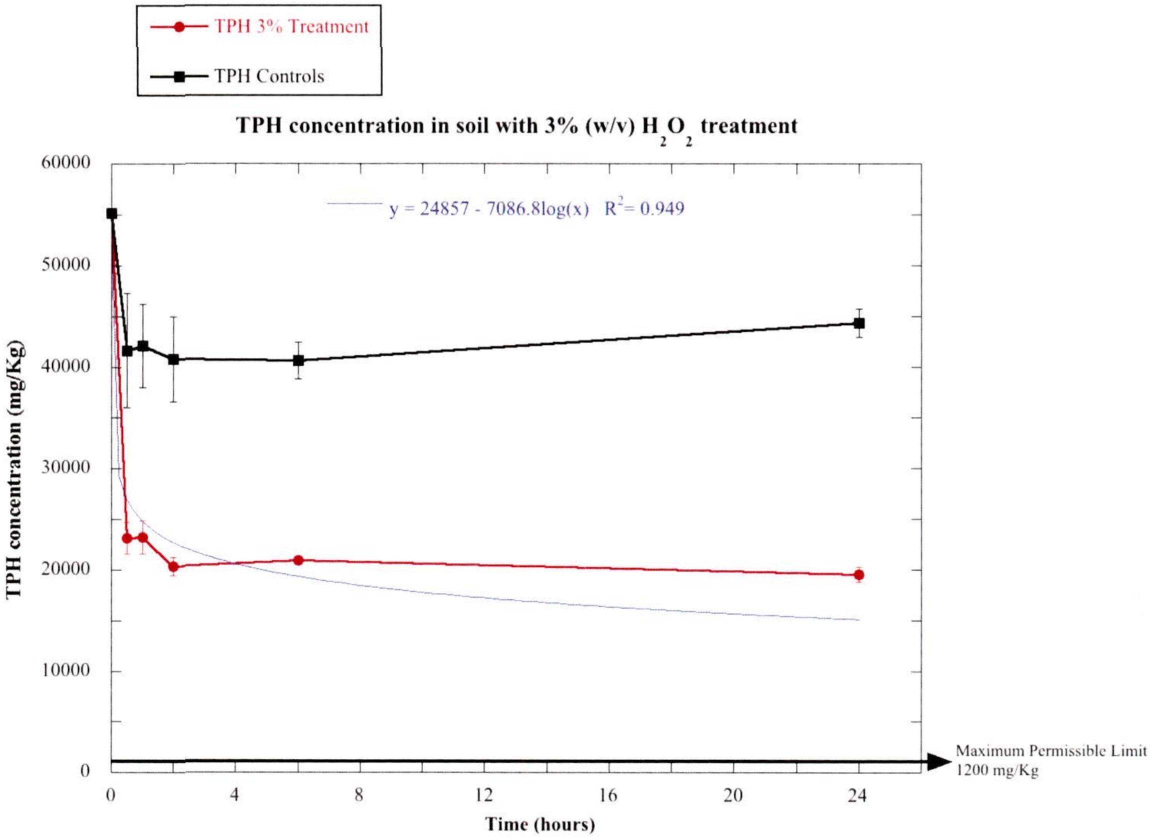

Figure 3.9 Changes of the TPH concentration in soil with 3% H_2O_2 treatment

Likewise, violent reactions were derived from the application of $FeSO_4$ as catalyst, which again could damage treatment systems. Furthermore, the reduction in the permeability reduced the contact of the oxidant with the soil and the contaminant, affecting of course, the degradation efficiency.

With an initial TPH concentration of 10 000 mg/Kg, Tsai & Kao (2009), reached a 96% removal efficiency of diesel with 15% H_2O_2 catalyzed with waste material from steel production containing iron. At a 3% H_2O_2 concentration without any catalyst, they reached a TPH removal of less than 10%.

Apul *et al.* (2016), with initial TPH of 16 156 mg/Kg and H_2O_2 doses ranging from 1 to 10%, had nearly 70% removal efficiency, with high TPH concentration in the supernatant, situation that is comparable to the 64% removal obtained in this research, along with the transference of the hydrocarbons to the supernatant. It is worth mentioning that these authors report higher removal efficiencies at higher concentrations of H_2O_2, but they also report damage in centrifugue tubes at high oxidant concentrations.

About persulfate ($S_2O_8^{2-}$), **Figure 3.10** shows the TPH degradation results on the oxidation experiment with 5% $K_2S_2O_8$. In this treatment, persulfate was no longer detected 48 hours after the treatment started, which shows the higher persistence of persulfate against hydrogen peroxide. As observed, total consumption of the oxidant occurred after 24 hours. Diesel removal reached a 60.02% efficiency, achieving a final hydrocarbon concentration of 22 449 mg/Kg, as observed in **Figure 3.11**.

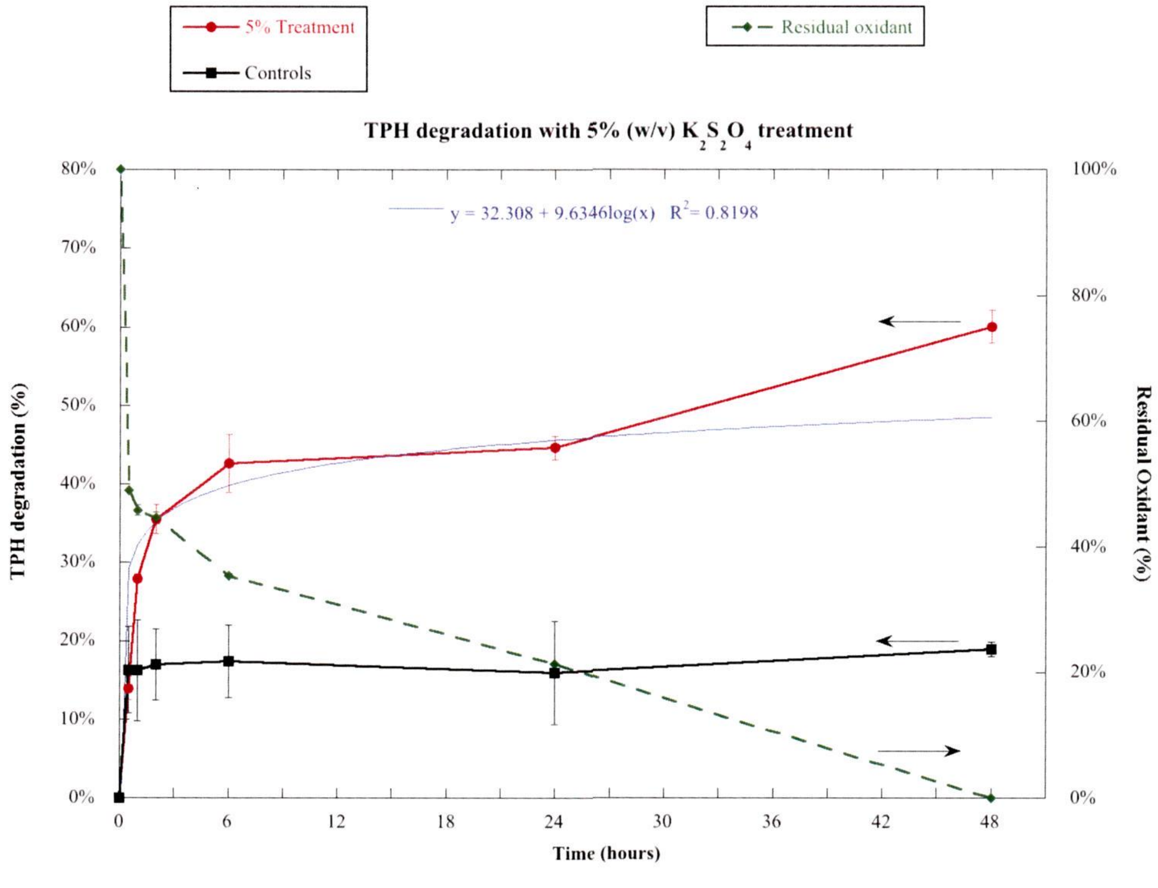

Figure 3.10 TPH degradation with 5% $K_2S_2O_8$ treatment. Green dotted line reads on the secondary Y axis

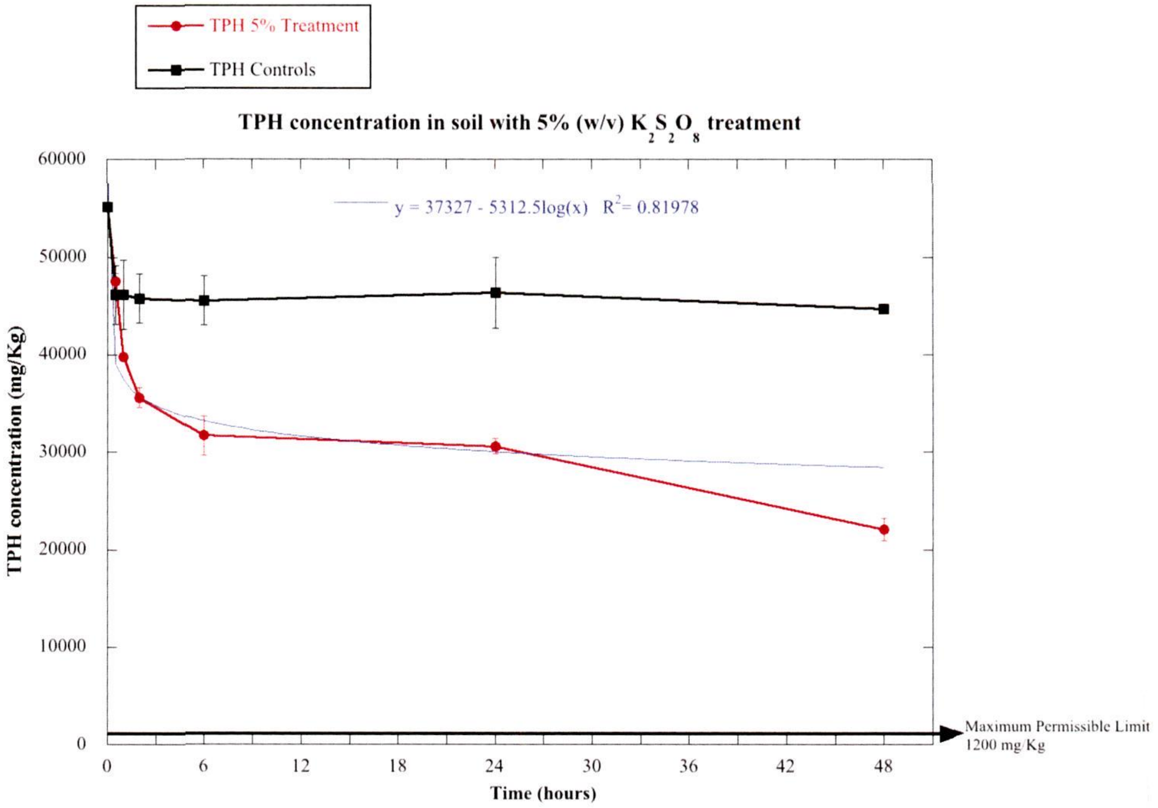

Figure 3.11 Changes of the TPH concentration in soil with 5% $K_2S_2O_8$ treatment

The treatment with 10% $K_2S_2O_8$, had a removal efficiency of 84.05% and a final concentration of TPH of 8 090 mg/Kg, the highest removal efficiency of all oxidation treatments. This can be observed in **Figures 3.12** and **3.13**. Again, the oxidant was completely consumed in the 48 hour time point.

Observations on $K_2S_2O_8$ treatments include that the low solubility of $K_2S_2O_8$ complicated the preparation of the oxidant solutions. Identically to the H_2O_2 treatment, the supernatant recovered for oxidant analysis was heavily acidified too, with a final pH of 0.2, the same as the H_2O_2 treatments. The initial pH of both $K_2S_2O_8$ solutions was 3.1, showing that the oxidant itself acidified the solution.

Again, the treatments of the first time points (0.5, 1, and 2 hours) exhibited iridescence on the surface of the liquid, indicating that some of the diesel that had not been oxidized yet, was transferred to the liquid. These supernatants also acquired an orange color, since the sixth hour of treatment in both cases. Again, this color is produced by the oxidation of iron, dissolved under the acidic conditions. The presence of this color was more notable in the 10% $K_2S_2O_8$ treatment, that stained the tubes. It should be noted that this color was produced from the oxidation of the iron originally present in the soil since no $FeSO_4$ was added.

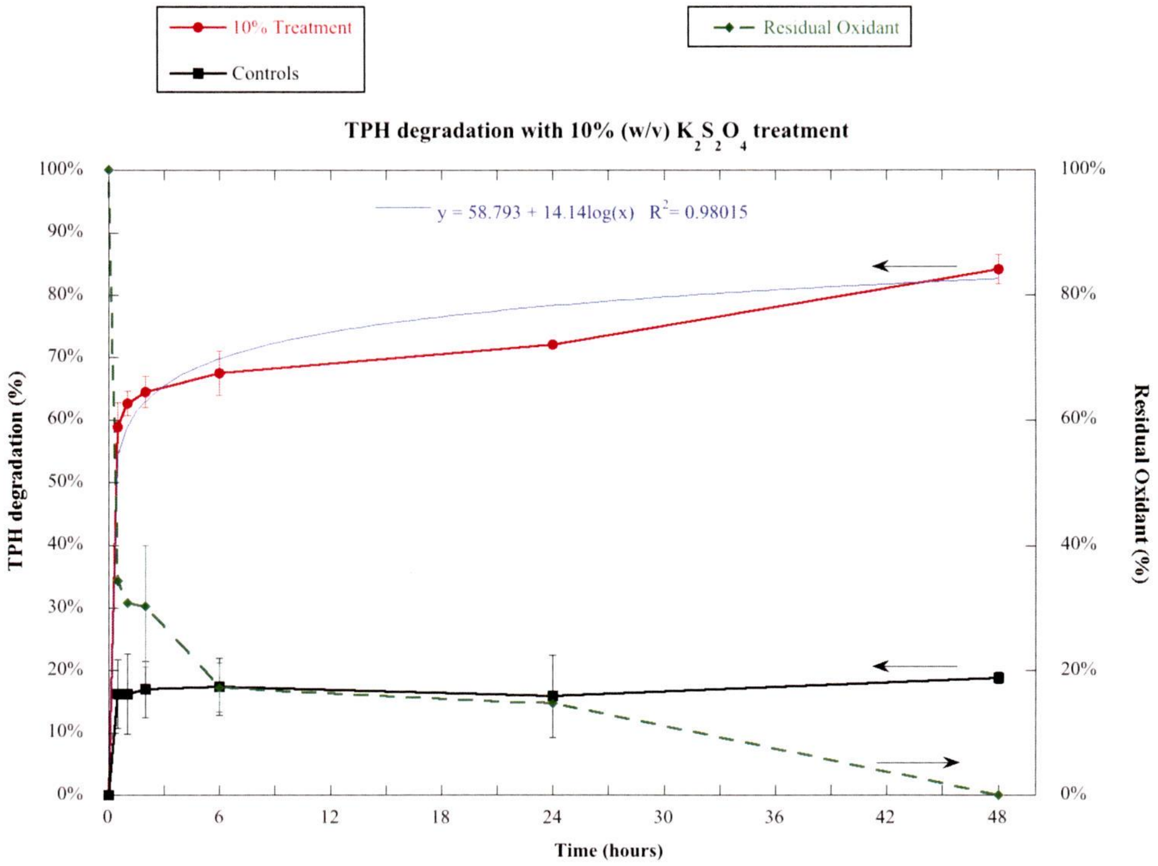

Figure 3.12 TPH degradation with 10% $K_2S_2O_8$ treatment. Green dotted line reads on the secondary Y axis

Despite the excellent removal efficiencies obtained for $K_2S_2O_8$ treatments, it is evident in **Figures 3.9** and **3.13**, that none of the treatments reached the maximum permisible limit of 1 200 mg/Kg established in NOM-138-SEMARNAT/SSA1-2012.

Apul *et al.* (2016), reported similar hydrocarbon-removal efficiencies (approximately 70%) using $Na_2S_2O_8$ and H_2O_2 in a 48 hour treatment. They report that for persulfate, the amount of TPH in the supernatant was much lower than with hydrogen peroxide.

Full oxidant consumption could have been achieved faster with higher activation temperatures. This is because according to Tsitonaki *et al.* (2010), reaction rates for the persulfate ion are much slower than for the sulfate radical, higher activation temperatures result in faster production of sulfate radicals, which results in faster reaction rates, although this hinders TPH degradation due to rapid oxidant depletion.

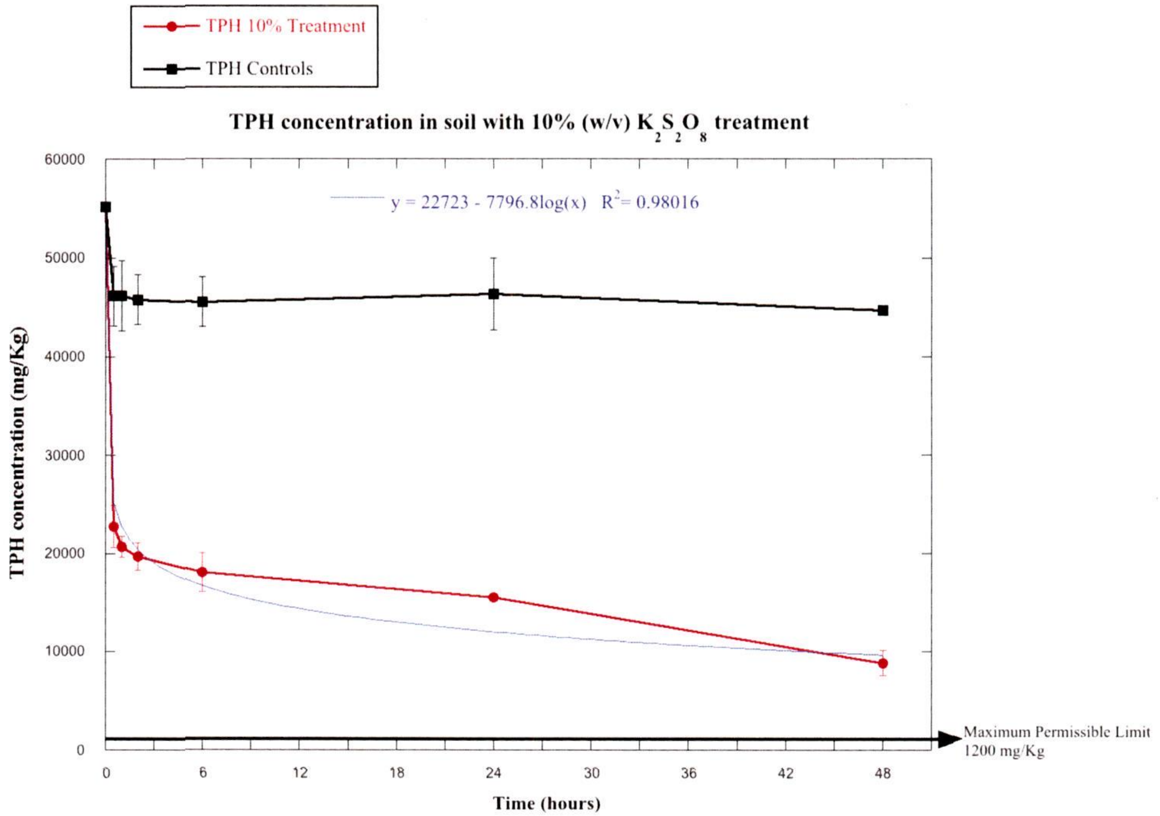

Figure 3.13 Changes of the TPH concentration in soil with 10% $K_2S_2O_8$ treatment

Regarding both treatments, H_2O_2 and $S_2O_8^{2-}$, Chen *et al.* (2016) report that persulfate had a better performance in diesel removal than peroxide, although the persistency of persulfate had more adverse effects on bacterial growth, than peroxide, due to low pH. However, the addition of oxidants at low concentrations (1 to 3%) still allowed intrinsic biodegradation.

Figure 3.14 summarizes the changes on the TPH concentration through all oxidation treatments performed. It is clear that the behavior of the oxidation of hydrocarbons follow a pattern, the degradation speed is higher at the beginning and then slows down until no further degradation can be achieved, probably because of the consumption of the oxidant or the complete mineralization of the contaminant. Plots were adjusted to a logarithmic model, which describes the kinetics of some redox reactions (Shi *et al.*, 2011; San Pio *et al.*, 2017).

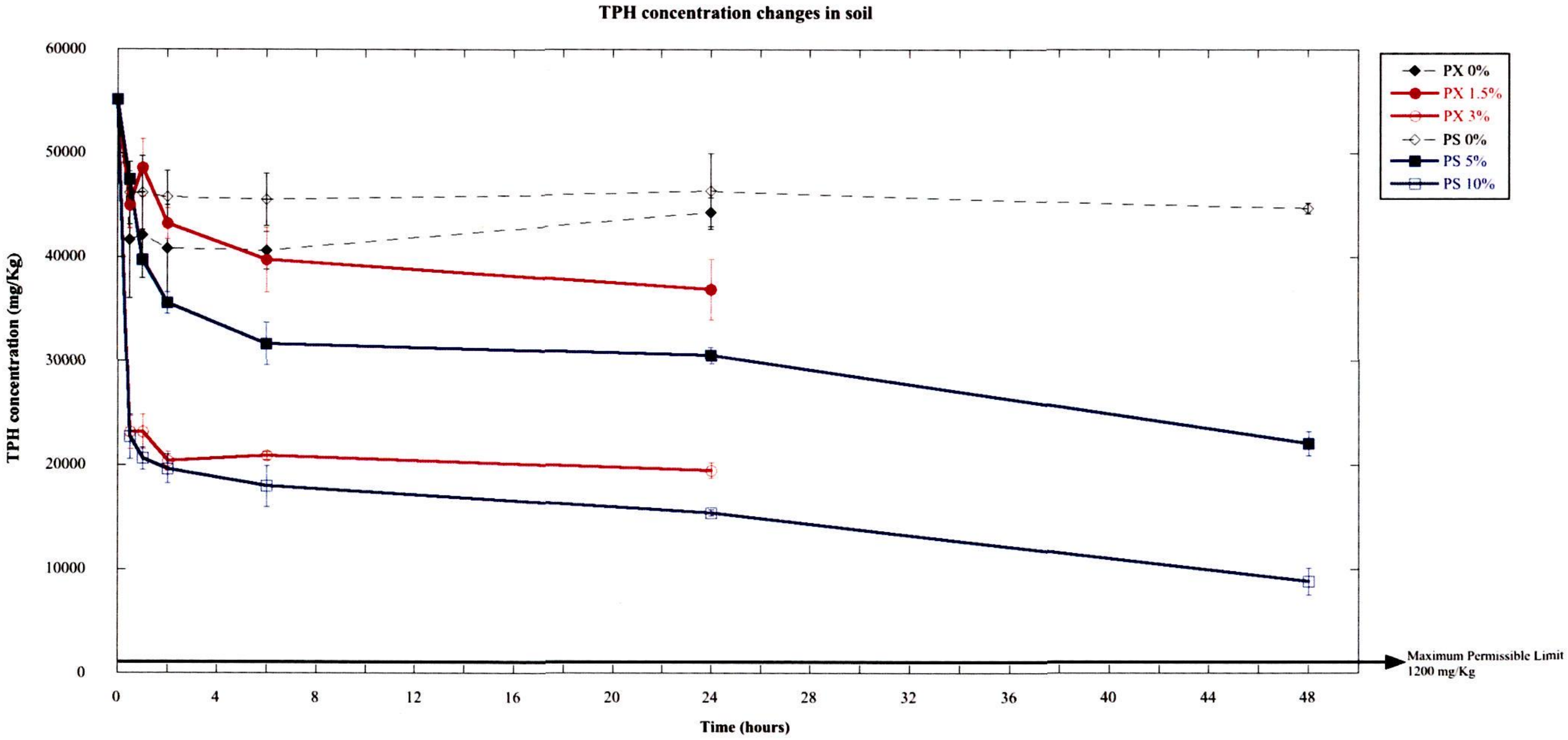

Figure 3.14 Summary of TPH concentrations in soil throughout advanced oxidation treatments

3.6 SORPTION TESTS

The results of the preliminary tests can be found in Table 3.13. As expected, controls did not present a significant TPH loss. On the other hand, the mixture of contaminated soil with 5% (w/w) AC reduced significantly the TPH concentration in the soil. After 15 days of contact, the AC removed almost 58% of the diesel in the soil and after 30 days up to nearly 62%. With a 15% AC concentration, a maximum removal of 75.64% was achieved, and after 30 days, the removal of TPH did not increase, on the contrary, it maintained around 71.32%.

Table 3.13 Preliminary sorption tests

AC concentration	Initial TPH (mg/kg)	TPH 15 days (mg/kg)	TPH removal	TPH 30 days (mg/kg)	TPH removal
0% (w/w)	55141	47816	13.28%	48499	12.05%
5% (w/w)	55141	23285	57.77%	21016	61.89%
15% (w/w)	55141	13433	75.64%	15812	71.32%

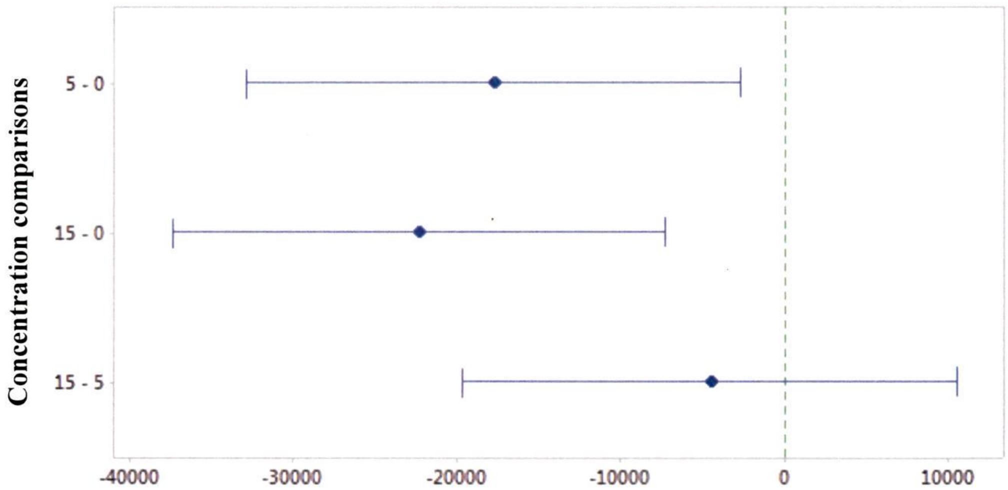

Figure 3.15 Mean comparison of sorption treatments through Fisher's method, individual confidence intervals of 95%

All mean comparison methods applied (Fisher, Dunnet and Tukey) were coincident in the following results. A significant difference was not observed between 5% and 15% AC treatments. When running the statistical analysis of this data, the comparisons of the obtained means confirmed that in fact, 5% and 15% AC treatments were significantly different when compared to the control treatment, but when compared with each other, they did not show significant differences. This can be observed in **Figure 3.15**, the first two represented intervals do not contain zero, so the corresponding means are significantly different. Given these results, 5% AC concentration was selected to carry out the subsequent sorption tests, in order to reduce the introduction of AC in the soil and optimize the use of the material.

The aspect of the soil after adding AC can be observed in **Figure 3.16**. The color of the soil changes significantly after AC addition, turning almost completely black with a 15% AC concentration in the mixture. Another effect observed was the formation of lumps of soil particles with AC. These effects were not as perceptible with 5% AC. Regarding soil microorganisms, according to Meynet *et al.* (2012), AC has no detrimental effects on soil microbiology and AC-amended soils still retain the potential to biodegrade contaminants.

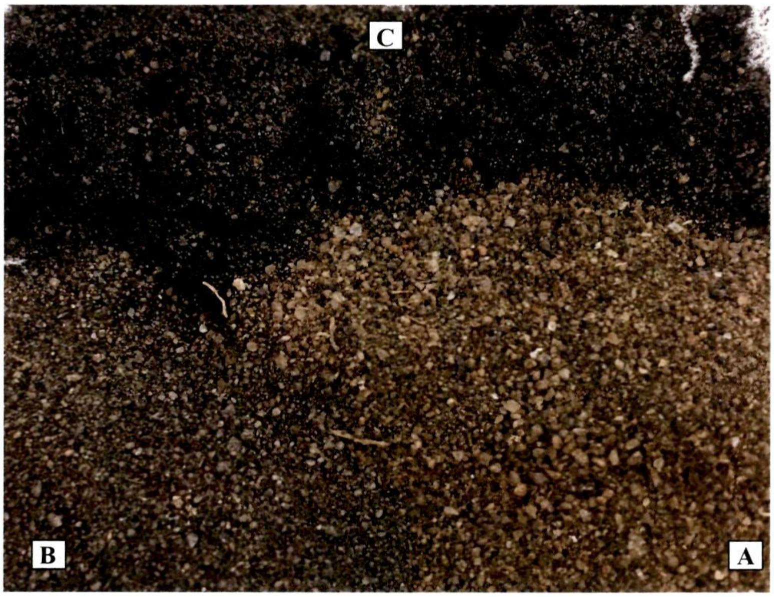

Figure 3.16 Aspect of soil-AC mixtures: A) 0% AC, B) 5% AC, C) 10% AC

Once the best AC concentration was set at 5%, following sorption tests were carried out in order to optimize the amount of time needed for TPH removal. First the sorption tests were carried out during 5 days. Results of this test are shown in **Figure 3.17**, where it is evident that the sorption of TPH from the soil to the AC stabilized from the first day to the fifth, with an average TPH removal of 58% (and 23 130 mg/Kg TPH remaining in the soil), the same amount removed in the 15-day treatment mentioned above. Although most soil treatment research with AC considers higher contact times (Hilber & Bucheli, 2010), that range from 35 days (Yu *et al.*, 2009) to over 1000 days (Vasilyeva *et al.*, 2009), the obtained results lead to the assumption that the sorption process was quite rapid, happening in less than 24 hours and probably minutes.

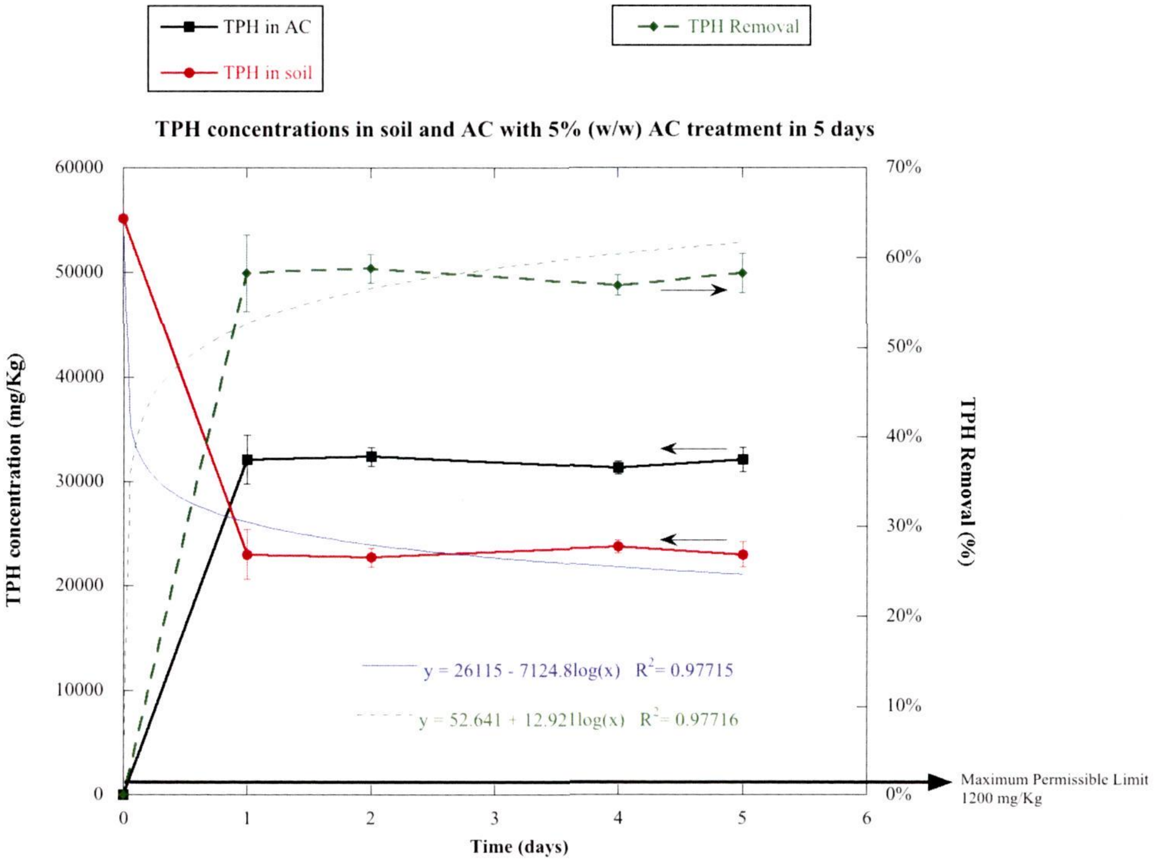

Figure 3.17 TPH concentrations and removal over 5 days sorption treatment. Green dotted line reads on secondary Y axis

The sorption experiment was repeated with 5% AC and monitored between 5 and 150 minutes, results are shown in **Figure 3.18**. Again, TPH removal stabilized around 58%, from 45 minutes, proving that indeed the sorption process with this semi-wasted AC, at a 5% concentration reaches a maximum of 58% TPH removal in a matter of minutes. As mentioned above, this valorized semi-wasted AC has a mesoporous structure, meaning contaminants with big-sized molecules, like hydrocarbons, can access the pores of the material.

Despite being a quick and highly efficient method for TPH removal, as seen in **Figures 3.17** and **3.18**, this sorption treatment alone is not enough to reach the maximum permisible limit of 1 200 mg/Kg, established in NOM-138-SEMARNAT/SSA1-2012.

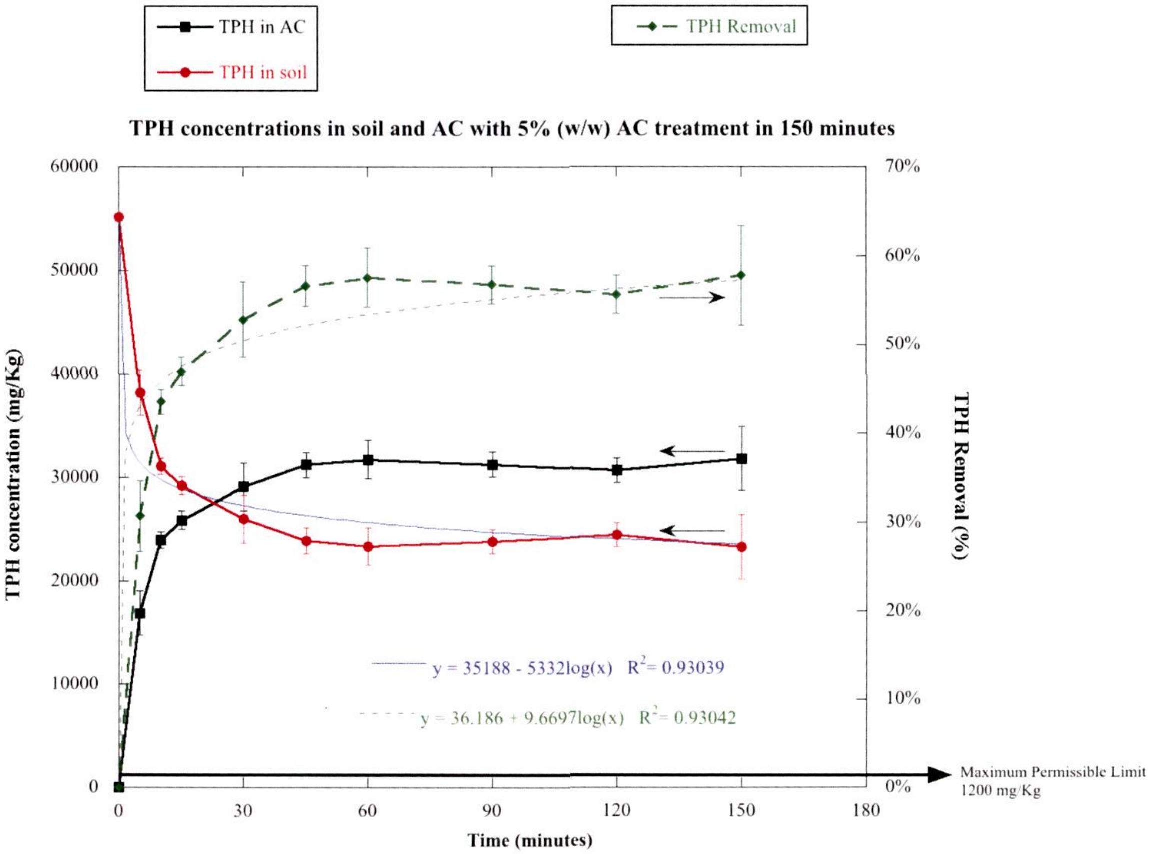

Figure 3.18 TPH concentrations and removal over 150 minutes sorption treatment. Green dotted line reads on secondary Y axis

Brändli et al. (2008) were able to reduce PAH in soil/water suspensions by 99%, they observed a high effectiveness of powdered AC in moderately contaminated soil. Given these results, the removal of hydrocarbons by AC with a 58% reduction is adequate since in this case the soil was heavily contaminated with 55 141 mg/Kg of TPH.

It is important to mention that the sorption process was not adjusted to any isotherm model since such models are suitable for contact between the adsorbent and fluids, not for solid-solid mixtures, as it was performed in this research. The behavior of the sorption process was only adjusted to a logarithmic model.

3.7 TREATMENT PAIRING

The treatments to be coupled, the best oxidation and sorption treatments were selected based on the following results of the statistical analysis of the obtained data.

First of all, the results of the effects of factors and interactions on the TPH removal are shown in **Figure 3.19**. All the bars that cross the line in number 2, correspond to the factors and interactions that influence the TPH removal. Since all bars cross the line, reaction time, oxidant substance, and oxidant concentration influence the outcome of the oxidation treatments, along with all their interactions, meaning that indeed oxidation is a complex process in which many factors should be taken into account.

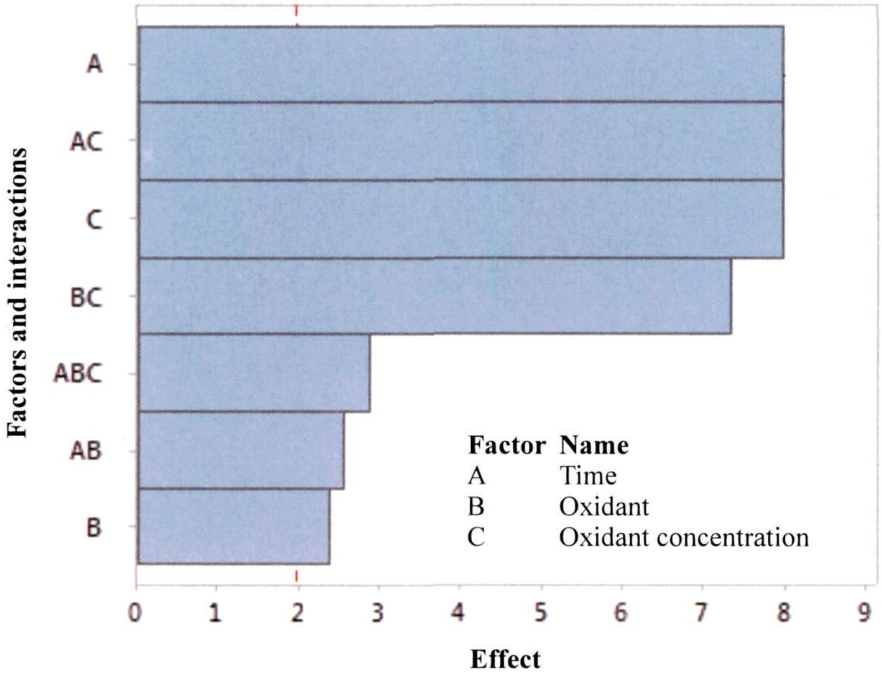

Figure 3.19 Effects of factors and their interactions on the TPH removal (α = 0.05), (48-hour time point was not considered to obtain these results)

Regarding the oxidation treatments, comparison results are shown in **Figures 3.20** and **3.21**, again all mean comparison methods applied (Fisher, Dunnet and Tukey) were coincident in the results. In the intervals that do not contain zero, the corresponding means are significantly different.

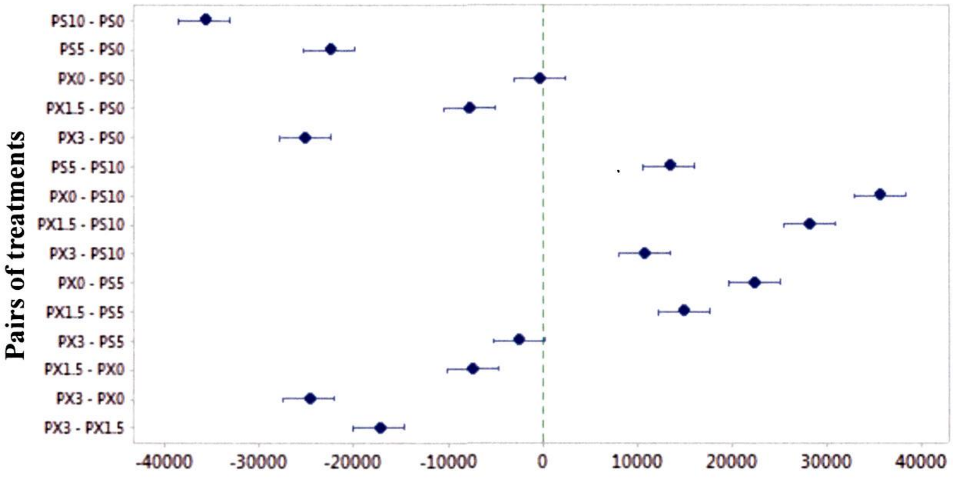

Figure 3.20 Mean comparison of oxidation treatments through Fisher's method, individual confidence intervals of 95%. PX = H_2O_2. PS = $K_2S_2O_8$

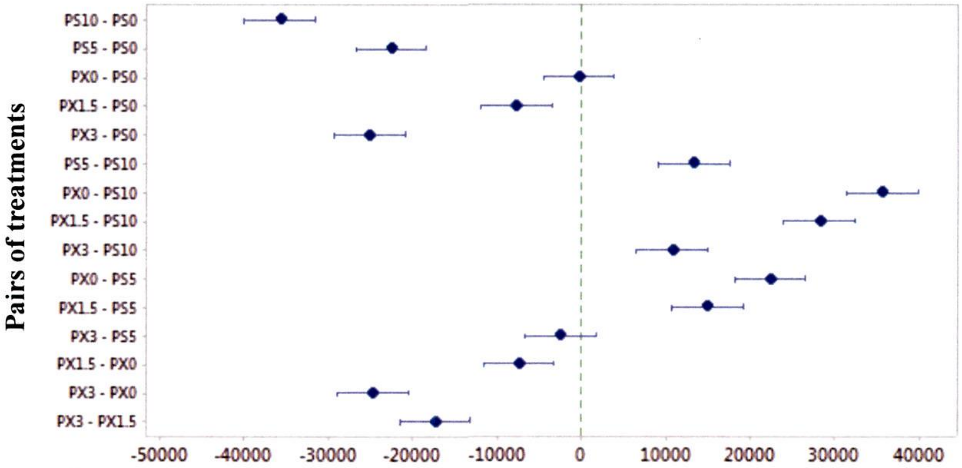

Figure 3.21 Mean comparison of oxidation treatments through Tukey's method, individual confidence intervals of 95%. PX = H_2O_2. PS = $K_2S_2O_8$

No significant difference was observed between the control treatments with 0% H_2O_2 and 0% $K_2S_2O_8$, this result shows that indeed the addition of the oxidant has a significant influence on the TPH removal. An interesting discovery is that treatments with 3% H_2O_2 and 5% $K_2S_2O_8$, had similar efficiencies, which also happened in the study carried out by Chen *et al.* (2015).

Figures 3.22 and **3.23** show the results on the comparisons between 5% AC treatment and all oxidation treatments. Most treatments show significant differences, except for 3% H_2O_2 & 5% $K_2S_2O_8$, and 0% H_2O_2 & 0% $K_2S_2O_8$, as mentioned above. Another significant finding was that treatment with 5% AC and 5% $K_2S_2O_8$ presented similar TPH removal efficiencies.

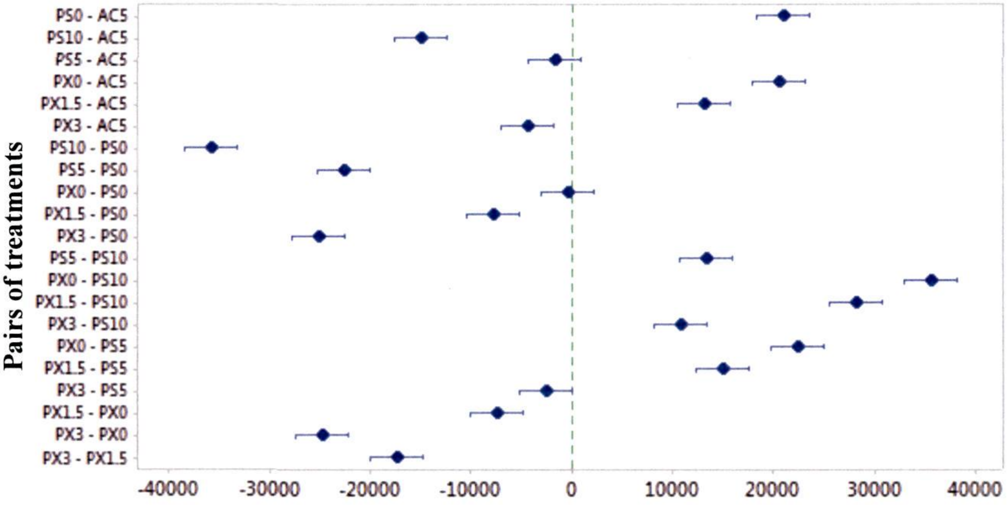

Figure 3.22 Mean comparison of sorption and oxidation treatments through Fisher's method, individual confidence intervals of 95%. PX = H_2O_2. PS = $K_2S_2O_8$. AC = Activated Carbon

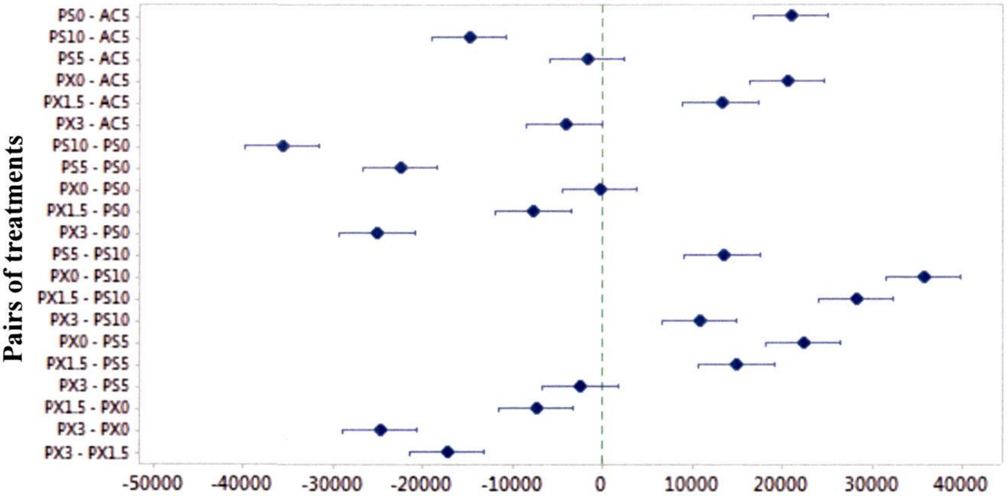

Figure 3.23 Mean comparison of sorption and oxidation treatments through Tukey's method, individual confidence intervals of 95%. PX = H_2O_2. PS = $K_2S_2O_8$. AC = Activated Carbon

Above, in section 3.6, the comparisons of between sorption treatments were discussed and it was found that the best AC concentration was 5% (w/w), since there was no significant difference between this treatment and the treatment with 15% (w/w) AC. To ensure that the sorption process reaches its maximum TPH removal efficiency during the treatment pairing, the 90-minute time point was selected for the pairing experiments and not the initial time point where TPH removal starts to stabilize.

On the other hand, the oxidation treatment selected for pairing was with 10% $K_2S_2O_8$, this decision was based on the data presented in Figure 3.12, in which the logarithmic curve fit had a higher R^2 value. Also, higher TPH degradation was achieved with this treatment in only 48 hours.

The results of paired treatments are summarized in **Table 3.14**. All paired treatments had better efficiencies than oxidation or sorption processes by themselves. The two-step treatments had similar removal efficiencies of over 97%. On the other hand, the simultaneous treatment had the lowest efficiency of the three experiments, with a final TPH concentration remaining in the soil of 5 273 mg/Kg. Even when this final TPH concentration is much lower than the initial TPH concentration in the soil of 55 141 mg/Kg, it is not enough to reach any of the maximum permissible limits of the NOM-138-SEMARNAT/SSA1-2012 for MFH, not even the limit for industrial use, which is 5 000 mg/Kg.

Table 3.14 Paired treatments results

Treatment	TPH remaining in soil (mg/kg)	TPH removed (%)
Sorption-Oxidation	1075	98.05
Oxidation-Sorption	1511	97.26
Simultaneous	5273	90.44

The oxidation-sorption treatment was able to reduce TPH to 1 511 mg/Kg, which means that according to the NOM-138-SEMARNAT/SSA1-2012, this soil is not suitable for agricultural or residential use, but it could still be used in industrial areas.

The sorption-oxidation treatment was the only one that successfully reached the goal of lowering the TPH concentrations in soil to the limit established in NOM-138-SEMARNAT/ SSA1-2012 for agricultural soils (1 200 mg/Kg). This sorption-oxidation treatment had a removal efficiency of 98.05% by pairing a 90-minute sorption treatment paired with a 48-hour oxidation treatment, meaning that in less than 50 hours, a heavily contaminated soil with an initial TPH concentration of 55 141 mg/Kg was efficiently treated.

To date, there are no precedents of pairing sorption and advanced oxidation processes to remediate hydrocarbon-contaminated soils. Although in recent years the use of persulfate for spent AC regeneration has been studied. UV activated persulfate can regenerate AC saturated with natural organic matter, by oxidizing it and completely mineralizing it, although highly acidic conditions (pH 1.6-2.4) result from this process along with sulfate residues (An *et al.*, 2015).

According to Hutson *et al.* (2012) these acidic conditions produced during the AC regeneration by persulfate AOP, generate blockage of the AC pores by the accumulation of persulfate residuals (sulfates, and potassium or sodium), therefore reducing the sorption capacity of the material. When the pH is adjusted to >5.5, the sulfur species are removed and the sorption capacity is improved.

These interactions between AC and persulfate shed some light on why the simultaneous sorption-oxidation treatment was not as efficient as the two-step treatments. It is likely that the materials adsorbed in the semi-wasted AC surface reduced the amount of oxidant available for hydrocarbon degradation, by consuming it themselves. Also, persulfate byproducts (sulfate and potassium) probably saturated the AC and lowered its sorption capacity, since the typical acidic conditions of persulfate oxidation were generated too.

Oxidation and sorption processes had not been paired to remediate hydrocarbon-contaminated soils, however both processes have been individually coupled with bioremediation to remove different contaminants in soil.

Regarding oxidation pairing with bioremediation, Gong (2012) reported a TPH reduction of 88.9% after a 20-week treatment in a loamy sand soil with an initial TPH concentration of 38 300 mg/Kg. According to the author, the soil toxicity was reduced by the oxidation process, but this process also caused cell death and inhibition of microbiologic activity in the soil.

On the other hand, a study pairing sorption with bioremediation was conducted by Vasilyeva *et al.* (2006). In such study, conducted for 420 days, the authors reported that the introduction of AC into the soil reduced the toxicity of organic contaminants (3,4-dichloroaniline, 2,4,6-trinitrotoluene, polychlorinated biphenyls) and promoted biodegradation processes.

These previous studies confirm that indeed, the developed sorption-oxidation treatment was fast and achieved high TPH removal from a heavily contaminated soil. Besides the objective of valorizing a semi-wasted AC residue was also reached and its residual sorption capacity was exploited.

3.8 TREATED SOIL CHARACTERIZATION

The fact that the sorption-oxidation treatment successfully reduced TPH concentrations in the soil, does not mean that the soil quality is good enough to continue its agricultural use. To assess this, the treated soil was characterized by carrying out the same analysis performed during the soil characterization stage of the project. The results of such characterization are summarized in **Table 3.15** and the aspect of the treated soil can be appreciated in **Figure 3.24.**

Table 3.15 Soil characteristics summary

Parameter (unit)	Uncontaminated soil	Contaminated soil	Treated soil
Texture	Loamy sand	-	-
pH	**6.6**	6.9	3.8
EC (dS/m) at 25 °C	0.203	0.159	2.430
Moisture content (%)	**1.11**	3.09	0.76
Oxidation potential (mV)	**320**	288	234
OM (%)	**2.78**	4.48	1.22
CEC (cmol(+)/Kg)	14.24	15.69	18.4
Available P (mg/Kg)	164.3	74.4	60.3
Total N (%)	**0.13**	0.06	0.04
K (cmol(+)/Kg)	**2.02**	1.64	6.67
Total Fe (mg/Kg)	3134	2499	810
Surface area (m^2/g)	2.2306	-	-
Total pore volume (cm^3/g)	0.0052	-	-
Average pore diameter (nm)	9.2957	-	-
TPH (mg/Kg)	-	55141	1075

The pH of the soil decreased drastically from a neutral to a highly acid value (3.8), this was by the action of the oxidant, that as discussed above, produces highly acidic conditions. When soil is highly acidic, major nutrients have a low availability and microbial activity decreases (Stirling et al., 2016; Oyem & Oyem, 2013). This pH level would need to be corrected in a field scale treatment since NOM-138-SEMARNAT/SSA1-2012 requires that the treated soil presents a similar pH value to a soil of a nearby uncontaminated area.

Figure 3.24 Treated soil

EC increased to a moderately saline level (2.4 dS/m), most likely due to the presence of sulfates, formed as byproducts of the oxidation treatment. Since this 2.4 dS/m value is higher than 1 dS/m, crops sensitive to salts are likely to be affected, but salt-tolerant crops that can grow with EC values of up to 5 dS/m, could stand this salinity (Stirling et al., 2016).

The moisture content decreased to a 0.76%, as well as the oxidation potential that decreased to 234 mV. This oxidation potential value could be an indicator that there is no significant microbial activity developing in the soil (Fernández-Linares *et al.,* 2006).

As expected, the OM content decreased to a low value of 1.22%, indicating that the TPH present in the soil were removed by the treatment. Although considering that the original OM value of the uncontaminated soil was 2.78%, the soil natural organic matter also decreased. This lowered the water-holding capacity of the soil, which is why the moisture content decreased drastically. Since the buffering capacity of the soil also depends on the OM content, this OM decrease is another reason why the soil pH went from 6.6 to 3.8. In accordance to Stirling *et al.* (2016) the decrease in OM also alters soil aeration, diffusion of nutrients, and of course the activity and diversity of soil fauna.

CEC basically maintained in the same level, meaning that the soil maintains its ability to hold nutrient cations, and prevent them from leaching (Stirling *et al.*, 2016). Despite the fact that OM is responsible for most of the CEC (Stirling *et al.*, 2016), the CEC increased when the OM content decreased, meaning that the CEC of this soil was altered by another factor like the interaction of the oxidant or the presence of AC residues that retained cations.

A significant change detected on the soil was the decrease of most nutrients. According to Sirguey *et al.* (2008), oxidation treatments produce significant changes in soil nutrients, specifically losses of organic carbon and nitrogen. Originally, the studied soil was rich in P, and even though a significant decrease of this element was observed, it still maintained at high levels, according to the NOM-021-RECNAT-2000. Still, most of the P loss was produced by the presence of the hydrocarbons itself and only a small fraction of it was lost by effect of the treatment.

Regarding total N, it presented an important decrease as well, to a very low nitrogen value. Although again, this decrease was mostly produced by the diesel spill than by the treatment applied. The C:N ratio of the treated soil changed to approximately 18:1, which was closer to the required 10:1 ratio for a plants and organisms development (Oyem & Oyem, 2013), than the contaminated soil.

As expected, K concentration increased drastically, which is logical since it is one of the components of the oxidant used. On the contrary, total Fe content decreased importantly, this was probably caused by its oxidation and dissolution in the acidic supernatant of the treatment, which was drained and discarded. Still, both concentrations, are still suitable for plant growth according to the levels established in NOM-021-RECNAT-2000.

These results indicate important changes in soil quality that would hinder the soil microbial activity and the development of plants. However it should be noted that as mentioned above, most of these changes occurred as a result of the contamination event and not as a result of the treatment. Anyhow, most nutrient levels in the soil are still adequate, except for nitrogen, which was reduced when the diesel spill occurred. Taking this into account, the parameters that were really impacted by the soil treatment, and that could inhibit plant and microorganisms growth, were pH, moisture content, EC, and OM content.

Regarding EC and pH, it is a known fact that persulfate increases conductivity and decreases pH. The measurement of these parameters post-oxidation treatment determine the following polishing treatment, depending on the expected land use (Rosansky *et al.*, 2015; Kueper *et al.*, 2014). After remediation, when soil is reintroduced into its original site, it tends to go back to equilibrium, meaning the oxidant is completely consumed and soil parameters like pH and ORP go back to their baseline levels (Interstate Technology & Regulatory Council, 2005). This is why post-treatment monitoring should be conducted at several time points after the treatment application and compared to the initial parameters to understand how the treatment really impacted the soil (Rosansky *et al.*, 2015).

About OM and moisture, organic amendments would increase soil fertility and its water-retention capacity. Introduction of organic matter leads to an improvement of soil biological functions, increases organic carbon content, improves aggregate stability, and it enhances soil organic nitrogen content (Diacono & Montemurro, 2011). The incorporation of humic substances into the soil, allows nutrient retention and availability for the plants (Mora-Delgado, 2006). These nutrient amendments are also a common approach to stimulate bacterial growth after chemical oxidation (Sutton *et al.*, 2011).

Finally, in relation to microbial activity, since soil is not a closed system, bacteria repopulate areas where they have been depleted (Chen *et al.*, 2015; ITRC, 2005; Sutton *et al.*, 2011). In most treatment areas where chemical oxidation is used, microorganisms are initially dormant due to the presence of the contaminant. When the soil is remediated and toxic levels are reduced, the environment becomes more acceptable for bacterial growth. Post-treatment populations have been demonstrated to grow rapidly within short periods after even the most aggressive treatments (ITRC, 2005).

CHAPTER 4. CONCLUSIONS

Although the social, economical and environmental context that surrounds these contaminated areas, heavily complicates soil treatment application and research, the hydrocarbon-contaminated soil, sampled in the municipality of San Martín Texmelucan, Puebla, Mexico, was successfully treated by coupling sorption and advanced oxidation processes.

The sampled soil was characterized as a loamy sand contaminated with an initial concentration of 55 141mg/Kg of diesel. The origin of the contamination was an illegal fuel intake in the Pemex's pipeline, a common origin of soil contamination in the area. This hydrocarbon-contaminated soil was heavily impacted by the contamination event and presented an important increase in its OM content and decreases in its soil nutrients.

All coupling arrangements reached over 90% TPH removal, nonetheless not all of them removed enough hydrocarbons to comply with the maximum permissible limits established in the Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012. Specifically, in a simultaneous sorption-oxidation treatment, the contact of the oxidant with the semi-wasted AC decreased the efficiency of the oxidation process.

The two-step treatment of sorption-oxidation resulted in an over 98% TPH removal, in less than 50 hours, which lowered the TPH in the soil enough to comply with the previously mentioned Official Mexican Standard. The treatment procedure started with a sorption process in which a semi-wasted AC residue was successfully valorized and its residual sorption capacity was exploited to remove hydrocarbons from the soil. After the sorption process, advanced oxidation with potassium persulfate was applied to degrade the remaining hydrocarbons in the soil.

Despite being an efficient and fast treatment to reduce the TPH concentrations, several changes in the soil were observed as a result of the sorption-oxidation treatment applied. The main changes observed were in pH, moisture, EC and OM, apart from further fluctuations in the content of nutrients, that were already impacted by the introduction of the hydrocarbons into the soil. It is likely that such variations in the characteristics of the soil will hinder the immediate development of plants and microorganisms in the soil, complicating its agricultural use. A polishing post-treatment could be needed to rapidly recover soil fertility.

PERSPECTIVES

Several matters emerged from this research and being outside of its scopes, they still need to be studied. First of all, the migration of the contaminant needs further assessment considering soil horizons and permeability.

Regarding the sorption treatment, other possible sources of semi-wasted AC could be considered, as well as the possibility of exploiting this material to prevent the contaminant migration. Possible secondary effects of AC amendment on soil microbiology, nutrients, ecology and fertility need further research. Also, an alternative to manage the spent AC by valorizing its calorific capacity needs further research.

The advanced oxidation process requires analysis of the produced by-products and their toxicity, including the produced gasses, and the by-products remaining in the soil. Also, the supernatant resulting from the treatment needs further analysis and a possible treatment.

The influence of certain factors not considered in this research, like pH, agitation, temperature, and oxidant demand need to be evaluated in order to optimize them and determine their effects on the treatment. Besides, different arrangements of the treatment could be evaluated, assessing its performance in different reactors or in columns.

Fertility and microbiological tests need to be carried out in order to assess the capacity of the treated soil to support life, and to determine wether the soil can still be used for agricultural purposes. Alternatives to improve the soil quality and reduce the effects of the treatment need to be assessed.

Finally, the viability of upscaling the technology should be considered once the questions that emerged from the research are answered. The viability of applying this technology at field scale should also be evaluated through a cost analysis and its comparison to other technologies and coupled treatments.

All of the above should be accomplished considering the social, economical and environmental context that surrounds these contaminated areas.

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APPENDIX A. SAMPLING DOCUMENTATION

A.1. Sampling Plan

Sampling plan

Objective

To obtain a representative sample of contaminated soil, following the procedures established in the Standard Operation Procedure 2012 of the US EPA, along with the requirements established in the Official Mexican Standards NOM-021-SEMARNAT-2000 and NOM-138-SEMARNAT/SSA1-2012, in order to carry out the characterization of the soil and the sorption and advanced oxidation processes experiments.

Sampling site and date

Site located in the suburb of San Martín de Labastida, in the municipality of San Martín Texmelucan de Labastida, in the central west area of the state of Puebla, in central Mexico.

- **UTM coordinates:** Zone 14 North, 561390.00 m E, 2132852.00 m N
- **Access to the site:** Parting from San Martín Texmelucan to Tlaxcala de Xicohtencatl through Federal Road San Martin Texmelucan - Tlaxcala, turn right to the street Domingo Arenas, located right after Independencia street. The contaminated site is located at the end of the Domingo Arenas street.
- **Date:** Thursday April 27th, 2017, 09:30 am

Name and signature of the responsible person

Sandra Ivonne Arroyo Sánchez
Environmental Engineering Student
Universidad Popular Autónoma del Estado de Puebla

Description of the sampling activities and execution times

Sampling activity	Execution time
1. Delimitation of the contaminated area	2 minutes
2. Mark the sampling points, according to the number required by the NOM-138-SEMARNAT/SSA1-2012, based on the extent of the contamination	3 minutes
3. Remove rocks and vegetation, if there are any	5 minutes
4. Dig V-shaped hole, 30 cm deep	2 minutes
5. Extract a slice of 5 cm thick and transfer into a labeled container	1 minute
6. Clean tools and repeat procedure (steps 3-5) for each sampling point	2 minutes

Characteristics of the sampling site considered for the sampling plan

- Extent of the contamination
- Spilled product (contaminant)
- Access to the site
- Land use (agriculture)

Hidrocarburos a analizar según el contaminante

- TPH
- Diesel-range hydrocarbons

Design of the sampling plan

Targeted method, when the extent of the contamination is evident through the physical characteristics of the soil (color).

Sampling approach

Systematic polar grid. The samples are located in a regular pattern in the studied area, starting from a randomly located point. Parting from this point, a certain distance is established to locate the rest of the sampling points (same distance between them). Camples can be arranged in a polar grid, or a rectangular grid.

Number of sampling points

The extent of the contaminated area is below 0.1 hectares, thus a minimum of 4 sampling points is required by the NOM-138-SEMARNAT/SSA1-2012. Six sampling points were selected: 1 sampling point for uncontaminated soil and 5 sampling points for contaminated soil (1 central sample and 4 radial samples).

Sample size

According to the NOM-021-SEMARNAT-2000, it has been observed that analyzing single samples may present more variation, and require more time and economic resources than composite samples. This composite sample must be prepared with subsamples that contain the same amount of soil, and could be submitted to homogenization and the quartering process.

To develop the entire research project approximately 4 Kg of soil are required. As a precaution, this quantity was doubled to 8 Kg, and to apply the quartering method, the double (16 Kg) is required. Since 5 subsamples will be taken, at least 3.2 Kg of soil should be extracted per sampling point.

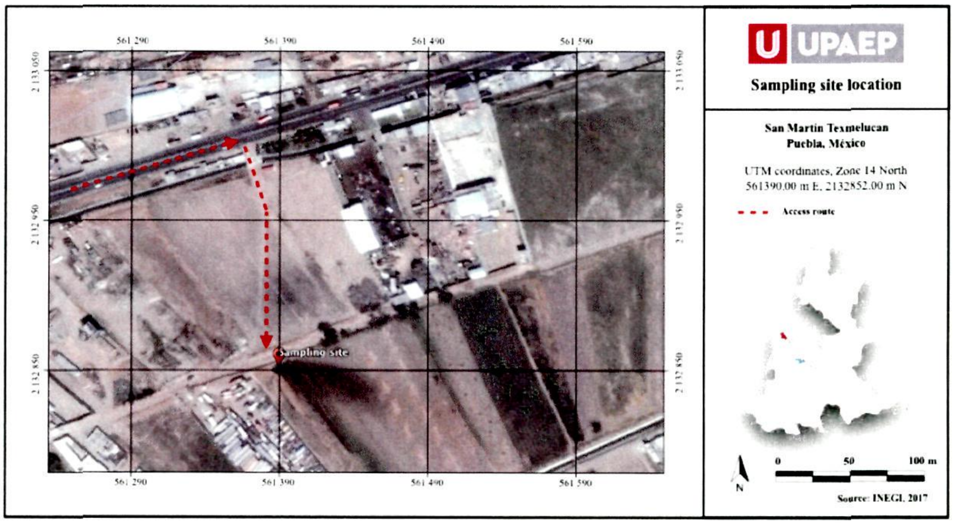
Justification for the location of the sampling points, depth, and sampling technique

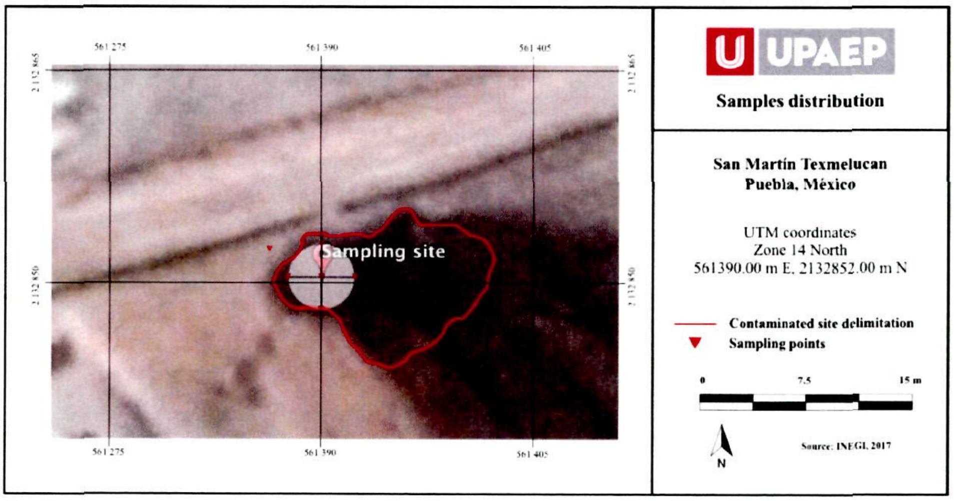
The sampling points were located to cover the area of the contamination systematically, covering the site from north to south, and from east to west; delimiting the horizontal distribution of the contaminant. The sampling depth was established at 30 cm in accordance to the NOM-021-SEMARNAT-2000, since the study will be carried out from an agricultural perspective, to determine the feasibility of the treatment to recover soil fertility. Since the root space of crops usually covers only the first 30 cm of the soil layer, that depth was selected. The selected sampling technique was manual due to the availability of the sampling equipment and the fact that the sampling depth is small.

Location of the sampling site and the sampling points

Sampling points

Sample No.	Soil type	Sample identification by sample code	Type of sample	UTM coordinates (UTM Zone: 14 N) X	Y
1	Uncontaminated	SS-01-U	Single sample	561392.4	2132860.9
2	Contaminated	SC-01-C	Subsample	561390.0	2132852.0
3	Contaminated	SC-02-S	Subsample	561390.0	2132849.7
4	Contaminated	SC-03-E	Subsample	561392.3	2132852.0
5	Contaminated	SC-04-N	Subsample	561390.0	2132854.3
6	Contaminated	SC-05-W	Subsample	561387.7	2132852.0





Sampling equipment

- Shovels
- Spatula
- Plastic bags
- Markers
- Labels
- Tape
- Water for cleaning
- Compass
- Measuring tape
- Wooden stakes
- Camera
- Sampling documents

Equipment decontamination procedure

1. Before sampling, wash throughly with soap and water
2. Rinse with distilled water
3. Air-dry

For equipment decontamination in the field, rinse with distilled water and dry with a clean cloth.

Types of containers, identification and storage

- Big resealable bags, and an opaque hermetic plastic box for transportation
- Labels for identification. These labels should include the following information: Sample No., Sample code, Date, Hour, Depth, Sampling point (coordinates), Name and signature of the responsible person
- Refrigeration if available, if not, store at room temperature, in the dark, inside a sealed container

Safety equipment

- Gloves
- Mask
- Boots
- Safety glasses

Instruments to ensure a good sampling quality

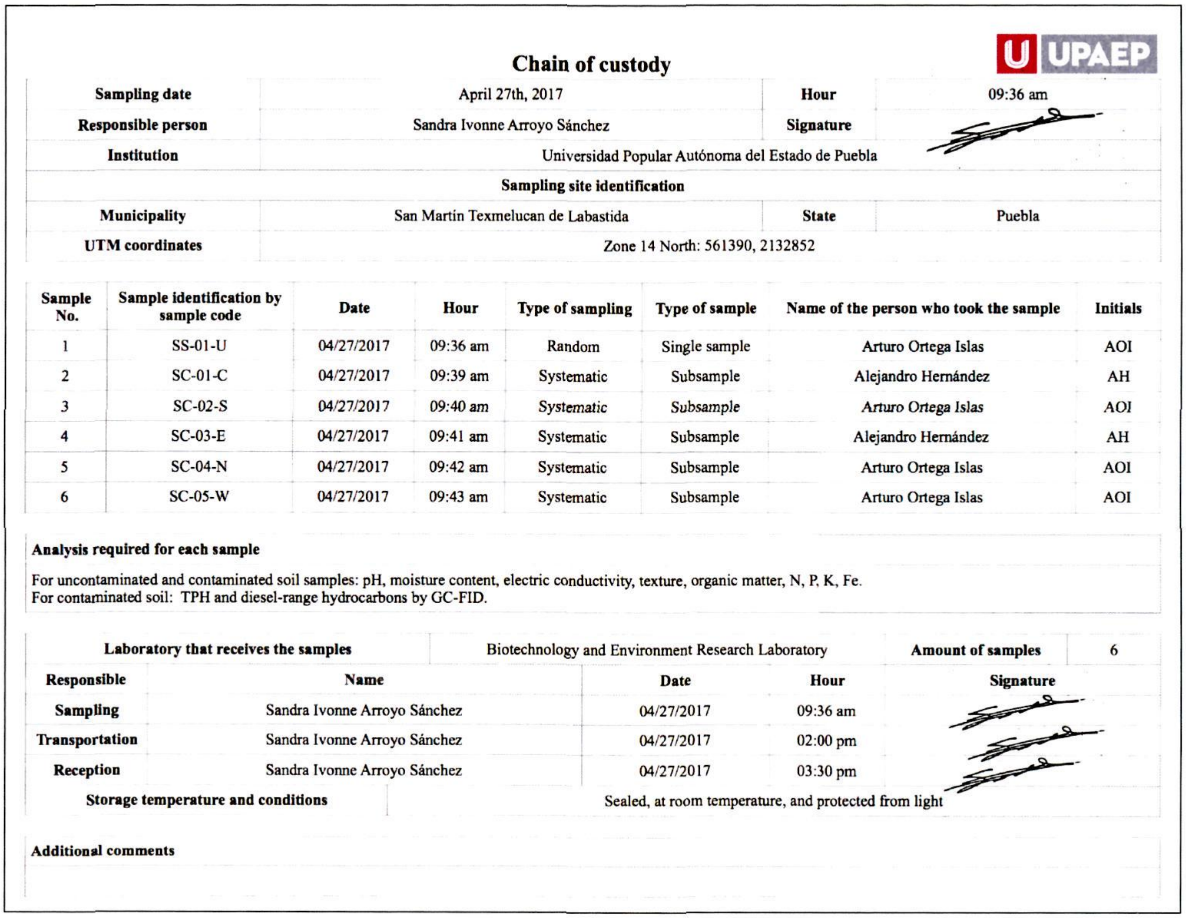
- Chain of custody and Sample record sheet
- Additional uncontaminated soil sample in an uncontaminated area near the sampling site
- New containers
- Sampling equipment decontamination

Historical background of the origin of the contamination

According to information provided by the personnel of *Protección Civil* of San Martín Texmelucan, who aided the sampling activities:

- The origin of the contamination was a fuel spillage due to a clandestine intake for fuel theft by organized crime groups
- The exact date of the spillage is unknown, but the fire department personnel who attended the emergency estimated the date of the spill about a month before the sampling date
- The Physical Security personnel from Pemex that attended to the sampling site assured that the product that is transported in the pipelines of the area is diesel

A.2. Chain of Custody



Chain of custody

Sampling date	April 27th, 2017	**Hour**	09:36 am
Responsible person	Sandra Ivonne Arroyo Sánchez	**Signature**	
Institution	Universidad Popular Autónoma del Estado de Puebla		
Sampling site identification			
Municipality	San Martin Texmelucan de Labastida	**State**	Puebla
UTM coordinates	Zone 14 North: 561390, 2132852		

Sample No.	Sample identification by sample code	Date	Hour	Type of sampling	Type of sample	Name of the person who took the sample	Initials
1	SS-01-U	04/27/2017	09:36 am	Random	Single sample	Arturo Ortega Islas	AOI
2	SC-01-C	04/27/2017	09:39 am	Systematic	Subsample	Alejandro Hernández	AH
3	SC-02-S	04/27/2017	09:40 am	Systematic	Subsample	Arturo Ortega Islas	AOI
4	SC-03-E	04/27/2017	09:41 am	Systematic	Subsample	Alejandro Hernández	AH
5	SC-04-N	04/27/2017	09:42 am	Systematic	Subsample	Arturo Ortega Islas	AOI
6	SC-05-W	04/27/2017	09:43 am	Systematic	Subsample	Arturo Ortega Islas	AOI

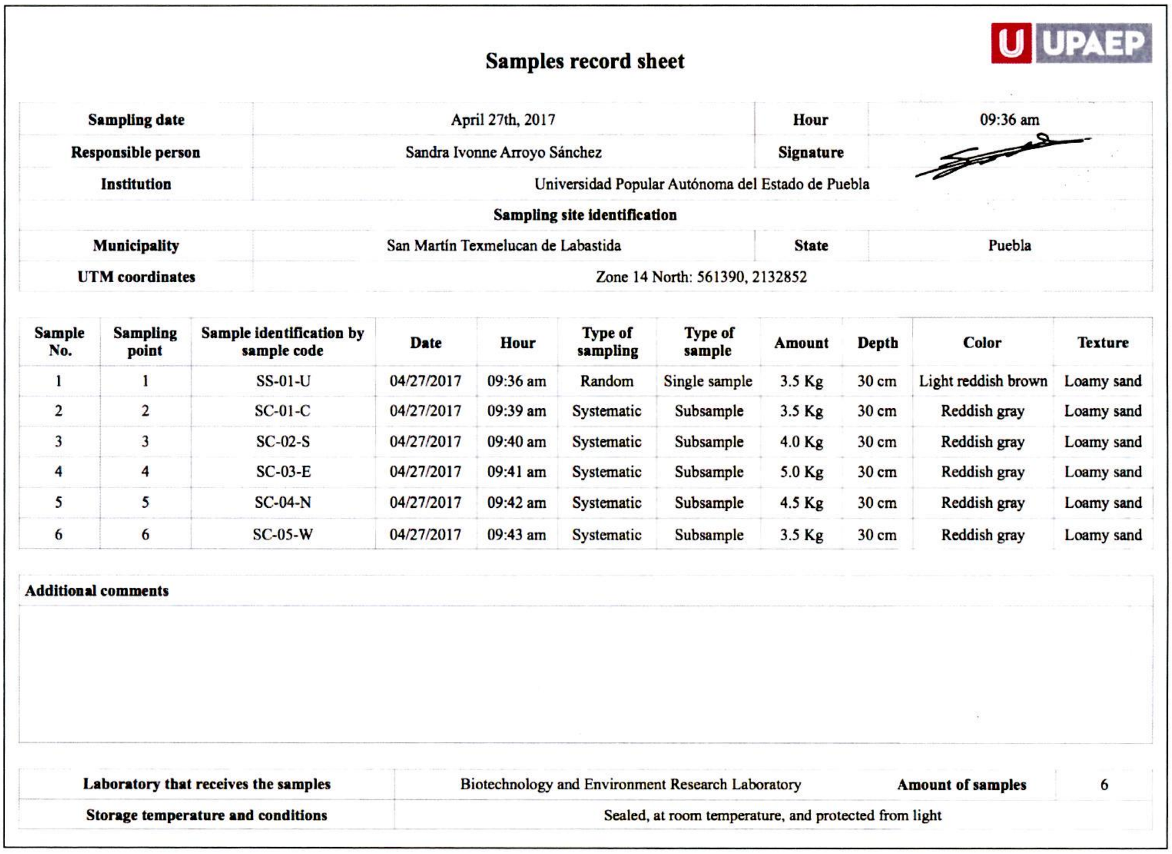
Analysis required for each sample

For uncontaminated and contaminated soil samples: pH, moisture content, electric conductivity, texture, organic matter, N, P, K, Fe.
For contaminated soil: TPH and diesel-range hydrocarbons by GC-FID.

Laboratory that receives the samples	Biotechnology and Environment Research Laboratory		**Amount of samples**	6
Responsible	**Name**	**Date**	**Hour**	**Signature**
Sampling	Sandra Ivonne Arroyo Sánchez	04/27/2017	09:36 am	
Transportation	Sandra Ivonne Arroyo Sánchez	04/27/2017	02:00 pm	
Reception	Sandra Ivonne Arroyo Sánchez	04/27/2017	03:30 pm	
Storage temperature and conditions	Sealed, at room temperature, and protected from light			

Additional comments

A.3. Samples Record Sheet



UPAEP

Samples record sheet

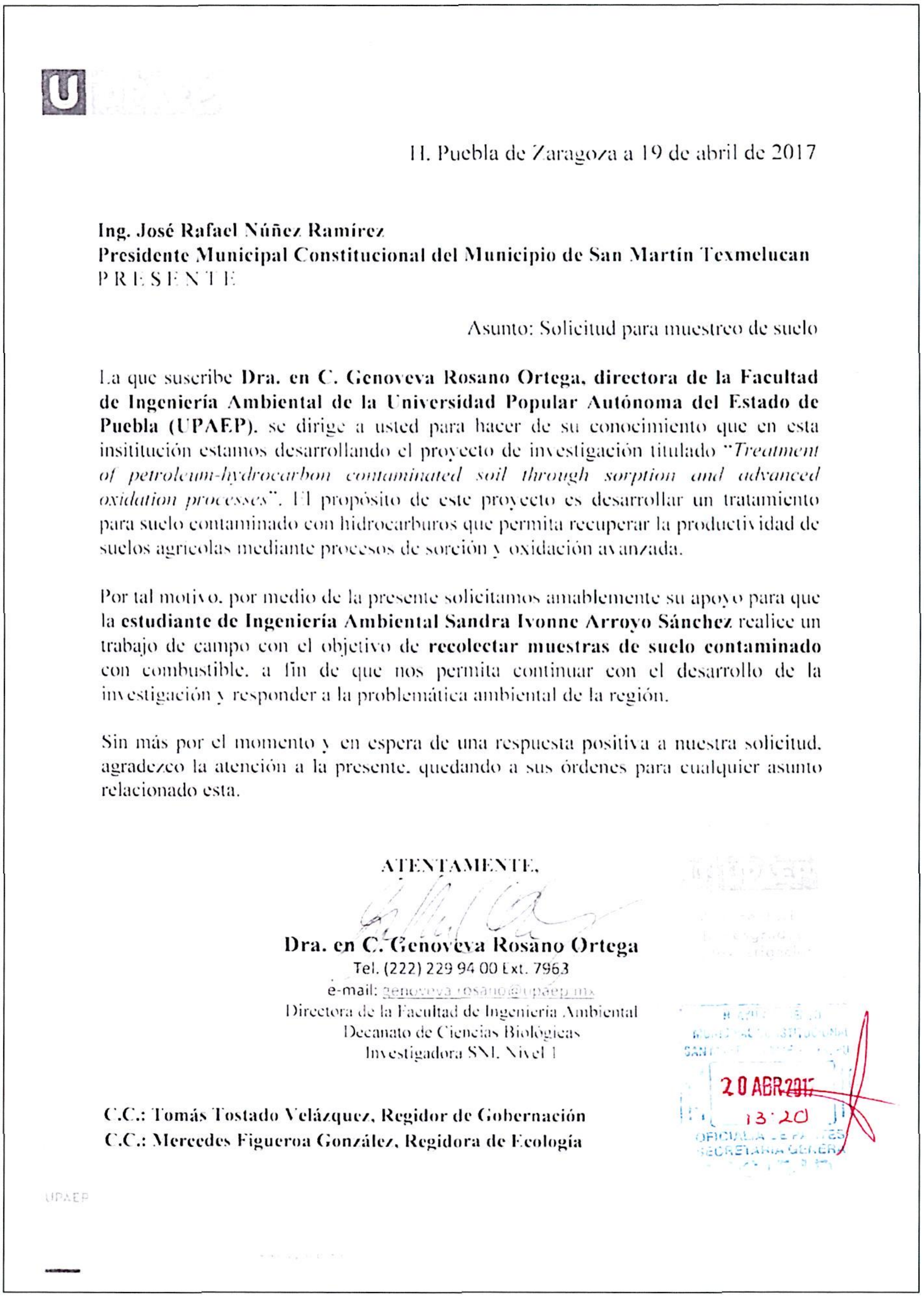
Sampling date	April 27th, 2017	**Hour**	09:36 am
Responsible person	Sandra Ivonne Arroyo Sánchez	**Signature**	
Institution	Universidad Popular Autónoma del Estado de Puebla		
Sampling site identification			
Municipality	San Martín Texmelucan de Labastida	**State**	Puebla
UTM coordinates	Zone 14 North: 561390, 2132852		

Sample No.	**Sampling point**	**Sample identification by sample code**	**Date**	**Hour**	**Type of sampling**	**Type of sample**	**Amount**	**Depth**	**Color**	**Texture**
1	1	SS-01-U	04/27/2017	09:36 am	Random	Single sample	3.5 Kg	30 cm	Light reddish brown	Loamy sand
2	2	SC-01-C	04/27/2017	09:39 am	Systematic	Subsample	3.5 Kg	30 cm	Reddish gray	Loamy sand
3	3	SC-02-S	04/27/2017	09:40 am	Systematic	Subsample	4.0 Kg	30 cm	Reddish gray	Loamy sand
4	4	SC-03-E	04/27/2017	09:41 am	Systematic	Subsample	5.0 Kg	30 cm	Reddish gray	Loamy sand
5	5	SC-04-N	04/27/2017	09:42 am	Systematic	Subsample	4.5 Kg	30 cm	Reddish gray	Loamy sand
6	6	SC-05-W	04/27/2017	09:43 am	Systematic	Subsample	3.5 Kg	30 cm	Reddish gray	Loamy sand

Additional comments

Laboratory that receives the samples	Biotechnology and Environment Research Laboratory	**Amount of samples**	6
Storage temperature and conditions	Sealed, at room temperature, and protected from light		

A.4. Sampling Solicitude Letter



H. Puebla de Zaragoza a 19 de abril de 2017

Ing. José Rafael Núñez Ramírez
Presidente Municipal Constitucional del Municipio de San Martín Texmelucan
PRESENTE

Asunto: Solicitud para muestreo de suelo

La que suscribe **Dra. en C. Genoveva Rosano Ortega, directora de la Facultad de Ingeniería Ambiental de la Universidad Popular Autónoma del Estado de Puebla (UPAEP)**, se dirige a usted para hacer de su conocimiento que en esta insititución estamos desarrollando el proyecto de investigación titulado *"Treatment of petroleum-hydrocarbon contaminated soil through sorption and advanced oxidation processes"*. El propósito de este proyecto es desarrollar un tratamiento para suelo contaminado con hidrocarburos que permita recuperar la productividad de suelos agrícolas mediante procesos de sorción y oxidación avanzada.

Por tal motivo, por medio de la presente solicitamos amablemente su apoyo para que la **estudiante de Ingeniería Ambiental Sandra Ivonne Arroyo Sánchez** realice un trabajo de campo con el objetivo de **recolectar muestras de suelo contaminado** con combustible, a fin de que nos permita continuar con el desarrollo de la investigación y responder a la problemática ambiental de la región.

Sin más por el momento y en espera de una respuesta positiva a nuestra solicitud, agradezco la atención a la presente, quedando a sus órdenes para cualquier asunto relacionado esta.

ATENTAMENTE,

Dra. en C. Genoveva Rosano Ortega
Tel. (222) 229 94 00 Ext. 7963
e-mail: genoveva.rosano@upaep.mx
Directora de la Facultad de Ingeniería Ambiental
Decanato de Ciencias Biológicas
Investigadora SNI, Nivel 1

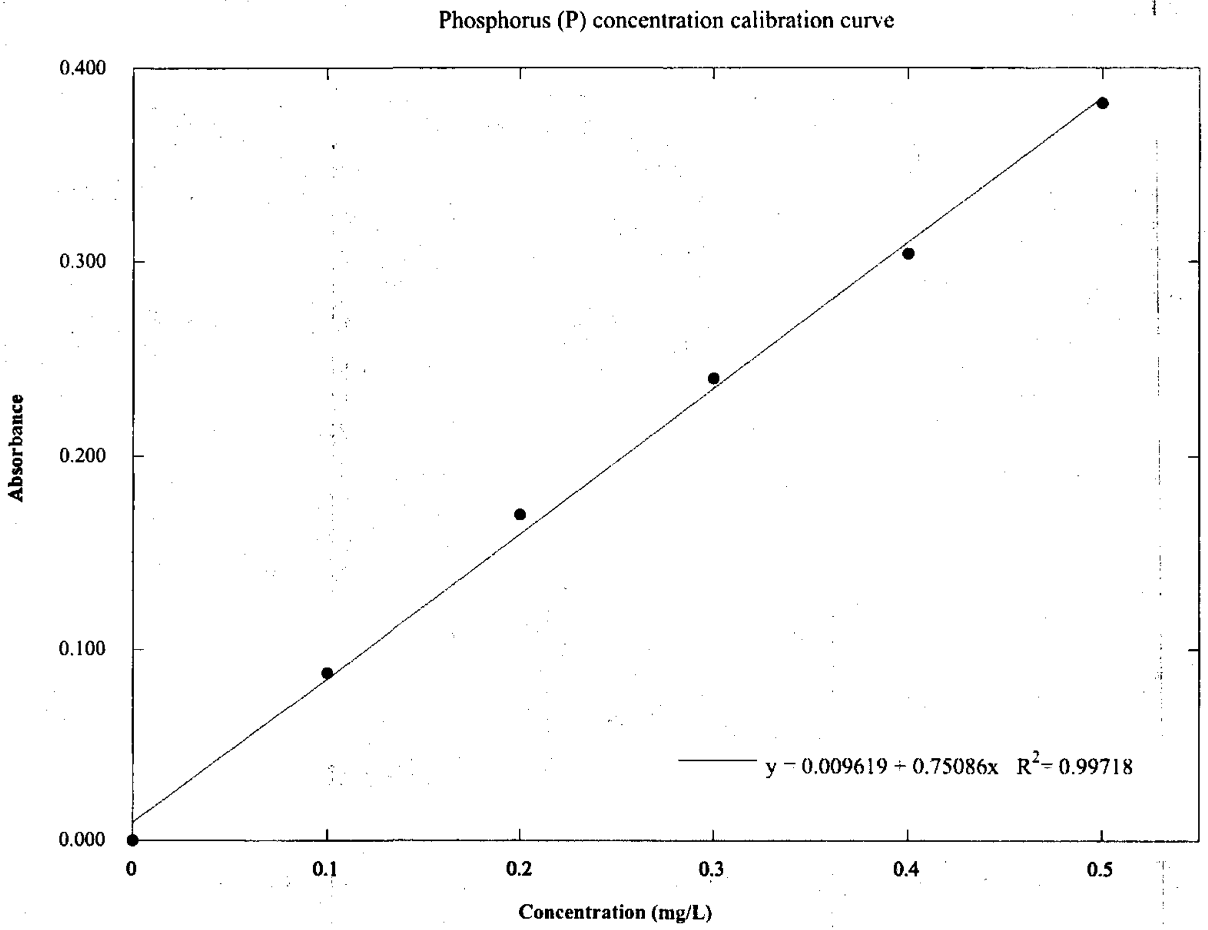
20 ABR 2017
13:20
OFICIALIA DE PARTES
SECRETARIA GENERAL

C.C.: Tomás Tostado Velázquez, Regidor de Gobernación
C.C.: Mercedes Figueroa González, Regidora de Ecología

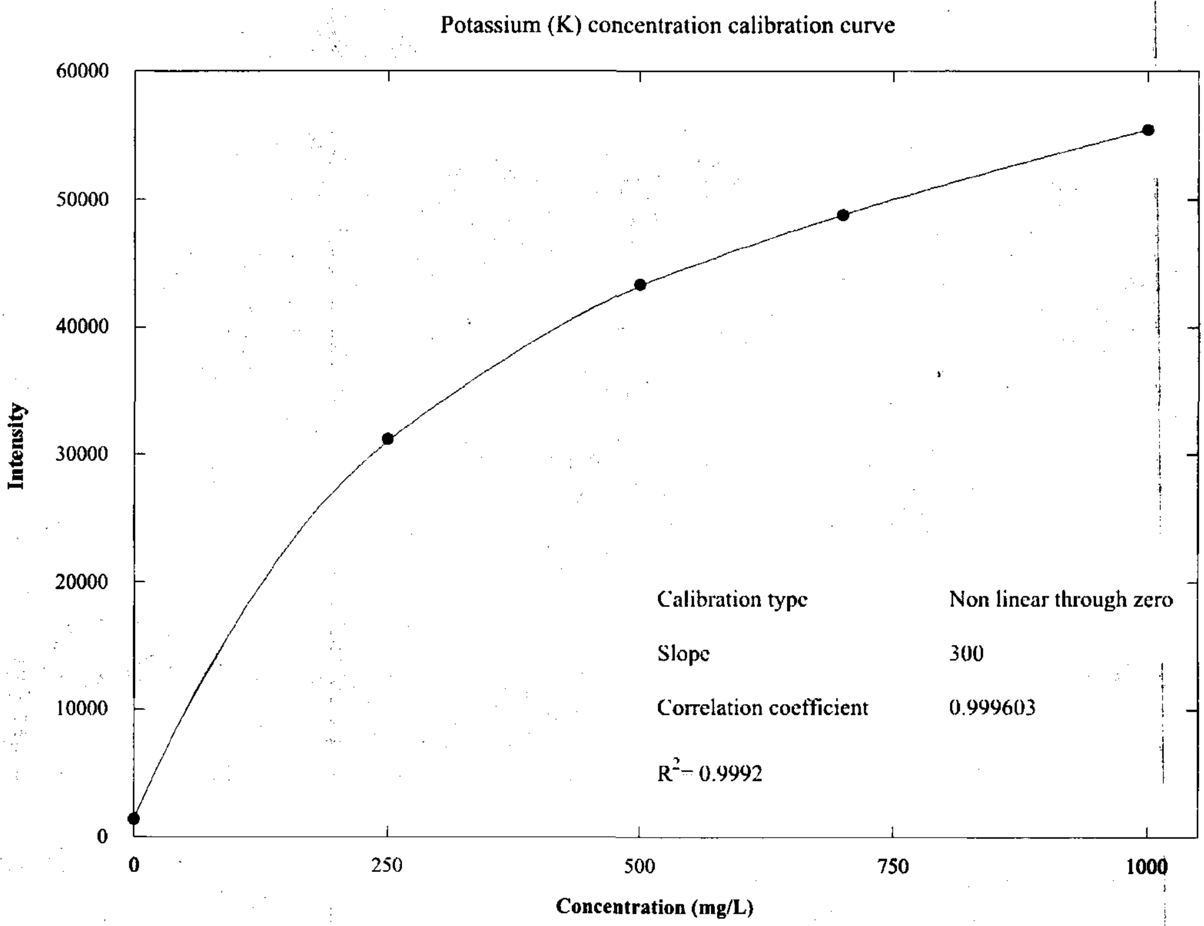
UPAEP

APPENDIX B. CALIBRATION CURVES

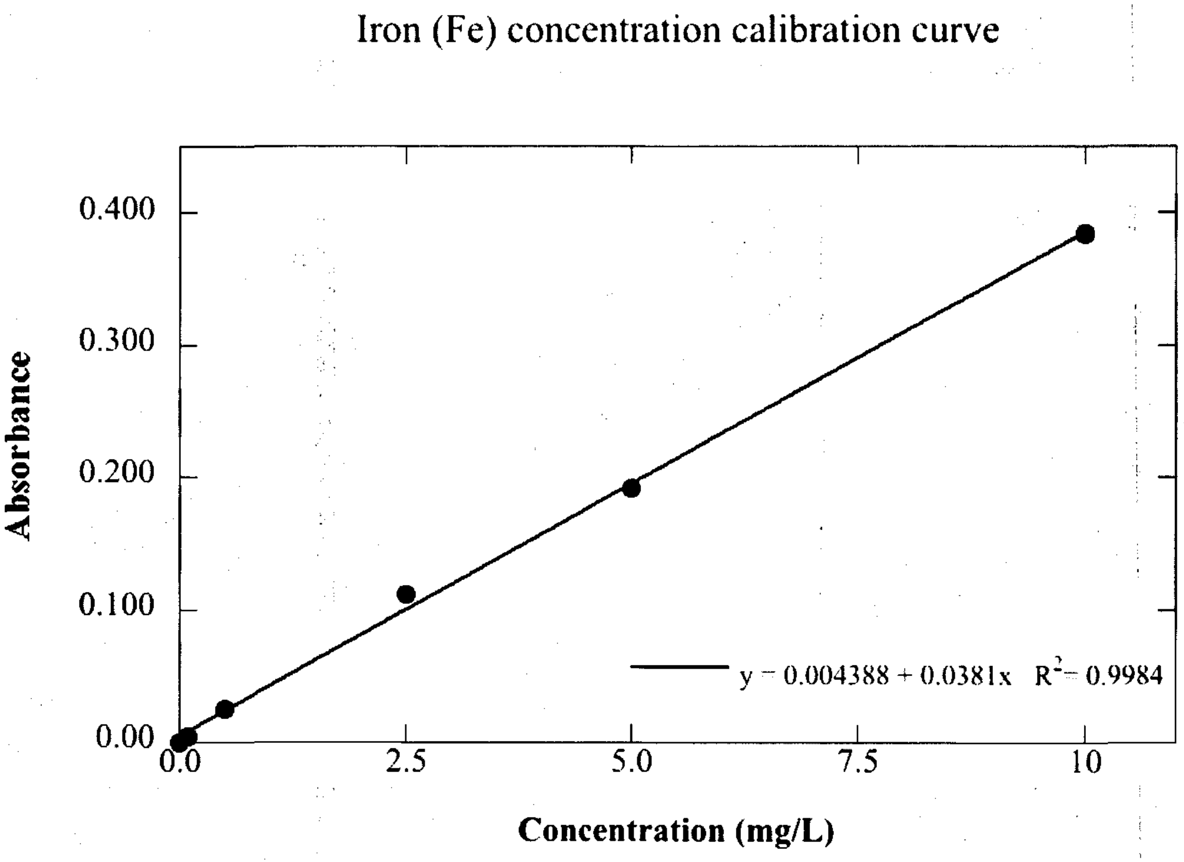
B.1. Available Phosphorus (P) Calibration Curve



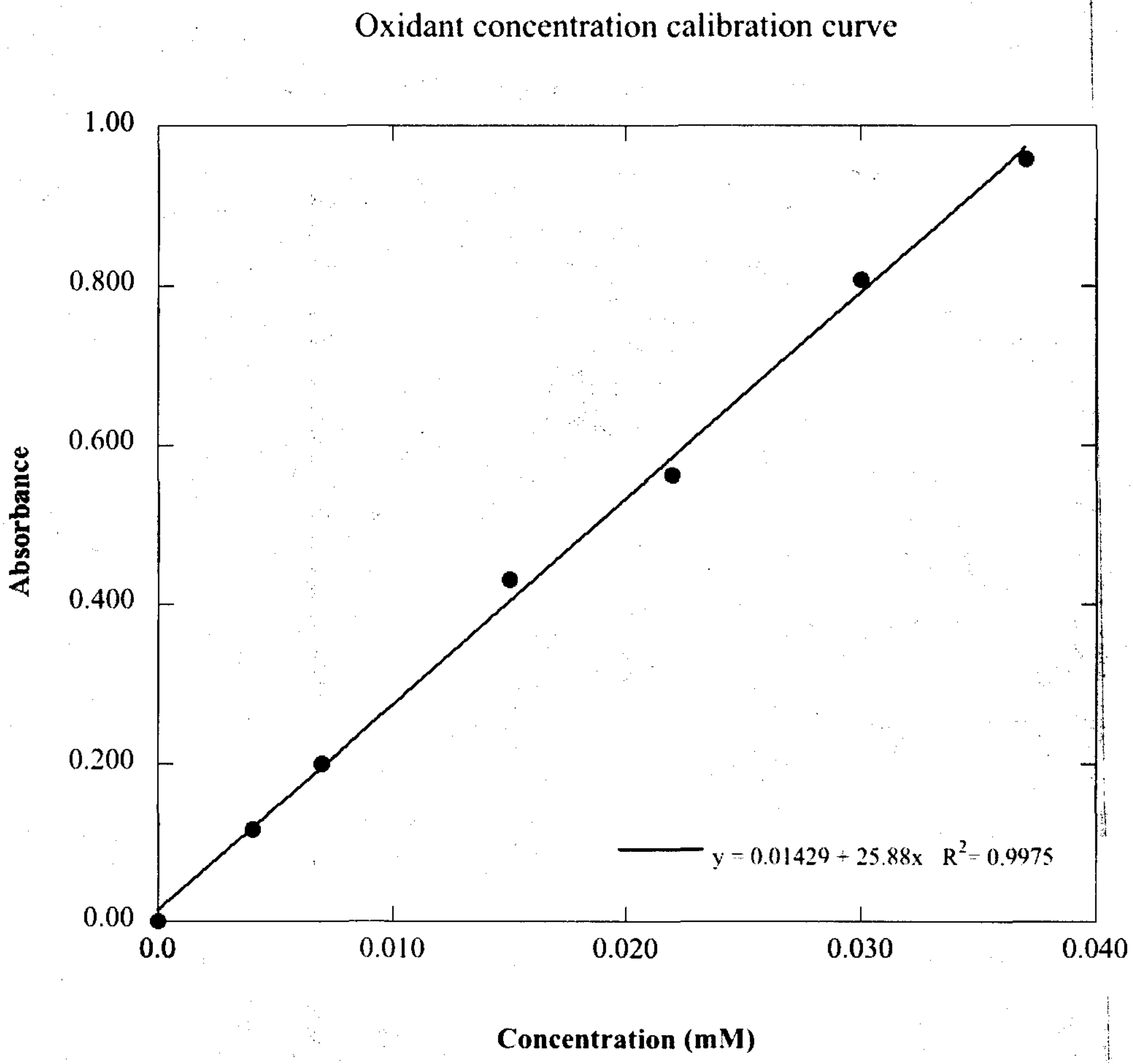
B.2. Potassium (K) Calibration Curve



B.3. Iron (Fe) Calibration Curve



B.4. Oxidant Calibration Curve



APPENDIX C. PARAMETERS FOR MOLECULAR SIMULATIONS

SE-PM3 (Semi-Empirical Options)

- Total Charge: 0 (-1 for $\cdot SO_4^-$, -2 for $S_2O_8^{2-}$)
- Spin Multiplicity: 1 (2 for $\cdot OH$ and $\cdot SO_4^-$)
- Spin Pairing: RHF (UHF for $\cdot OH$ and $\cdot SO_4^-$)
- State: Lowest
- Convergence Limit: Default
- Interaction Limit: Default
- Accelerate Convergence: Yes
- Polarizability: No

Geometry Optimization (Semi-Empirical Optimization)

- Algorithm: Polak-Ribiere
- Termination Condition: Default
- In Vacuo
- Screen Refresh Period: 1 cycles

EP plot (Plot Molecular Properties Options)

- Molecular property: Electrostatic Potential
- Representation: 3D Mapped Isosurface
- Grid Mesh Size: Coarse
- Isosurface Grid: Default
- Contour Grid Starting Value: Default
- Contour Grid Increment: Default
- Mapped Function Options: Default
- Total Charge Density 0.015
- Rendering: Wire Mesh

APPENDIX D. COMPLETE REDUCTANT - OXIDANT INTERACTIONS SIMULATED

Table D1. Reductant - Oxidant interactions from modelled molecules

Reductant	Oxidant	HOMO	LUMO	BG	E-	E+	EP	ETC
n-decane	**$OH\cdot$**	-11.275	4.239	15.514	0.018	0.179	0.161	96.361
n-decane	**$OH\cdot$**	-11.275	-0.760	10.515	0.018	0.179	0.161	65.311
n-decane	**H_2O_2**	-11.275	1.580	12.855	0.018	0.179	0.161	79.846
n-decane	**$SO_4^{\cdot-}$**	-11.275	6.603	17.878	0.018	0.091	0.073	244.906
n-decane	**$SO_4^{\cdot-}$**	-11.275	3.470	14.745	0.018	0.091	0.073	201.988
n-decane	**$S_2O_8^{2-}$**	-11.275	7.948	19.223	0.018	-0.023	0.041	468.857
n-dodecane	**$OH\cdot$**	-11.265	4.239	15.504	0.017	0.179	0.162	95.706
n-dodecane	**$OH\cdot$**	-11.265	-0.760	10.505	0.017	0.179	0.162	64.848
n-dodecane	**H_2O_2**	-11.265	1.580	12.845	0.017	0.179	0.162	79.292
n-dodecane	**$SO_4^{\cdot-}$**	-11.265	6.603	17.868	0.017	0.091	0.074	241.465
n-dodecane	**$SO_4^{\cdot-}$**	-11.265	3.470	14.735	0.017	0.091	0.074	199.127
n-dodecane	**$S_2O_8^{2-}$**	-11.265	7.948	19.213	0.017	-0.023	0.040	480.335
n-tetradecane	**$OH\cdot$**	-11.267	4.239	15.506	0.016	0.179	0.163	95.131
n-tetradecane	**$OH\cdot$**	-11.267	-0.760	10.507	0.016	0.179	0.163	64.462
n-tetradecane	**H_2O_2**	-11.267	1.580	12.847	0.016	0.179	0.163	78.818
n-tetradecane	**$SO_4^{\cdot-}$**	-11.267	6.603	17.870	0.016	0.091	0.075	238.271
n-tetradecane	**$SO_4^{\cdot-}$**	-11.267	3.470	14.737	0.016	0.091	0.075	196.497
n-tetradecane	**$S_2O_8^{2-}$**	-11.267	7.948	19.215	0.016	-0.023	0.039	492.700
n-eicosane	**$OH\cdot$**	-11.266	4.239	15.505	0.017	0.179	0.162	95.709
n-eicosane	**$OH\cdot$**	-11.266	-0.760	10.506	0.017	0.179	0.162	64.851
n-eicosane	**H_2O_2**	-11.266	1.580	12.846	0.017	0.179	0.162	79.296
n-eicosane	**$SO_4^{\cdot-}$**	-11.266	6.603	17.869	0.017	0.091	0.074	241.472
n-eicosane	**$SO_4^{\cdot-}$**	-11.266	3.470	14.736	0.017	0.091	0.074	199.134
n-eicosane	**$S_2O_8^{2-}$**	-11.266	7.948	19.214	0.017	-0.023	0.040	480.348
benzene	**$OH\cdot$**	-9.751	4.239	13.990	-0.005	0.179	0.184	76.033
benzene	**$OH\cdot$**	-9.751	-0.760	8.991	-0.005	0.179	0.184	48.864
benzene	**H_2O_2**	-9.751	1.580	11.331	-0.005	0.179	0.184	61.582
benzene	**$SO_4^{\cdot-}$**	-9.751	6.603	16.354	-0.005	0.091	0.096	170.354
benzene	**$SO_4^{\cdot-}$**	-9.751	3.470	13.221	-0.005	0.091	0.096	137.719
benzene	**$S_2O_8^{2-}$**	-9.751	7.948	17.699	-0.005	-0.023	0.018	983.278

Table D1. Reductant - Oxidant interactions from modelled molecules (Cont.)

Reductant	Oxidant	HOMO	LUMO	BG	E-	E+	EP	ETC
naphthalene	**$OH^{\cdot}$**	-8.837	4.239	13.076	-0.005	0.179	0.184	71.065
naphthalene	**$OH^{\cdot}$**	-8.837	-0.760	8.077	-0.005	0.179	0.184	43.896
naphthalene	**H_2O_2**	-8.837	1.580	10.417	-0.005	0.179	0.184	56.614
naphthalene	**$SO_4^{\cdot -}$**	-8.837	6.603	15.440	-0.005	0.091	0.096	160.833
naphthalene	**$SO_4^{\cdot -}$**	-8.837	3.470	12.307	-0.005	0.091	0.096	128.197
naphthalene	**$S_2O_8^{2-}$**	-8.837	7.948	16.785	-0.005	-0.023	0.018	932.497
anthracene	**$OH^{\cdot}$**	-8.249	4.239	12.488	-0.005	0.179	0.184	67.872
anthracene	**$OH^{\cdot}$**	-8.249	-0.760	7.489	-0.005	0.179	0.184	40.703
anthracene	**H_2O_2**	-8.249	1.580	9.829	-0.005	0.179	0.184	53.421
anthracene	**$SO_4^{\cdot -}$**	-8.249	6.603	14.852	-0.005	0.091	0.096	154.713
anthracene	**$SO_4^{\cdot -}$**	-8.249	3.470	11.719	-0.005	0.091	0.096	122.077
anthracene	**$S_2O_8^{2-}$**	-8.249	7.948	16.197	-0.005	-0.023	0.018	899.857

APPENDIX E. ANOVA TABLES

E.1. Factorial General Regression: TPH vs Blocks, Time, Oxidant and Oxidant Concentration

E.1. Factor Information

Factor	Levels	Values
Time	6	0.0, 0.5, 1.0, 2.0, 6.0, 24.0 (hours)
Oxidant	2	Peroxide (PX), Persulfate (PS)
Oxidant Concentration	3	0, -, + (none, low, high)

E.1. ANOVA

Source	DOF	SS Adjust.	MS Adjust.	F Value	P Value
Model	37	17175047490	464190473	92.57	0.000
Blocks	2	2476753	1238377	0.25	0.782
Linear	8	1466431030	1833045129	365.53	0.000
Time	5	6687468495	1337493699	266.71	0.000
Oxidant	1	28685515	28685515	5.72	0.019
Oxidant concentration	2	7948207020	3974103510	792.48	0.000
2-term interactions	17	2367029111	139237007	27.77	0.000
Time*Oxidant	5	78943114	15788623	3.15	0.013
Time*Oxidant concentration	10	1981647993	198164799	39.52	0.000
Oxidant*Oxidant concentration	2	306438004	153219002	30.55	0.000
3-term interactions	10	141180596	14118060	2.82	0.005
Time*Oxidant*Oxidant concentration	10	141180596	14118060	2.82	0.005
Error	70	351032131	5014745		
Total	107	17526079621			

E.1. Model summary

S	R squared	R squared (adjusted)	R squared (predicted)
2239.36	98.00%	96.94%	95.23%

When P value is higher than α = 0.05, that factor does not influence on the result of the treatment. Blocks do not influence the TPH removal from the treatments.

E.2. One-way ANOVA: Remaining TPH vs. Oxidation Treatment

E.2. Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	$\alpha = 0.05$

E.2. Factor Information

Factor	Levels	Values
Oxidation Treatment	6	PS0, PS5, PS10, PX0, PX1.5, PX3

E.2. ANOVA

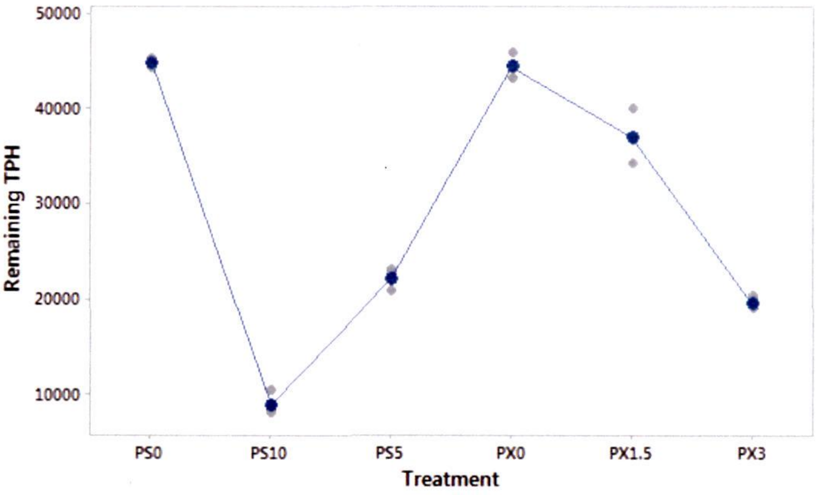
Source	DOF	SS Adjust.	MS Adjust.	F Value	P Value
Treatment	5	3268553178	653710636	275.97	0.000
Error	12	28425413	2368784		
Total	17	3296978590			

E.2. Model summary

S	R squared	R squared (adjusted)	R squared (predicted)
1539.09	99.14%	98.78%	98.06%

Since P value (0.000) is lower than $\alpha = 0.05$, the null hypothesis is rejected, meaning not all means are equal.

E.2. Individual Values Plot of Remaining TPH vs. Oxidation Treatment



E.3. One-way ANOVA: Remaining TPH vs. Treatment

E.3. Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

E.3. Factor Information

Factor	Levels	Values
Treatment	7	AC5, PS0, PS5, PS10, PX0, PX1.5, PX3

E.3. ANOVA

Source	DOF	SS Adjust.	MS Adjust.	F Value	P Value
Treatment	6	3347305160	557884193	249.86	0.000
Error	14	31259367	2232812		
Total	20	3378564527			

E.3. Model summary

S	R squared	R squared (adjusted)	R squared (predicted)
1539.09	99.07%	98.68%	97.92%%

Since P value (0.000) is lower than α = 0.05, the null hypothesis is rejected, meaning not all means are equal.

E.3. Individual Values Plot of Remaining TPH vs. Treatment