Chapter 7 Remediation of soils contaminated by hydrocarbons using a polymeric material (carboxymethylcellulose gel)

Capítulo 7 Remediación de suelos contaminados por hidrocarburos mediante un material polimérico (gel de carboximetilcelulosa)

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Abstract

In recent years, the pollution caused by hydrocarbon spills has increased, and this leads to research to mitigate the deterioration caused to the environment, therefore, this work has the purpose of remedying a contaminated soil due to the explosion of the Well Terra 123 of Mexican Oil (PEMEX) occurred in October 2013, which left in its wake contamination, death of animals and diseases in the population, causing both environmental and health effects on the inhabitants of the region such as vitiligo, problems vision, throat, cough and flu (Reporte Indigo, 2019). The studies carried out by Duran in 2015 on "Environmental impact on the indigenous communities of Nacajuca, Tabasco, due to the explosion of the Well Terra 123", gathered evidence of the impact that this oil accident had on the health of those close to it to the facilities and the environment. This chapter will deal with the remediation of soil contaminated by hydrocarbons due to the explosion of the Terra 123 Well, using a polymeric material (carboxymethylcellulose gel), which was synthesized at the laboratory level using carboxymethylcellulose (CMC), glutaraldehyde (GA) as agent of crosslinking and hydrochloric acid (HCl) as a catalyst for synthesis. The CMC gel was incorporated into the contaminated soil for the absorption of the hydrocarbon for a period of three months. The samples were collected from the soil contaminated with hydrocarbon from Terra 123 well, located in Oxiacaque, Nacajuca, Tabasco, and the effectiveness was studied in two stages: (1) The soil particle was decreased by sieving and (2) Pre and post soil analyzes were carried out (moisture percentage and fat content). In addition, the CMC gels were analyzed using infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques before and after being incorporated into the contaminated soil. The amount of hydrocarbon initially contained in the soil was made using the Soxhlet method, obtaining 0.99 mg of hydrocarbon / kg of soil.

Remediation, Gel, Carboxymethylcellulose, Hydrocarbons, Polymers

Resumen

En los últimos años se ha incrementado la contaminación provocado por derrames de hidrocarburos, y esto conlleva a realizar investigaciones que permitan mitigar el deterioro provocado al medio ambiente, por lo tanto, este trabajo tiene la finalidad de remediar un suelo contaminado debido a la explosión del Pozo Terra 123 de Petróleos Mexicanos (PEMEX) ocurrido en el mes de octubre del año 2013, lo cual dejó a su paso contaminación, muerte de animales y enfermedades en la población, provocando afectaciones tanto ambientales como de salud en los pobladores de la región como vitíligo, problemas de visión, de garganta, tos y gripa (Reporte Indigo, 2019). Los estudios realizados por Duran en el 2015 de "Impacto ambiental en las comunidades indígenas de Nacajuca, Tabasco, a causa de la explosión del Pozo Terra 123", acudieron a recoger evidencias del impacto que tuvo este accidente petrolero en la salud de las personas cercanas a las instalaciones y en el medio ambiente. El presente capítulo tratará sobre la remediación del suelo contaminado por hidrocarburos debido a la explosión del Pozo Terra 123, empleando un material polimérico (gel de carboximetilcelulosa), el cual se sintetizó a nivel laboratorio utilizando carboximetilcelulosa (CMC), glutaraldehído (GA) como agente de entrecruzamiento y ácido clorhídrico (HCl) como catalizador de la síntesis. El gel de CMC se incorporó al suelo contaminado para la absorción del hidrocarburo por un periodo de tres meses. Las muestras fueron recolectadas del suelo contaminado con hidrocarburo proveniente del pozo Terra 123, ubicado en el ejido Oxiacaque, municipio de Nacajuca, Tabasco y, se estudió la efectividad en dos etapas: (1) Se disminuyó la partícula de suelo mediante tamizado y (2) Se realizaron análisis previos y posteriores al suelo (porcentaje de humedad y contenido de grasa). Además, los geles de CMC se analizaron mediante las técnicas de espectroscopia de infrarrojo (FTIR) y microscopia electrónica de barrido (SEM) antes y después de ser incorporados al suelo contaminado. La cantidad de hidrocarburo que contenía inicialmente el suelo se realizó mediante el método Soxhlet, obteniendo 0.99 mg de hidrocarburo/kg de suelo.

Remediación, Gel, Carboximetilcelulosa, Hidrocarburos, Polímeros

1 Introduction

The petrochemical industry in Mexico has developed rapidly, generating diverse economic benefits. However, its expansion and development has also given rise to serious environmental problems, resulting in environmental emergencies, with serious repercussions on the health of the population and the ecological balance of ecosystems (Quadri 1994).

Among the causes that have generated this environmental deterioration due to the contamination of water bodies and soils throughout the country are the following: (i) improper handling and abandonment of hazardous materials and waste; (ii) inadequate maintenance or lack thereof in oil facilities; (iii) explosions in high-risk facilities; (iv) leaks in pipelines; and (v) hydrocarbon spills (CENAPRED 2001, PROFEPA 2002).

In PEMEX's final inventory of hazardous waste, with a total of 19.6 thousand tons at the end of 2020 (SISPA, 2021), the inventory increased 16% over 2019. During 2020, 56 thousand tons were generated and 53.2 thousand tons were disposed of, resulting in a disposal to generation ratio of 0.95. Pemex Transformación Industrial's activities account for 76% of the hazardous waste inventory, where 45% corresponds to oily sludge, 14% to solid waste impregnated with hydrocarbons, 13% to spent soda and the rest to others (laboratory, sewage treatment sludge, etc.).

On the other hand, the total number of leaks and spills in Pemex in 2020 was 931 events (not including those due to clandestine outlets), with respect to 2019, showing a 15% decrease, mainly due to a reduction in the number of events presented in Pemex Logística and Pemex Exploración y Producción (PEP). Of these events, 77% correspond to PEP, 13% to Pemex Logística, 8% to Pemex TRI (Transformación Industrial) and 2% to PMI (Comercio Internacional, S.A. de C.V.).

Among the most serious environmental disasters that threaten biodiversity are oil spills, and it is estimated that 3,800 million liters enter the oceans each year as a result of human activities. Of these, only 8 percent are due to natural sources; at least 22 percent to intentional operational discharges from ships, 12 percent to spills from ships, and another 36 percent to sewage discharges (Suchanek, 1993).

In a biodiversity report in 2006, it published that in 2002, Mexico spilled 160 barrels of hydrocarbons, thus increasing the area of contaminated soil. On the other hand, the Procuraduría de Protección al Ambiente (PROFEPA, 2016), published that, in the state of Tabasco, only in the last 11 years, a total of 385 oil spills have been registered.

Garcia *et al*. in 2010, conducted a study on the removal of polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) in a soil contaminated with crude oil, using two types of agro-industrial residues, cachaza and sugarcane bagasse as amendments and texturizers, where cachaza was highly effective for the removal of PAH and TPH hydrocarbons, obtaining similar results with sugarcane bagasse. On the other hand, the cachaza, besides obtaining good results in the repair, has as an additional advantage the contribution of microorganisms to the soil, which have the capacity to bio-transform the toxics and provide nutrients in higher concentration.

At the Instituto Tecnológico de Durango in 2011, the evaluation of the aerobic bioremediation process of a soil contaminated with petroleum hydrocarbons using residual sludge (biosolids) from a domestic wastewater treatment plant (WWTP) as an alternative source of macro and micronutrients was carried out, which resulted in the conclusion that sewage sludge is a viable alternative for the removal of petroleum hydrocarbons, in addition to being an alternative source of nutrients, also mentioning that the mineralization or maturity of the sludge influenced the rate of hydrocarbon removal (Martínez *et al*. 2011).

Ordaz *et al*. in 2011 conducted bioremediation tests at the microcosm level on a clay soil contaminated with crude oil, with different concentrations of total petroleum hydrocarbons (TPH) and used sugarcane bagasse as a texturizer and amendment, being sugarcane bagasse a profitable alternative for the development of microcosms, in addition to being effective in the removal of TPH.

By obtaining favorable results with these types of techniques, in Peru in 2013, the Soil Fertility Laboratory of the National Agrarian University La Molina, conducted a bioassay experiment where manure and sawdust were used, having as substrate the "corn" indicator plant (*Zea mays L.*), for the elimination of total petroleum hydrocarbons, obtaining as a result that the greatest reduction in the concentration of petroleum hydrocarbons was obtained with the use of manure; however, with the use of sawdust there is also a reduction in the concentration, but in smaller quantities (Buendía, 2013).

On the other hand, the Institute of Biotechnology and Applied Ecology of the University of Veracruz, conducted a research, in which they used endogeous earthworms (*Pontoscolex corethururs*) for the removal of the polyaromatic hydrocarbon Benzo(a)Pyrene, affirming that the endogeous species *P. corethururs* can be used in the remediation of soils contaminated with polyaromatic hydrocarbons in tropical areas (Hernández, 2013).

Quijano in 2015 conducted a study to evaluate the degradation of total petroleum hydrocarbons (TPH) in contaminated soil under nursery conditions. In which two tree species Swietenia macrophylla (mahogany) and Tabebuia rosea (macuilis) were planted in combination with bat guano vermi-compost, and cachaza and sheep manure composts in different doses, being the species S. macrophylla and T. rosea, those that improve the chemical parameters of the soil, helping to restore the contaminated soil.

Hydrocarbons are the most demanded petroleum products in the world, as they are the main energy generators for human beings and constitute the essential elements of petroleum; their molecules contain only carbon and hydrogen and are divided into several chemical families according to their structure. All these structures are based on the tetravalency of carbon (Wauquier, 2004).

Garcia *et al*. in 2010 studied the removal efficiency of polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) from a soil contaminated with crude oil, using two types of agroindustrial wastes, cachaza and sugarcane bagasse as amendments and texturizer. They conducted tests in solid culture microcosms for the bioremediation of a soil contaminated with 14,300 mg/kg of TPH and 23.14 mg/kg of PAH. The soil:residue ratios used in the tests were as follows (%): 100:0, 98:2, 96:4 and 94:6, and the addition of macro-nutrients based on a carbon/nitrogen/phosphorus ratio of 100:10:1. TPH removal was 60.1 % for bagasse and 51.4 % for cachaza. The cachaza turns out to be an alternative for bioremediation processes of soils contaminated with hydrocarbons.

Buendía in 2012 conducted a study in which he used manure and sawdust as substrate for the indicator plant "corn" (*Zea mays L*.), planted and controlled for a period of two months. Taking as a reference sample 36 pots in which 12 treatments were evaluated with three replicates each, obtaining as results an average decrease of 22.5% of the hydrocarbon content in the soil, using only manure decreased 16.5% and using only sawdust decreased 9.6%.

Arrieta *et al*. conducted a study in 2010 in which they isolated and characterized biochemically and molecularly a bacterial consortium capable of degrading the different hydrocarbons present in diesel, made up of the following genera: Enterobacter sp, Bacillus sp, Staphylococcus aureus, Sanguibacter soli, Arthrobacter sp, and Flavobacterium sp, using soil contaminated with diesel at laboratory scale, using two bioremediation technologies: natural attenuation and biostimulation. They defined as a control parameter the concentration of total hydrocarbons (TPH), concluding with a reduction in concentration over a period of 4 months of 36.86% for natural attenuation and 50.99% for biostimulation.

Anza *et al*, in 2016 conducted a research where they used biopiles as a method of bioremediation of soil contaminated with used oils from automotive service workshops, using four soil samples and analyzed moisture, organic matter, texture, pH, temperature, total nitrogen and phosphorus, they built four biopiles, developing three treatments with three replicates and a control, and were contaminated in concentrations for control 30,000 ppm, first treatment 10,000 ppm, second 30,000 ppm and third 50,000 ppm of total petroleum hydrocarbons (TPH). The strains used were: Acinetobacter Sp, Sphingobacterium Sp and Stenotrophomona Sp and they concluded that the treatment obtained high percentages of removal of the aliphatic fractions from 93.7 to 87.1% in 90 days.

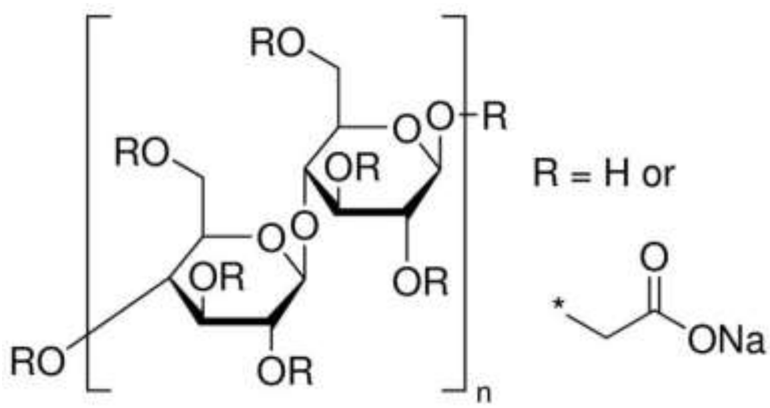
Martinez *et al*., in 2011, conducted a study in which they evaluated the aerobic bioremediation process of a soil contaminated with petroleum hydrocarbons using residual sludge (biosolids) from a domestic wastewater treatment plant (WWTP) as an alternative source of macro and micronutrients. The results showed that the residual sludge stimulated the stimulation of native soil microorganisms, which in turn were responsible for degrading the hydrocarbons. The soil subjected to aerobic remediation reached the maximum permissible limit (MPL) established in current Mexican regulations (NOM-138-SEMARNAT/SS-2003).

Cartaya *et al*. in 2011 conducted trials to study the uptake and distribution of heavy metals (Cu) in tomato seedlings treated with natural polymers (oligo¬galacturonides, Ogal) grown in a medium with toxic levels of copper. They analyzed the assimilable metals in the soil in order to determine the residual effect and mobility of these elements and concluded that the use of the oligogalacturonide mixture counteracts the effect of heavy metal toxicity and produced changes in the pattern of metal accumulation in plants treated with natural polymers, even though the low mobility and bioavailability of heavy metals are mainly due to soil characteristics. Manzano *et al*. in 2011, analyzed the use of cattle manure in the decontamination of diesel contaminated soil (1.4% by weight). Applying an ex-situ methodology of diesel contaminated soils and the characterization of hydrocarbon contamination, and the diesel fraction in particular can determine the doses of manure and wastewater to be contributed initially. The decontamination behavior of a diesel contaminated soil using biopiles with the addition of cattle manure can be modeled using a logistic curve type, and thus it is estimated that at 183 days 99.8% of diesel was removed from the soil.

Carboxymethyl cellulose (CMC)

Figure 7.1 shows the structure of carboxymethylcellulose (CMC), an organic compound derived from cellulose, consisting of carboxymethyl groups linked to some hydroxyl groups, which is present in the polymer. CMC is similar to cellulose, but unlike cellulose, it is soluble in water and appears as a white or almost white granular powder, hygroscopic after drying.

Figure 7.1 Structure of carboxymethylcellulose



Source: (Guise & et al., 2014)

Among its most important physical properties are its hydrophilic nature of action, its high viscosity in diluted solutions, being practically insoluble in acetone, ethanol and toluene, it also has similar uses to methylcellulose, has the ability to form gels with good consistency, but without great transparency and caramel brown color with high adhesiveness, which makes them very useful as semi-solid oral excipients. Table 7.1 shows the various industrial areas where CMC is used.

Table 7.1 Industrial uses of Carboxymethylcellulose

Application	Dispersant	Protective Colloid	Water Retainer	Thickener	Film Forming
Water-based paints	X	X	X	X	X
Construction products	X		X	X	
Adhesives for wallpapering				X	X
Paper coatings	X	X		X	X
Detergents		X		X	
Emulsions		X		X	
Ceramics	X	X	X	X	X
Tobacco					X
Cosmetics and Pharmaceuticals	X	X	X	X	
Food products	X	X	X	X	X
Oil sludge		X	X	X	

Source: *https://www.quiminet.com/articulos/las-diversas-aplicaciones-de-la-carboximetilcelulosa-cmc-16089.htm*

Hydrocarbons

A hydrocarbon is an organic compound that arises by combining hydrogen atoms with carbon atoms. These chains of carbon atoms can be open or closed and linear or branched. The great majority of hydrocarbons come from petroleum and because it is the result of the decomposition of organic matter, it offers a great quantity and concentration of carbon and hydrogen. Being these parts of a very important industry for the economy since from them fossil fuels are obtained, used in the industry to produce lubricants, plastics and other products.

Among the main characteristics it is worth mentioning that their boiling point increases as the size of the molecule increases, their density also increases when the molecule is larger, they are insoluble in water because they are polar substances, i.e. the electrical charges of each molecule are separated, they are mostly used as fuels, they are highly polluting and toxic.

They are also one of the main sources of soil and water pollution in the world, due to accidents during transportation, usually by pipeline, but a substantial volume of the oil that reaches the markets is transported by tanker or road.

Oil spills

An oil spill also known as an oil slick is caused by an oil spill that occurs due to an accident or improper practice that pollutes the environment.

These spills affect the entire ecosystem where the spill occurs, seriously damaging the fauna and flora with effects that can be very persistent over time. Hydrocarbon contamination is caused by spills in transportation, loading and unloading operations, leaks from pipelines or industrial facilities, and accidents.

The oil spill affects the soil structure, increasing its water retention capacity, in the surface layer the hydrocarbons decrease the soil pH, increase the available manganese, iron and phosphorus, making it acidic and therefore less suitable for cultivation or the growth of wild plants. Due to the drastic changes that occur after the spill, various forms of recovery have been implemented in order to restore the affected territory.

Soil remediation

Remediation is the treatment or set of operations carried out with the objective of recovering the quality of the contaminated subsoil as shown in Figure 7.2, there are different techniques that allow the recovery of the soil for its use and guarantee the health of people and ecosystems.

Figure 7.2 Soil remediation

Source: (Burnett, 2014)

Remediation techniques are applied depending on the type of pollutant. Treatment systems can be classified into three main areas.

1. Non-recovery, for which the properties of the soil must be modified and the affected space must be perfectly delimited, in addition to monitoring to ensure the impossibility of affecting third parties.
2. Isolation of contamination, consists of establishing correct safety measures to prevent the progression of contamination and mitigating the adverse effects related to the dispersion of contaminating substances.
3. Remediation, remediation measures are divided into in situ treatment, which involves the removal of contaminants without removing the soil, and ex situ where the material to be treated is taken to a confined space or treated in appropriate facilities.

Gels

A gel is a material made from cross-linked polymers in the form of a network, hydrophilic in nature, i.e. it has the capacity to absorb liquids. They can be classified into two types, depending on the nature of the junctions of the three-dimensional network that constitute them.

1. Chemical gels: These are those in which the network is formed through covalent bonds. This type of bond is very strong and its rupture leads to the degradation of the gel.
2. Physical gels: They present a three-dimensional network formed by bonds that are not completely stable. Generally, the bonds are of the Van der Waals type, much weaker than covalent bonds.

The objective of this chapter is to calculate the maximum amount of hydrocarbon absorption by means of a polymeric material (carboxymethylcellulose gel) for the remediation of a contaminated soil due to the explosion of PEMEX's Terra 123 well, performing several analyses (maximum swelling percentage, amount of hydrocarbon removed, pH, conductivity, etc.), where the results will constitute a basis for the remediation of hydrocarbon-contaminated soils.

In addition, it will contribute to and, if necessary, solve different national problems identified by the National Council of Science and Technology (CONACYT), among the areas related to PRONACES that affect the social welfare, sustainability and economic and cultural development of Mexico, among which the following stand out:

1. Social-ecological systems and sustainability.
2. Toxic agents and polluting processes.
3. Risk and disaster prevention
4. Sustainable cities
5. Sustainable, safe, culturally and environmentally relevant housing

2 Methodology

Sampling área

The sampling area was in the town of Oxiacaque in the municipality of Nacajuca, Tabasco in the facilities of the Terra 123 well of Petróleos Mexicanos (PEMEX), where an explosion occurred in one of the pipelines, affecting 120 by 160 m^2 of industrial land, as well as surrounding areas (agricultural land) as a result of the spill of crude oil (PROFEPA, 2015).

Soil sampling

Samples were taken in accordance with the guidelines of the NOM-021-SEMARNAT-2000 standard "Establishing specifications for fertility, salinity and soil classification, study, sampling and analysis", selecting two points. Samples were taken with a shovel at a depth of 50 cm and placed in transparent plastic bags for transport to the laboratory. The samples were dried in the sun for 12 hours, after which time they were crushed using a mortar with a pestle to reduce the particle diameter of the sample and then sieved to obtain uniform particles of approximately 2 mm in diameter, in order to carry out the pertinent analyses.

Moisture determination

For moisture content determination, 2 g of sieved soil was placed in an aluminum container and placed in the Labrem Thermobalaza for 10 minutes for analysis.

Determination of the amount of hydrocarbons

Two g of dry and sieved contaminated soil were weighed and placed in a 100 ml volumetric flask, this was done in triplicate and the flasks were placed inside an extraction hood, then 25 ml of ethylene tetrachloride was added and the flasks were volumetrized with distilled water, finally they were left to stand for a period of 48 hours. After this time, the substrates were filtered using a cone-shaped Whatman filter over a beaker to obtain the samples and were analyzed five times to obtain absorbance records and calculate the hydrocarbon content present in the contaminated soil with the INFRACAL equipment using the EPA method (Infrared Spectrometry).

Determination of the amount of fats (Soxhlet)

This analysis was carried out according to the standard, using a 250 ml flat bottom flask and 90 ml of hexane was added. A homogeneous mixture of 10 g of sieved contaminated soil sample and 10 g of sodium sulfate was introduced into the cellulose capsule and placed in the cornet of the Soxhlet equipment. Subsequently, the Soxhlet equipment was correctly installed and a temperature of 75°C was set for a period of 8 hours, until the sample performed 6 cycles. At the end of the process, the flask was removed and placed in an oven at 60°C for 45 min to remove the remaining steam, after which time it was placed in a desiccator until a constant weight was obtained.

Synthesis of carboxymethyl cellulose (CMC) gel:

In a glass batch reactor with a capacity of 500 ml, 10 g of CMC and distilled water were added until obtaining a 5% solution in weight and it was stirred for a period of 1 hour with constant agitation at 80°C in an electric grill with agitation and controlled temperature, once the solution was diluted, 4 ml of glutaraldehyde was added as crosslinking agent and 4 ml of hydrochloric acid as catalyst, and it was maintained in constant agitation at 80°C during a reaction time of 2 h. After that time, the mixture was placed in molds and dried in an oven maintaining a slow drying at a temperature of 60°C for 48 h, to obtain the CMC gel film. Finally, the films were removed from the molds for use in the remediation treatment of hydrocarbon-contaminated soils.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is a technique that works with a small sample that is placed in an infrared cell, where it is subjected to an infrared light source,which scans from wavelengths of 4000 cm^{-1} to 600 $cm^{-1.}$

The intensity of the light transmitted through the sample is measured at each wavenumber, which allows the amount of light absorbed by the sample to be calculated by the difference between the intensity of the light before and after passing through the sample cell.

This analysis was performed on the carboxymethyl cellulose gel film to determine the characteristic functional groups of the polymer before and after exposure to the contaminated soil, in order to observe if there are significant changes in the structure of the polymeric material.

Scanning electron microscopy (SEM)

Scanning electron microscopy is a technique based on the principle of optical microscopy in which the light beam is replaced by an electron beam used for the visualization and analysis of the characteristics of high-resolution solid samples. It works by scanning a beam of electrons over the sample, the sample is coated with a very thin layer of gold or carbon, which gives it conductive properties.

This analysis was performed on the carboxymethyl cellulose gel film to determine the morphological surface of the polymer before and after being exposed to the contaminated soil, in order to observe if there are significant changes in the morphology of the polymeric material.

3 Results

Moisture determination

Two sampling points (samples 1 and 2) of the hydrocarbon contaminated soil were selected and the percent moisture content was determined with the data provided by the Labrem thermobalance. Table 7.2 presents the results before and after drying, according to ASTM D-2216, moisture content determination shall be performed as soon as possible after sampling, especially if corrodible containers (such as thin-walled steel tubes, paint cans, etc.) or plastic bags are used.

Table 7.2 Moisture content of oil-contaminated soil

Sample	Maximum particle size	Initial weight (g)	Final weight (g)	% humidity
1	2 mm	350	20	5.7
2	2 mm	350	21	6.0

Source: Own Elaboration

Determination of hydrocarbons

A soil analysis was performed prior to treatment in order to determine the amount of hydrocarbons contained in samples 1 and 2, as shown in Table 7.3 To obtain a valid result, the samples were run in the INFRACAL equipment five times, and an average was obtained, this being the actual amount of hydrocarbons in mg/l.

Table 7.3 Hydrocarbon content of contaminated soil

Sample	Test 1	Test 2	Test 3	Test 4	Test 5	Average	Co (mg/l)	MCo (mg/kg)
1	0.1	0.1	0	0	0	0.04	0.0792	0.99
2	8.1	8.1	8.5	8.2	8.2	8.22	16.498	206.225

Source: Own Elaboration

In this analysis, two standard equations were used, equation 1 refers to the conversion of the milliliters of Tetrachloroethylene obtained by running the samples in units of mg/l of hydrocarbons, and equation 2 is the conversion of mg/l to mg/kg of soil.

$$Co = \frac{(1.9807\ x\ abs)}{[1-(0.0016\ x\ abs)]} \qquad (1)$$

Where:
Co = level of concentration in mg/l
1.9807 = value given by the standard
abs = absorbance obtained from the equipment INFRACAL

$$MCo = \left({}^{1}/_{1000}\right)\left({}^{25}/_{g\ de\ suelo}\right)(1000) \qquad (2)$$

Where:
MCo = level of concentration in mg/kg

Fat extraction

The determination of fats was performed by the Soxhlet method and consisted of the differences in weights between the flask before and after analysis by bringing them to constant weight using equation 3 provided by the standard.

$$MED = \left[\frac{(Pf-Pi)}{kg\ base\ húmeda}\right] x\ 100 \qquad (3)$$

Where:
MED = amount of fat in percent (%)
Pf = peso final
Pi = Peso inicial
kg wet basis = amount of sample analyzed

The results of the analysis are shown in Table 7.3 for the initial and final weights of samples 1 and 2.

Table 7.3 Amount of grease in soil contaminated with oil

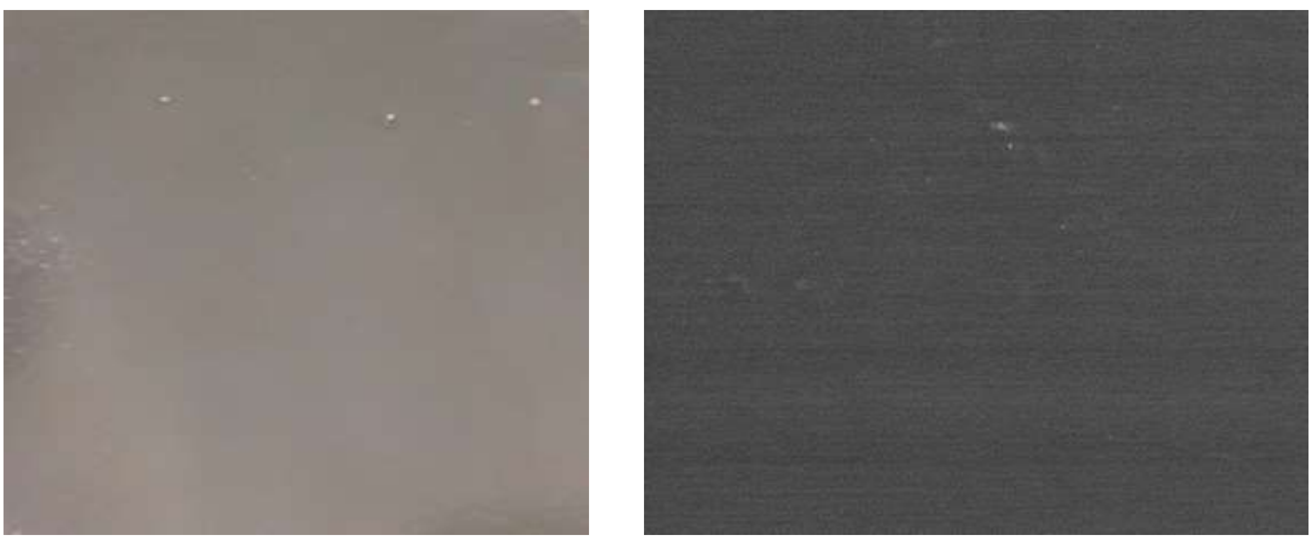
Sample	Initial weight (g)	Final weight (g)	Amount of fat (%)
1	103.51	106.20	26.9
2	104.18	112.22	80.4

Source: Own Elaboration

Once the hydrocarbon contaminated soil was analyzed, the CMC gel was incorporated for a period of three months, after which the film was removed and the soil was analyzed again using the INFRACAL equipment in order to determine the amount of hydrocarbons absorbed by the CMC gel, the fat content was also determined using the Soxhlet method and the percentage of moisture. The results obtained after removing the CMC gel film in the soil contaminated with hydrocarbon from Terra 123 well did not show a decrease in the readings obtained, due to the fact that the exposure time was not adequate to decrease the amount of hydrocarbon present in the soil. Therefore, a study would have to be done extending the exposure time to 4, 6 and 9 months to determine the adequate time for the decrease of hydrocarbon in a contaminated soil.

Figure 7.3 shows the CMC gel film before being incorporated into the soil contaminated with hydrocarbon showing a clear tone, with smooth surface and little flexibility to the touch and also shows the SEM analysis of the CMC gel film after being removed from the contaminated soil presenting a homogeneous, smooth surface and without significant change in its pores, so we can deduce that the exposure time was not adequate.

Figure 7.3 CMC gel film (a) before exposure and (b) after exposure to hydrocarbon contaminated soil



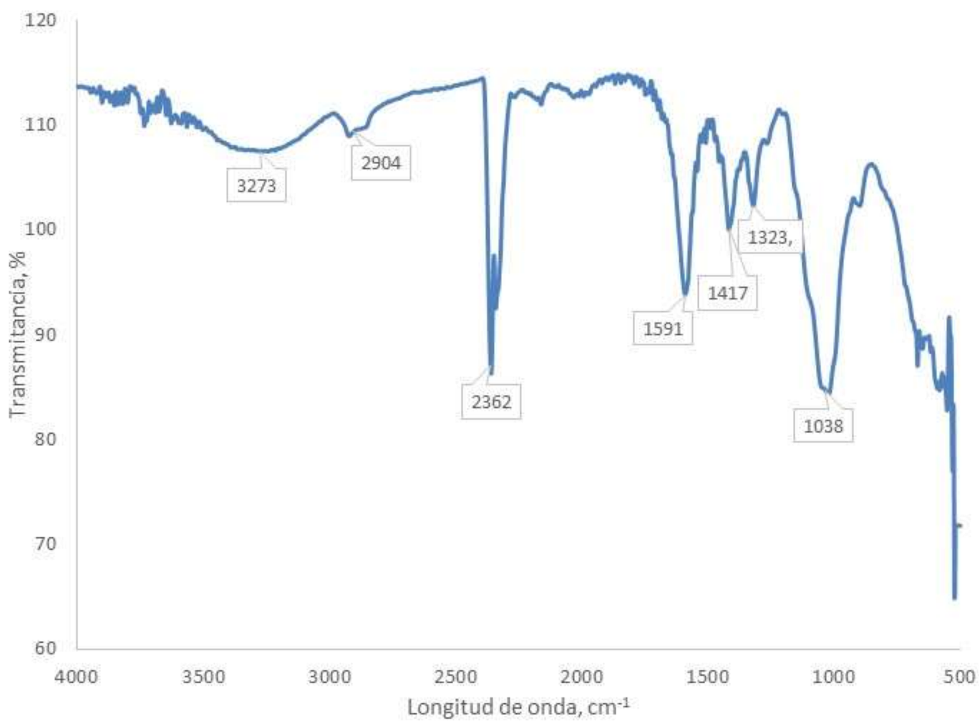
(a) (b)

Source: Own Elaboration

Figure 7.4 the FTIR spectrum of the synthesized carboxymethyl cellulose gel is observed, where the characteristic functional groups of the material can be appreciated and at the wavelength of 3276 cm-1 a wide and pronounced band is observed due to the -OH group characteristic in the CMC structure, at 2362 cm^{-1} a signal appears characteristic of the CO_2 present in the environment at the moment of the equipment calibration, at 1591 cm^{-1} a stretching of the carbonyl group is shown and in the band of 1417 cm^{-1} it is attributed to the carboxyl group.

On the other hand, at 1323 cm^{-1} a bending of the $-CH_2-$ group is observed and in the 1038 cm^{-1} region it is due to the C-C bond. The results agree with those reported by Antonio *et al*. in 2008, where the identification of the different functional groups characteristic of hydrogels was carried out and the wavelengths of the FTIR spectrum of the gel synthesized in this research work are very similar. It is worth mentioning that after 600 cm^{-1} wavelength there is a decrease in the spectrum, due to noise interference in the equipment, which often happens in some cases to voltage variation. However, it does not affect the analysis of the main groups of the CMC gel.

Figure 7.4 FTIR spectrum of the carboxymethylcellulose gel



Source: Own Elaboration

Conclusions

The purpose of this chapter was to prove that a carboxymethyl cellulose gel can be employed as a remediation method in a hydrocarbon contaminated soil and that it allows the recovery of the soil for further use. According to the results, it can be concluded that the synthesized CMC gel did not reduce the amount of hydrocarbon found in the contaminated soil during the exposure period, because the moisture analysis, fat determination and hydrocarbon content did not decrease during the exposure period. Therefore, it is recommended to increase the exposure period of the CMC gel in the hydrocarbon contaminated soil.

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