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# Use of the governor (*Larrea tridentata*), as a surfactant in the treatment of soils contaminated with hydrocarbons

# Utilización de la gobernadora (*Larrea tridentata*), como tensioactivo en el tratamiento de suelos contaminados con hidrocarburos

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**Abstract**

In Mexico, the oil industry has been one of the mainstays of the economy, but it has had a negative impact on the environment since pipeline breakage and the dispersion of chronic spills have been detected. Likewise to clandestine taps, which have affected large areas. Phytoremediation has emerged as a cost-effective technology for contaminant removal. Some plant species have shown remarkable resistance to polluted environments. This ability is believed to be due to the evolution of chemical functional groups that inhibit toxicological effects. Therefore, plants growing in contaminated areas can be a good source of natural biological compounds that have potential for contaminant remediation. Such is the case of Larrea tridentata. In the present project, its surfactant effect is compared to decontaminate the soil of oil and its derivatives; with the following findings: The extract of Larrea tridentata obtained from the leaf turned out to have a better surfactant effect than that obtained from the stem. The leaf extract at a temperature of 50°C, turned out to have a better surfactant effect than the extract obtained at 21°C. Comparing the removal percentage, the Larrea tridentata extract is less effective with a removal percentage of 62%, compared to: humic acids 74%, fulvic acids 77%, lechuguilla extract obtained at 50°C, 79%, lechuguilla extract obtained at room temperature 90%.

**Phytoremediation, Surfactant, *Larrea tridentata***

**Resumen**

En México, la industria petrolera ha sido uno de los sustentos de la economía, pero ha tenido un impacto negativo para el ambiente ya que se han detectado rotura de oleoductos, la dispersión de los derrames crónicos. Así mismo a tomas clandestinas, que han afectado grandes extensiones. La fitorremediación ha aparecido como una tecnología rentable para la remoción de contaminantes. Algunas especies de plantas han mostrado una notable resistencia a ambientes contaminados. Se cree que esta capacidad se debe a la evolución de grupos funcionales químicos que inhiben los efectos toxicológicos. Por lo tanto, las plantas que crecen en áreas contaminadas pueden ser una buena fuente de compuestos biológicos naturales que tienen potencial para la remediación de contaminantes. Tal es el caso de *Larrea tridentata*. En el presente proyecto se compara su efecto surfactante para descontaminar el suelo de petróleo y sus derivados; con los siguientes hallazgos: El extracto de *Larrea tridentata* obtenido de la hoja resultó tener mejor efecto surfactante que el obtenido del tallo. El extracto de la hoja a temperatura de 50°C, resultó tener mejor efecto surfactante que el extracto obtenido a 21°C. Comparando el porcentaje de remoción el extracto de *Larrea tridentata* es menos efectivo con un porcentaje de remoción del 62%, comparado con: ácidos húmicos 74%, fúlvicos 77%, extracto de lechuguilla obtenido a 50°C ,79%, extracto de lechuguilla obtenido a temperatura ambiente 90%.

**Fitorremdiación, Surfactante, *Larrea tridentata***

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## Introduction

Undoubtedly, one of the great challenges for humanity is to convert production processes into clean and energy efficient processes. Environmental pollution caused by oil and petrochemical products (complex mixtures of hydrocarbons) is recognized as one of the most serious problems today, especially when associated with large-scale accidental spills (Plohl K, and Leskovsek H., 2002).

In Mexico, the oil industry has considerably increased its infrastructure in the last three decades (García et al., 2006), it has had a negative impact on the environment, due to its extensive exploitation, since it has been for several years one of the mainstays of the economy, the activities are oriented to the exploration, exploitation, storage and transportation of hydrocarbons. The sources of contamination of the soils by oil are due to the rupture of oil pipelines, the dispersion of chronic spills, the spills of sewage coming from the refining processes, spills of drilling mud and maintenance work of the wells ( Riveroll-Larios et al., 2015). Also to clandestine intakes, which have affected large areas of land, mainly for agricultural use (Pérez *et al*., 2006).

Oil is a mixture of paraffinic, cycloparaffinic, aromatic hydrocarbons and low amounts of sulfur, nitrogen and oxygen compounds (Ortiz-Salinas et al. 2021), as well as metals such as V, Ni, Pb and Fe. (Figueruelo and Dávila 2001, Owamah 2013), its effects on the soil depend on the components of the ecosystem, the physical and chemical properties of the oil hydrocarbons and the type of environmental emergency (García-López *et al*., 2006, Pinkus-Rendón and Contreras-Sánchez 2012).

Given the problem of contamination by oil and its derivatives in the soils of Mexico, alternatives have been sought to solve this situation. There are remediation technologies, physical and chemical, that may be more practical and effective, from the point of view of times, which are shorter, to remediate contaminated sites. In recent years, bioremediation and phytoremediation technologies are being applied in soils affected by oil and its derivatives (Fiorenza *et al*., 2000).

Remediation is the set of corrective operations aimed at avoiding the harmful effects that a contaminated soil causes or may cause. The choice of remediation technology should be based on the results of previous environmental studies conducted on site sampling. Remediation can be *on-site;* elimination of pollutants on the ground itself, without removal from it, and *ex situ*; the soil is transferred to other facilities for its treatment or confinement (Jiménez, 2017).

Bioremediation has emerged as an inexpensive solution (Atlas, 1995). More recently, phytoremediation has emerged as a cost-effective technology for the removal of metals from contaminated areas. Some plant species have shown remarkable resistance to contaminated environments (Delgadillo-López et al. 2011). This ability to grow in highly contaminated areas is believed to be due to the evolution of chemical functional groups that inhibit toxicological effects (Lue-Kim and Rauser, 1986). Therefore, plants growing in contaminated areas can be a good source of natural biological compounds that have potential for remediation of contaminants.

Another relevant factor intervenes in the biodegradation of oil: the availability of hydrocarbons for the microorganism, since some compounds have low solubility in water, which makes their transport difficult within the microorganism. This aspect is very relevant since oil and its derivatives are insoluble in water.

Considering that bioremediation has been favored with the presence of surfactants and / or biosurfactants, where bioavailability has been considered as one of the most beneficial factors for bioremediation and possible inhibition and / or toxicity as the adverse factors to consider, This project focuses on the analysis of the effectiveness of extracts of *Larrea tridentata* (governor) as a surfactant agent for the effective extraction of hydrocarbons from soils contaminated with hydrocarbons.

## Hypothesis

The use of the flat *Larrea tridentata* as a surfactant agent could help the extraction of hydrocarbons present in contaminated soils.

## Objectives

### General

To evaluate the effect of the extract of the *Larrea tridentata plant* as a surfactant agent for the extraction of hydrocarbons present in soils contaminated with hydrocarbons.

### Specific

1. Obtain soil from the surroundings of the Miguel Hidalgo Refinery and determine its fat and oil content.

2. Obtain governor extract by hot and cold method (room temperature 20 ° C) and hot (50 ° C).

3. Wash the soil contaminated with hydrocarbons.

4. Monitor the effectiveness of the removal by comparing the fat and oil content, before and after washing.

5. Monitor the effectiveness of the removal by measuring the Chemical Oxygen Demand (COD) of the solutions of the biosurfactant used in the washing of each of the soil samples.

6. Analyze advantages and disadvantages of the governor, as a surfactant agent.

## Theoretical framework

In accordance with NOM-138-SEMARNAT / SSA1-2012, below, we review the following definitions:

Unconsolidated

**Soil**: material composed of inorganic particles, organic matter, water, air and organisms, which comprises from the upper layer of the earth's surface to different levels of depth.

**Soil contaminated with hydrocarbons**: The one in which the hydrocarbons included in table 1 are present, in a concentration greater than the maximum permissible limits established in tables 2 and 3.

**Hydrocarbons**: Organic chemical compounds, consisting mainly of carbon atoms and hydrogen.

**Light fraction hydrocarbons**: A mixture of hydrocarbons whose molecules contain between five and ten carbon atoms (C5 to C10).

**Middle fraction hydrocarbons**: A mixture of hydrocarbons whose molecules contain between ten and twenty-eight carbon atoms (C10 to C28).

**Heavy fraction hydrocarbons**: A mixture of hydrocarbons whose molecules contain between twenty-eight and forty carbon atoms (C28 to C40).

| POLLUTANT PRODUCT | HYDROCARBON | | | | |
|---|---|---|---|---|---|
| | FRACTION HEAVY | FRACTION MEDIA | HAP | FRACTION LIGHT | BTEX |
| Mixture of unknown products derived from oil | X | X | X | X | X |
| Crude oil | X | X | X | X | X |
| Fuel Oil | X | | X | | |
| Paraffins | X | | X | | |
| Petrolates | X | | X | | |
| Petroleum derived oils | X | | X | | |
| Diesel oil | | X | X | | |
| Diesel | | X | X | | |
| Jet fuel | | X | X | | |
| Kerosene | | X | X | | |
| Creosote | | X | X | | |
| Gasaplane | | | | X | X |
| Gas solvent | | | | X | X |
| Gasoline | | | | X | X |
| Naphtha gas | | | | X | X |

**Table 1** Hydrocarbons that must be analyzed according to the polluting product
*Source: NOM-138-SEMARNAT / SSA1-2012*

| FRACTION HYDROCARBON | PREDOMINANT SOIL USE (mg / kg DRY BASE) | | | ANALYTICAL METHOD |
|---|---|---|---|---|
| | Agricultural, forestry, livestock and conservation | Residential and recreational | Industrial and commercial | |
| **Light** | 200 | 200 | 500 | NMX-AA-105-SCFI-2008 |
| **Medium** | 1 200 | 1 200 | 5 000 | NMX-AA-145-SCFI-2008 |
| **Heavy** | 3 000 | 3 000 | 6 000 | NMX-AA-134-SCFI-2006 |

**Table 2** Limits Maximum allowable for fractions of hydrocarbons in soil. NOM-138-SEMARNAT / SSA1-2012PREDOMINANT

| HYDROCARBONS SPECIFIC | SOIL USE (mg / kg DRY BASE) | | | ANALYTICAL METHOD |
|---|---|---|---|---|
| | Agricultural, forestry, livestock and conservation | Residential and recreational | Industrial and commercial | |
| Benzene | 6 | 6 | 15 | NMX-AA-141-SCFI-2007 |
| Toluene | 40 | 40 | 100 | NMX-AA-141-SCFI-2007 |
| Ethylbenzene | 10 | 10 | 25 | NMX-AA-141-SCFI-2007 |
| Xylenes (sum of isomers) | 40 | 40 | 100 | NMX- AA-141-SCFI-2007 |
| Benzo [a] pyrene | 2 | 2 | 10 | NMX-AA-146-SCFI-2008 |
| Dibenzo [a, h] anthracene | 2 | 2 | 10 | NMX-AA-146-SCFI-2008 |
| Benzo [a] anthracene | 2 | 2 | 10 | NMX-AA-146-SCFI-2008 |
| Benzo [b] fluoranthene | 2 | 2 | 10 | NMX-AA-146-SCFI-2008 |
| Benzo [k] fluoranthene | 8 | 8 | 80 | NMX-AA-146-SCFI-2008 |
| Indene (1, 2, 3-cd) pyrene | 2 | 2 | 10 | NMX-AA-146-SCFI-2008 |

**Table 3** Maximum permissible limits for specific hydrocarbons in soil
*Source: NOM-138-SEMARNAT / SSA1-2012*

## HPA

Polycyclic aromatic hydrocarbons Polycyclic aromatic hydrocarbons can be classified as light (3-4 rings) or heavy (5 or more rings). Some of these compounds have proven carcinogenic properties, such as benzo-**α**-pyrene (WHO, 1993).

They come from the incomplete combustion of certain organic compounds, they are compounds of low solubility in water and also in the soil. Once in the sediment, PAHs can undergo UV photo-decomposition, being also totally or partially degraded by some microorganisms (Marín, 2003).

Surfactant agents are also known as surface active substances.

## Surfactant agents Surfactants

Are amphipathic molecules that accumulate at the interfaces, gas / liquid (air-water), liquid / liquid (oil-water) or liquid / solid (water / surface of solids), causing a decrease in surface tension. and interfacial of the medium. From certain concentrations these molecules tend to form aggregates such as micelles, bilayers and vesicles (Van Hamme et al., 2006). Surfactants have two clearly differentiated regions in their chemical structure, which gives them the dual character characteristic of all amphipathic substances (see figure 1).

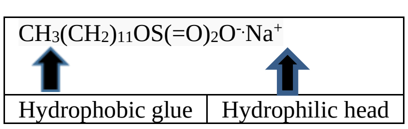


**Figure 1** Sodium dodecyl ester sulfate molecule
*Source: Own source*

One region is the hydrophilic fraction (polar head), which has a strong affinity for polar solvents, especially water, while the other hydrophobic fraction (apolar tail), has a higher affinity for organic or non-polar solvents (Burgos-Díaz et al., 2011). The hydrophobic part can be constituted by hydrocarbon chains, saturated hydrocarbon rings and aromatic rings, and the hydrophilic part by polar groups of different nature. Surfactants are available in many forms, and are generally classified depending on the charge on the polar head as anionic, non-ionic, cationic, and amphoteric (Pramauro and Pelizzetti, 1996; Rieger, 1997; Rosen, 2004).

## Classification *tensoac*Tive

Surfactants can be classified accordingtheir applications: soaps, detergents, dispersants, emulsifiers, foaming agents, bactericides, corrosion inhibitors, antistatic agents, etc .; or by the structures they form: membranes, microemulsions, liquid crystals, liposomes or gel. Many surfactants can be used in different applications, therefore, it is preferred to classify them according to the form of dissociation of their molecule in water (Salager, 2002). According to the type of dissociation of the hydrophilic group in the aqueous phase, these are classified as:

Anionic surfactants are those compounds that have a negative charge in their polar group. They are molecules with organic and inorganic cations ($Na^+$, $K^+$, $Ca^{2+}$, $Ba^{2+}$, $Mg^{2+}$, $NH_4^+$, etc.) and in their hydrophilic part they contain the anionic groups ($-COO^-$, $-SO_3$, -O-PO $^{2-}$, etc), attached to the organic fraction. They are important for use in the formulation of detergents for domestic and industrial use. Most anionic surfactants are alkyl carboxylates (better known as soaps), sulfonates (powdered detergents) and sulfates (foaming agents) (Salager and Fernández, 2004).

Cationic surfactants are those that have a positive charge on the polar group. Most are made up of quaternary ammonium salts or alkylamine salts, where the hydrophobic group is the long chain (8 to 25 carbon atoms) and the hydrophilic group is made up of the quaternary nitrogen.

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Due to the positively charged nitrogen, quaternary ammoniums have antistatic, softening and disinfectant properties, caused by the electrostatic adsorption of the surfactant on surfaces (fabrics, skin, hair ... usually with a negative surface charge) (García *et al.*, 2001; Esumi, 2001; García *et al.*, 2000; Esumi *et al.*, 1998).

**Amphoteric surfactants** are those that have anionic and cationic groups within the same molecule, such is the case of amino acids, betaines and phospholipids. Of the latter, the main representatives are lecithins, which constitute the majority of the structural elements of biological membranes. These surfactants are characterized by their behavior dependent on the pH of the medium (Uphues, 1998). At acidic pH they behave as cationic surfactants, at alkaline pH they behave as anionic and at the isoelectric point (more or less close to neutral pH) they behave as non-ionic. They are stable products in acid and alkaline systems, very important in cosmetics because they have good tolerance on the skin and in the formulation of alkaline cleaning products or as corrosion inhibitors.

**Non-ionic surfactants**

Nonionic surfactants do not ionize in aqueous solution, since they possess hydrophilic groups of the alcohol, phenol, ether or amide type. A high proportion of these surfactants are relatively hydrophilic thanks to the presence of a polyethylene oxide chain. Among these are Tween and Span (ethoxylated and non-ethoxylated sorbitan esters respectively), used in food and cosmetic applications due to their low toxicity (Roberts, 2000; Holmberg et al., 2002; Rosen, 2004).

**Properties and characteristics of surfactants**

The most interesting properties of synthetic surfactants and bio-surfactants are mainly associated with their amphipathic character, which gives them the ability to reduce the surface and interfacial tension of two phases, and form micro-emulsions of two immiscible compounds, where hydrophobic compounds can be solubilized in water or where water can be solubilized in hydrophobic compounds. As mentioned above, these characteristics give them properties such as excellent detergents, emulsifiers, foaming agents and dispersants that make surfactants one of the most used products in chemical processes (Desai and Banat, 1997).

In addition to these properties, four more parameters characterize surfactants: critical micellar concentration (CMC), emulsifying capacity, hydrophilic-hydrophobic balance (HLB) and liquid crystal formation.

a) Surface and interfacial activity

The intermolecular forces of any liquid cause a tension membrane to be generated on the surface that is difficult to break. This is due to the fact that within a liquid each molecule is subjected to attractive forces in all directions that on average are canceled. However, the molecules that are on the surface are only attracted inwards, forming a kind of film on the surface that allows light objects to float on it Mathematically, the work necessary to bring the molecules to the surface per unit area, N / m or J / m$^2$, is what is called the surface tension of a liquid and is represented by a Greek letter gamma or sigma (Desai and Banat, 1997; Rosen, 2004), and is expressed with the following formula :

$$\gamma rs = \_dW \quad (Nm - 1)$$

dA

b) Critical micellar concentration (CMC)

As the surfactant concentration increases, the number of surfactant monomers on the surface increases, decreasing the surface tension until reaching a critical value, called micelle concentration critical (CMC). At this concentration, the interface is sutured with surfactant and the molecules begin to aggregate to form structures such as micelles, bilayers, and vesicles. CMC is a characteristic parameter for each surfactant and is used to measure the efficiency of a surfactant (Jiménez Islas *et al.*, 2009).

c) Formation of aggregates

The aggregates formed by surfactants can be constituted by a single surfactant, a single aggregate, or by several surfactants, mixed aggregates. The morphology of surfactant aggregates depends, among other factors, on the chemical structure of the compound and the nature of the medium in which it is dissolved.

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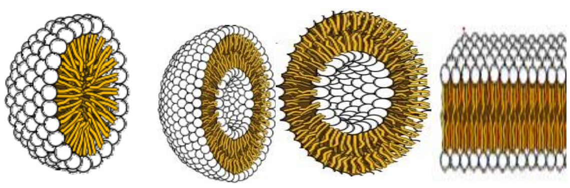
The formation of the aggregates occurs through non-covalent intermolecular interactions, such as hydrophobic interactions, hydrogen bonding, etc., producing in each case, the set of interactions that give rise to the most stable structure. In addition to the molecular structure of the surfactant and the polarity of the medium, there are other factors such as ionic strength, pH and the procedure used for the formation of the aggregate that decisively influence the type of aggregate formed (Morigaki *et al*., 2003). The most characteristic simple aggregate types formed by surfactants are spherical micelles, vesicles, bilayers and inverse micelles (see figure 2).



Micelle Reverse micelle vesicle
Bilayera

**Figure 2** Different types of simple aggregates formed by surfactants

The tendency of surfactants to adsorb at the interface of a system and to form molecular aggregates within the liquid from a certain concentration, It is also responsible for the series of classical properties of surfactants such as surface tension reduction, emulsification, foaming, detergency, wettability, etc.

d) Formation of lyotropic liquid crystals by surfactants

Lyotropic liquid crystals appear in a certain temperature and concentration range when certain amphiphilic substances, such as surfactants, are dispersed in water. As the surfactant concentration increases, the micelles clump together in an ordered structure and form a lyotropic liquid crystal. (Pasquali, 2006).

**Biotensoactivesactive**

In addition to the chemical compounds that possess surface-properties, there are compounds of biological origin that can also have this capacity, and which are called Biotensoactive (BT).

BTs are molecules that can be produced and secreted by different types of microorganisms and their interest has increased considerably in recent years due to their applications in industry and the environment (Nitschke *et al*., 2005 and Mukherjee *et al*., 2006). In addition, by presenting low toxicity, being biodegradable and having a better compatibility with the environment, they make them candidates to replace chemically synthesized surfactants.

Bio-surfactants (BT) are amphipathic molecules produced by a wide variety of microorganisms (bacteria, fungi and yeasts). These are classified into two groups, those of high molecular weight and low molecular weight. Low molecular weight BTs are generally glycolipids or lipopeptides and are more effective in lowering the surface and interfacial tension of the medium. High molecular weight BTs, polysaccharides, proteins, lipopolysaccharides and lipoproteins, are more effective in stabilizing oil-in-water emulsions (Pacwa-Plociniczak *et al*., 2011).

**Governor**

According to Jerzy Rzedowski (1987), the governor (Larrea tridentata) is the Mexican plant best adapted to arid conditions, since it can live in the most extreme conditions that occur in Mexico, without being a succulent plant, nor presenting spines, nor tomentum and also being evergreen.

*Larrea tridentata*, is ecologically dominant and widely distributed in the semi-arid regions of North America that extend from the southern United States to northern Mexico (Downum et al., 1988). In Mexico it is known as "governor", but also as a creosote bush, sonora, beef jerky, jarilla and smelly odor due to the peculiar smell it has, especially after a rain. It is an evergreen xerophytic evergreen shrub (Brinker, 1993). The major compounds in extracts of L. *tridentata* are numerous, in table 4 a summary of the most important is presented. Phenolic lignans stand out, followed by saponins, flavonoids, amino acids and minerals. The most important compound found in leaf and stem cells is nordihydroguaiaretic acid (NDGA), one of the best-known antioxidants (Seigler *et al*., 1974).

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| Dry weight percent | Type | Compound |
|---|---|---|
| 16-21 | Lignans Phenolic | acid Dihidroguaiarético Hemi-norisoguaiacin nordihydroguaiaretic acid Nordihidroguaiacin |
| 5 - 7.5 | Flavonoids | Apigenin Kaempferol |
| 10 to 15 | Saponins and Terpene | Larreagenin A Larréico Acid |
| 0.1 - 0.2 | Monoterpenes Volatile Hydrocarbons 35 | Alpha penene Delta-3-carene Limonene |
| | Aromatics | Benzaldheido Benzyl acetate Benzylbutane Methyl naphthalene |
| | Steroids | Beta-sitosterol Cholesterol Campesterol |
| | Tannins Carbohydrates | Glucose Sucrose |
| 70.1 (from stems) | Lipids | Alkyl esters (C46-C56) |
| 16.6 | Amino acids | Phenylalanine, Isoleucine, Glutamic acid,Aspartic acid Glycineand GlycineGlycine |
| 15.6 19.8 mg /19.8 / 100 mgmg / 100 mg /g | Vitamins | Carotenes Vitamin C |
| 13.7 | Minerals | Sodium, Potassium, Calcium, Magnesium, Iron, Sulfur and Phosphorus |

**Table 4** Main phytochemical constituents of *Larrea tridentata*
*Source: (Brinker, 1993)*

The nordihydroguaiaretic acid, also known as β, γ-Dimethyl-α, δ-bis (3,4-dihydroxyphenyl) butane; (see figure 3). There is a difference in the mean concentration of the NDGA, depending on the geographic area where the governor grew up; in the Chihuahuan desert they report 2.62%, while those of the Sonoran Desert contain 3.84% (Gisvold, 1948).

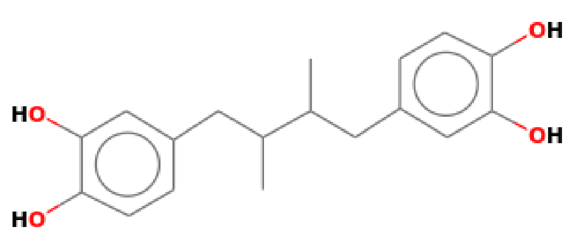


**Figure 3** β, γ-Dimethyl-α, δ-bis (3,4-dihydroxyphenyl) butane (Nordihydroguaiaretic acid) NDGA
*Source: Retrieved from https://webbook.nist.gov/cgi/cbook.cgi?ID=500-38-9*

Governor extracts have antioxidant, anti-inflammatory, cytotoxic, antimicrobial and enzyme inhibitor properties (Mabry *et al*., 1977; Fernández, 1979; Brinker, 1993).

The combined effect of these constituents is synergistic, which means that better results are obtained from an extract containing leaves and branches than from the use of purified NDGA.

Experiments have shown that the biomass of the governor can adsorb ions Cu (II), Ni (II), Cd (II), Pb (II), Zn (II), Cr (III) and Cr (VI), from solutions watery. When the heavy metal tolerant plant was compared with plants grown in uncontaminated areas, the uncontaminated plant showed a higher copper binding capacity. The difference in absorption is due to the occupation of the chemical binding sites by previously absorbed ions (Gardea, 1998).

Different applications derived from its chemical content have been described; some of its uses are described in Table 5.

| Species | Uses |
|---|---|
| **Gobernadora *Larrea tridentata*** | Forajero: the branches and leaves of the governor contain large amounts of proteins and other nutrients, which indicates that the plant could serve as livestock feed once the resins it contains are extracted. |
| | Food: its main component is norhydroguaiaretic acid (NDGA), which acts as a powerful antioxidant, which is why it is used in the food industry. |
| | Industry: to reduce saline incrustations in boilers and containers; for the preparation of phenolic type polymers and organic fungicides and insecticides. The resins are used to manufacture footwear greases. Glue (from sheets) for plywood and compressed cardboard. |
| | Cosmetics: Manufacture of soaps |
| | Medicine: used for urinary tract conditions such as kidney stones; kidney pain and bladder inflammation. In gynecological problems such as female sterility; for postpartum and to regularize menstruation; as an infusion in baths for hemorrhoids, fever, malaria, pimples, bumps; promote healing and cure rheumatism; as a remedy for rheumatism, gallstones and kidney stones, dermatitis, hepatitis, measles, erysipelas and as an antiseptic. Properties and actions against gastric discomfort, venereal diseases and tuberculosis are attributed to it. It is used to treat mycosis. It has anti-amoebic |
| | insecticidal and fungicidal activity: the resins of the governor plant show antifungal activity against *Rhizoctonia solana*, *Fusarium oxysporum*, *Pythium spp*. and other phytopathogenic fungi. The insecticidal activity is used against the brown bean weevil (*Acanthoscelides obtectus*, Coleóptera: *Bruchidae*); major grain borer (*Prostephanus truncatus*, Coleoptera: *Bostrichidae*) |

**Table 5** Uses of *Larrea tridentata*
*Source: Own elaboration based on a review of the literature*

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**Materials and Methods**

The focus of the study is quantitative descriptive experimental since it seeks to analyze the effectiveness of the flat *Larrea tridentata* as a surfactant agent

**Origin and taking the soil**

The samples were taken from soils contaminated with hydrocarbons in the surroundings of the Miguel Refinery Hidalgo, which were conserved in sterile amber jars and processed within 24 h of their collection / kept in refrigeration.

**Obtaining the governor (*Larrea tridentata*)**

Theplant *Larrea Tridentata* was obtained from the Progreso de Obregón municipality, Hidalgo.

**Theoretical Methods**

The methods used were those described in the Official Mexican Standards: Determination of pH in water (NMX-AA-008-SCFI-2011), and for COD the EPA 5220 D method; APHA, 1989. NMX-AA-005-SCFI-2013-Analysis of water - measurement of fats and oils

**Obtaining hot and cold extract of the governor (*Larrea Tridentata*), extraction of humic and fulvic acids and washing of soil contaminated with hydrocarbons**

In this stage the following materials were used: 250ml Pyrex brand graduated cylinder, perilla, 500ml beakers (Kimax), Potentiometer, Conductimeter, heaters with stirring, magnets, Refrigerants and the following procedures were followed:

Cold extraction and hot stem and leaf separately.

**Cold extract**

It is obtained separately and 220 grams of leaves and stems are placed in mortars. It is ground in a blender adding 240 ml of de-ionized water, it was passed through a sieve to eliminate solid residues (see figure 4A and B).

**Hot extraction**

In the flat-bottomed ball flask add 250gr of the governor (stems and leaves separately), and 240 ml of de-ionized water. It is placed in a closed reflux system for 2 hours. The extract is passed through a sieve to remove residues (see Figure 4C).

**Soil washing**:

4 washes were carried out in triplicate:

**Washing with extract *Larrea tridentata*, obtained by method at room temperature (cold method) and hot**

Sift the contaminated soil with a sieve number 18 and 10, We weigh 10 grams of the sample for each beaker, using the extracts obtained in a 5: 1 ratio (extract / soil), it is subjected to agitation for a period of 2 hours. The hydrocarbon-free washed soil and the contaminated residual solution are filtered and recovered separately (see figure 1), they are labeled for determination of fats and oils and Chemical Oxygen Demand (COD). These determinations are made on the soil samples before and after washing. Likewise, a triplicate series was used in each case of a wash blank with uncontaminated soil and a reagent blank with deionized water. (See figure 4D).

**Determination of fats and oils in the soil; before and after washing**

Bring the balloon flask to constant weight. Weigh the sample and place it in the cartridge, Install the Soxhlet, add 185ml of hexane, perform the extraction for 4 hours, once completed, recover the hexane by distillation, let it cool in a desiccator and obtain the amount of fats and oils by difference. weight (see figure 5A).

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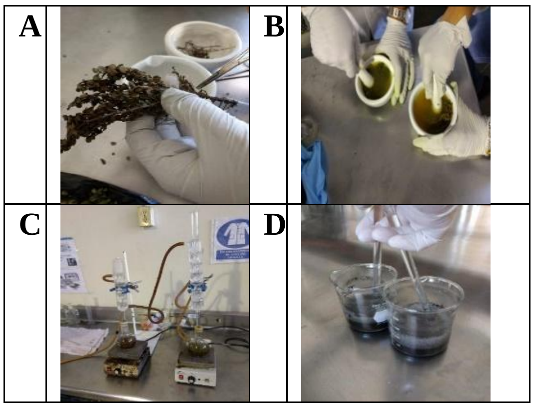



**Figure 4** Obtaining extracts of *Larrea tridentata* and washing the soil contaminated with hydrocarbons A. Separation of stems and leaves of *Larrea tridentata* (governor), B. Obtaining the cold extract. C. Obtaining the extract in hot. D. Washing of soils contaminated with hydrocarbons

### COD determination

Glass tubes with a Teflon stopper were used, to which 2.5ml of sample, 1.5ml of digester solution (10.216g of $K_2Cr_2O_7$ + 33.3 $HgSO_4$ and 167ml of$H_2SO_4$) and 3.5ml of sulfuric acid solution ( 10.142g of $Ag_2SO_4$ of $H_2SO_4$), once the samples are prepared, they are digested within a heating block at 150 ° C for 2 hours. Subsequently, allow the samples to cool to room temperature and read the absorbance at 600nm. (EPA 5220 D; APHA, 1989) (see figure 5B).

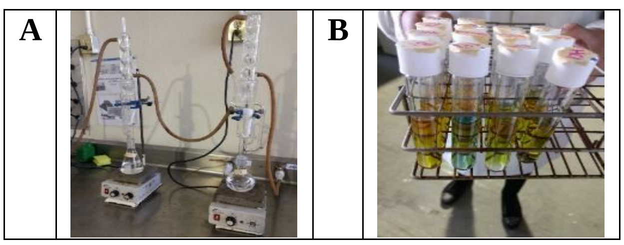
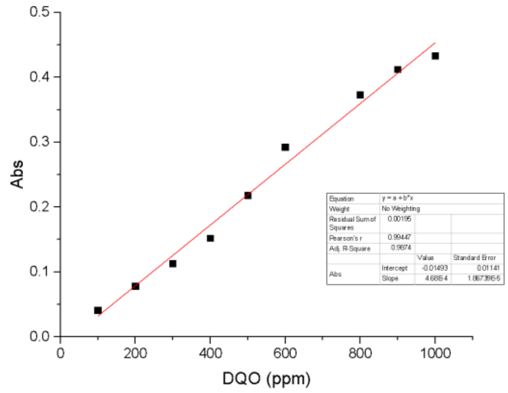



**Figure 5** Determination of fats (A) and oils and COD (B)

## Results

### CODofextracts *Larrea tridentata* before and after washing soil contaminated with hydrocarbons

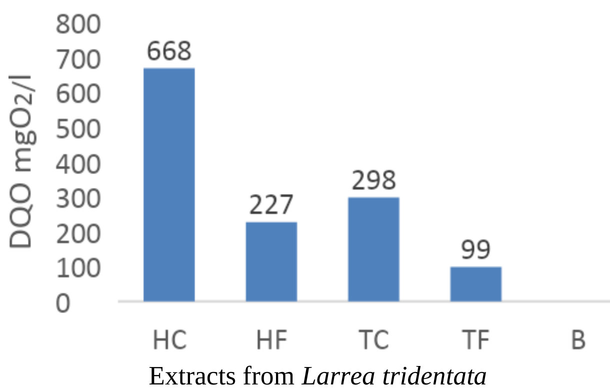
The COD values are obtained from a calibration curve made with potassium biphthalate (0-681mg / l, equivalent to 0-800 mgO2 / l). (See Graph 1).




**Graphic 1** Calibration Curve for COD
*Source: Own elaboration*

From the graph, the formula to determine the COD of the studied samples was defined.

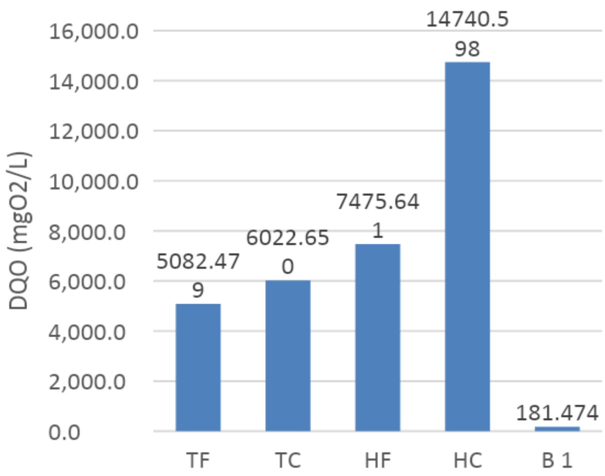
The COD values of the leaf and stem extracts, obtained separately through processes at 21 ° C and 50 ° C, are shown in graph 2, in which we can see that the extract of the Governor Leaf, obtained in hot has a higher content of organic matter, this is explained, since, according to literature, the leaf has numerous lignans, saponins, terpene and flavonoids present in its resinous exudates, among others, one of the most abundant acid nordihydroguaiaretic. The cold extract presents a lower quantity in both cases: stem and leaf extract.




**Graphic 2** COD of the governor extracts before washing

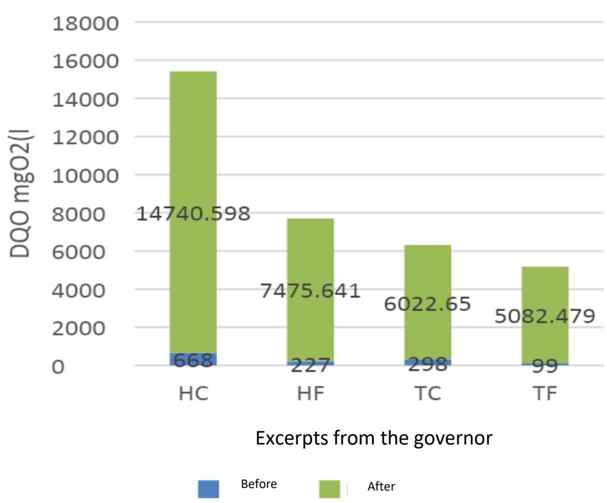
Once the soil was washed with the different extracts: TF has a COD of 5082,478 mgO2 / l, TC of 6022,650 mgO2 / l. HF of 7475,641 mgO2 / l, and HC of 14740,598 mgO2 / l (see graph 3), although the 4 extracts tested removed organic matter from the soil, there is a greater removal in the case of soil washed with the HC extract, every time that a greater amount of organic matter passed into the aqueous extract.

In this case, a sample of soil from the gardens of the Tula-Tepeji University was used for the blank, which was washed with distilled water, said sample contained 181,474mg$O_2$/ l, this may be due to herbicides that are used in garden areas or contaminated irrigation water, (see graphic 3).




**Graphic 3** COD after soil washing with extracts from different parts of the plant, cold stem (TF), hot stem (TC), cold leaf (HC) and White (B1)

We can see that with the HC extract, 14,072,598 mgOwere removed$_2$/ l of oxidizable matterfrom the contaminated soil (see graph 4).




**Graphic 4** COD before and after soil washing with extracts from different parts of the plant, cold stem (TF), hot stem (TC), cold leaf (HC) and White (B1)

## Fat and oil content in the contaminated soil, before and after washing with the extracts

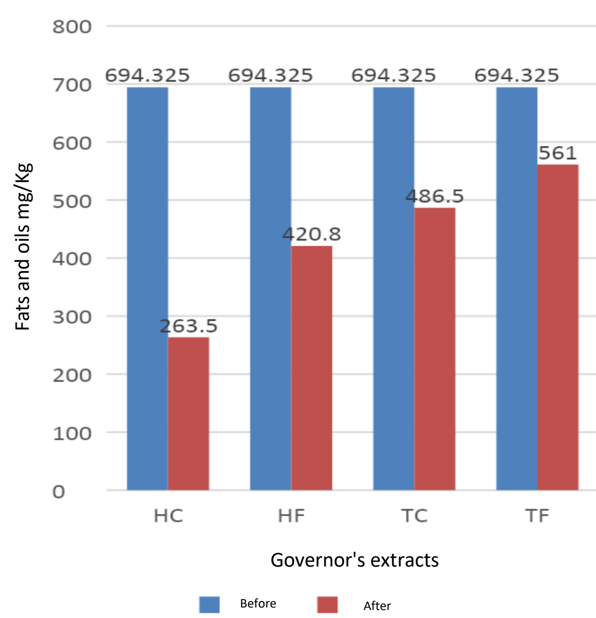
Once the soil was washed, fats and oils were determined, finding a lower amount in the soil washed with HC extract (see graph 5).

The soil initially had a fat and oil content of 694,325 mg / Kg, when it was washed, this amount decreased. With CH at 263.5 mg / Kg, HF at 420.8 mg / Kg, TC at 486.5 mg / Kg, and with TF at 561.0 mg / Kg. There was a greater removal of fats and oils in the case of the governor leaf extract obtained in hot 50 ° C. (see graphic 5).

Returning to the data from Reséndiz-Vega and García-Melo (2019), where 3 surfactant agents were tested: humic and fulvic acids and hot and cold extracts of lechuguilla (*Agave lechuguilla* Torrey), the following results were obtained:

Reséndiz-Vega and García-Melo, 2009… "in the case of soil washed with a humic acid solution from 694.7 g / Kg to 178g / Kg, in the case of soil washed with a solution of fulvic acids it dropped from 694.7 g / Kg to 155.5 g / Kg, in the case of the hot lettuce extract the decrease was from 694.7 g / Kg to 139.2g / Kg and in the case of washing with the lettuce extract obtained at room temperature (cold lettuce) the decrease was 694.7g / Kg to 65.6g / Kg"

The 4 biosurfactants are effective since a percentage of removal of: humic acids 74%, fulvic acids 77%, extract of lettuce obtained at 50 ° C 79%, extract of lettuce obtained at room temperature 90 % and the governor leaf extract obtained at 50 ° C 62%.




**Graphic 5** Fat remaining in the soil washed with the different extracts obtained from the governor Cold leaf (HF), hot leaf (HC), cold stem (TF) and hot stem (TC)

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## Conclusions

The extract of *Larrea tridentata* obtained from the leaf turned out to have a better surfactant effect than that obtained from the stem.

Theextract *Larrea tridentata* obtained from the leaf at a temperature of 50 ° C, turned out to have a better surfactant effect than the extract obtained at 21 °C.

Comparing the removal percentage, the extract of *Larrea tridentata* is less effective with a removal percentage of 62%, compared to: humic acids 74%, fulvic acids 77%, lechuguilla extract obtained at 50°C 79%, lechuguilla extract obtained at room temperature 90%.

The extract of *Agave lechuguilla* Torrey is the most effective and economical since it is obtained at room temperature.

The effectiveness of *Larrea tridentata*, as a surfactant agent varies, depending on the place from where it is collected, since, if it is a contaminated place, its effectiveness in bioremediation has been observed to decrease.

The effectiveness of *Agave lechuguilla* Torrey may be due to the fact that it contains saponins in higher concentration; if we compare it with the content of *Larrae tridentata*. *Agave lechuguilla* Torrey contains 9 saponins (smilagenin, yucagenin, gitogenin, hecogenin, tigogenin, diosgenin, gentrogenin, chlorogenin and ruizgenin), which have a surfactant effect. Hernández *et al*., (2005), extract was a better option for washing soils contaminated with hydrocarbons *Agave lechuguilla* Torrey, compared to the other biosurfactant agents tested.

Finally, it is necessary to treat the extracts contaminated with hydrocarbons, for which a system that encourages their biodegradation will be adapted.

## References

Atlas RM y Unterman, R. (1999). Bioremediation. In: Demain AL & Davies JE (Eds) Manual of Industrial Microbiology and Biotechnology 2nd ed (pp 666-681), ASM Press, Washington DC

A. y Marqués, AM (2011). Isolation and partial characterization of a biosurfactant mixture produced by *Sphingobacterium* sp. isolated from soil. *J Colloid Interface Sci* 361, 195-204

Bautista, FZ (1999). *Introducción al estudio de la contaminación del suelo por metales pesados. México: UADY, (Capítulo 1).*

Botello, AV, Von, JR, Gold-Bouchot, G., & Agraz, CH (2005). *Golfo de México: contaminación e impacto ambiental: diagnóstico y tendencias.* (2da ed.). México: Universidad Autónoma de Tabasco. (Capítulo 17).

Botkin, CW and Duisberg, PC 1949. The nordihidroguayeretic acid content of the creosotebush. Bul, 349, New Mexico State College. 15 p.

Brinker, F. 1993. *Larrea tridentata* (DC) Coville (Chaparral or Creosote Bush). British Journal of Phytotherapy 3:10- 30.

Burgos-Díaz, C., Pons, R., Espuny, MJ, Aranda, FJ, Teruel, JA, Manresa, A., Ortiz, Desai, JD y Banat, IM (1997). Microbial production of surfactants and their commercial potential. *Microbiol Mol Bio R* 61, 47-64

CCA (2014), La quema de residuos agrícolas: fuente de dioxinas, Comisión para la Cooperación Ambiental, Montreal, Canadá, 6 pp.

Coronado-Ortega y col., 2011. Hacia la sustentabilidad: Los residuos sólidos como fuente de energía y materia prima: 270-274.

Dávila G, Vázquez-Duhalt R. Enzimas lignolíticas fúngicas para fines ambientales. Mensaje Bioquímico. 2006; XXX: 29-55.

Delgadillo-López, Angélica Evelin, González-Ramírez, César Abelardo, Prieto-García, Francisco, Villagómez-Ibarra, José Roberto, & Acevedo-Sandoval, Otilio. (2011). Fitorremediación: una alternativa para eliminar la contaminación. *Tropical and subtropical agroecosystems,14*(2), 597-612. Recuperado en 30 de julio de 2021, de http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1870-04622011000200002&lng=es&tlng=es.

Delgadillo Ruíz, Lucía, Bañuelos Valenzuela, Rómulo, Delgadillo Ruíz, Olivia, Silva Vega, Mónica, & Gallegos Flores, Perla. (2017). Composición química y efecto antibacteriano in vitro de extractos de *Larrea tridentata*, origanum vulgare, artemisa ludoviciana y ruta graveolens. *Nova scientia*,*9*(19), 273-290.https://doi.org/10.21640/ns.v9i19.1019

Esumi, K. (2001). Adsorption and adsolubilization of surfactants on titanium dioxides with functional groups. *Colloids Surf Physicochem Eng Aspects* 176, 25-34.

Esumi, K., Toyoda, A., Goino, M., Suhara, T., Fukui, H. y Koide, Y. (1998). Adsorption Characteristics of Cationic Surfactants on Titanium Dioxide with Quaternary Ammonium Groups and Their Adsolubilization. *J Colloid Interface Sci* 202, 377-384.

Figueruelo EJ y Dávila MM (2001). Química física del me- dio ambiente. Ed. Reverté, México DF, México, 619 pp

Fiorenza, S., Oubre, CL, & Ward, CH (2000). *Phytoremediation of Hydrocarbon-Contaminated Soil.*United States: Lewis Publishers, (Chapter 2).

García-López, E., Zavala-Cruz, J. y Palma-López, DJ (2006). Caracterización de las comunidades vegetales en un área afectada por derrames de hidrocarburos.*Terra Latinoamericana*,*24*(1), 17-26

García, MT, Ribosa, I., Guindulain, T., Sánchez-Leal, J. y Vives-Rego, J. (2001). Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment. *Environ Pollut* 111, 169-175.

García, MT, Campos, E., Sanchez-Leal, J. y Ribosa, I. (2000). Anaerobic degradation and toxicity of commercial cationic surfactants in anaerobic screening tests. *Chemosphere* 41, 705-710

Gardea-Torresdey, JL; Hernandez, A.; Tiemann, KJ; Bibb, J.; and Rodriguez, O. (1998) "Adsorption of Toxic Metal Ions From Solution by Inactivated Cells of *Larrea tridentata* Creosote Bush,"Journal of Hazardous Substance Research: Vol. 1.https://doi.org/10.4148/1090-7025.1002

González García, Yolanda, González Reynoso, Orfil, Nungaray Arellano, Jesús. Potencial del bagazo de Agave tequilero para la producción de biopolímeros y carbohidrasas por bacterias celulolíticas y para la obtención de compuestos fenólicose-Gnosis [en linea] 2005,[Fecha de consulta: 10 de julio de 2021] Disponible en:<http://www.redalyc.org/articulo.oa?id=73000314> ISSN

Guerrero, (2002). *Curso de suelos. Centro de Gestión y Tecnología Ambiental*. UNALM-Perú.

Hernández S., Rosa, & Lugo C., Eugenia C., & Díaz J., Lourdes, & Villanueva, Socorro (2005). Extracción y cuantificación indirecta de las saponinasde agave lechuguilla Torrey. e-Gnosis, (3),0.[fecha de Consulta 30 de Julio de 2021]. ISSN:Disponible en: https://www.redalyc.org/articulo.oa?id=73000311

Holmberg, K., Jonsson, B., kronberg, BI y Lindman, B. (2002). Surfactants and polymeric in aquos solution. 2ª Ed wiley and Sons, New York.

Jiménez Islas, D., Medina Moreno, SA y Gracida Rodríguez, JN (2010). Propiedades, aplicaciones y producción de biotensoactivos. *Rev Int Contam Ambient* 26 (1), 65-84

Jiménez, RB (2017). *Introducción a la contaminación de suelos.* España: Mundi-Prensa, (Capítulo 26).

Lue-Kim H., Rause WE r, Partial Characterization of Cadmium-Binding Protein from Roots of Tomato ,Plant Physiology, Volume 81, Issue 3, July 1986, Pages 896–900,https://doi.org/10.1104/pp.81.3.896

Lira, RH (2003). Estado Actual del Conocimiento Sobre las Propiedades Biocidas de la Gobernadora [*Larrea tridentata* (DC) Coville]. *Revista Mexicana de Fitopatología, 21 (2), 214-222.*

Morigaki K., Walde P., Misran M. y Robinson BH (2003). Thermodynamic and kinetic stability. Properties of micelles and vesicles formed by the decanoic acid/decanoate system. *Colloids Surf A* 213, 37-44

Mukherjee, S., Das, P. y Sen, R. (2006). Towards commercial production of microbial surfactants. *Trends Biotechnol* 24, 509-515

National Institute of Standards and Technology (NIST). Libro del Web de Química del NIST. DOI:https://doi.org/10.18434/T4D303 https://webbook.nist.gov/

Nitschke, M., Costa, SG y Contiero, J. (2005). Rhamnolipid surfactants: an update on the general aspects of these remarkable biomolecules. *Biotechnol Prog* 21, 1593-1600.

Ortiz-Salinas R., Cram S. y Sommer I. (2012). Hidrocar- buros aromáticos policíclicos (HAPs) en suelos de la llanura aluvial baja del estado de Tabasco, México. Revista Universidad y Ciencia 28 (2), 131-144.

Owamah HI (2013). Heavy metals determination and assessment in a petroleum impacted driver in the niger delta región of Nigeria. J. Pet. Environ. Biotechnol. 4, 135-138. DOI: 10.4172/2157-7463.1000135

Pasquali, RC, Bregni, C. y Serrao, R. (2006). Características e identificación de los cristales líquidos liotrópicos. Revisión bibliográfica. Revista Mexicana de Ciencias Farmacéuticas 37 (2), 38-53

Peñuelas-Rubio, Ofelda, Arellano-Gil, Maritza, Verdugo-Fuentes, Abel Alberto, Chaparro-Encinas, Luis Abraham, Hernández-Rodríguez, Sharon Elena, Martínez-Carrillo, José Luis, & Vargas-Arispuro, Irasema del Carmen. (2017).

Peñuelas-Rubio, O., Arellano-Gil, M., Verdugo-Fuentes, A., Chaparro-Encinas, L., Hernández-Rodríguez, S., Martínez-Carrillo, J., & Vargas-Arispuro, I. (2017). Extractos de *Larrea tridentata* como una estrategia ecológica contra Fusarium oxysporum radicis-lycopersici en plantas de tomate bajo condiciones de invernadero.Revista Mexicana De FitopatologíA, Mexican Journal Of Phytopathology, 35(3). doi:http://dx.doi.org/10.18781/R.MEX.FIT.1703-3

Pérez, GC, Iturbe, RA, & Flores, RM (2006). Cambio en las propiedades físicas de un suelo contaminado con hidrocarburos debido a la aplicación de una tecnología de remediación. *Revista AIDIS de ingeniería y ciencias ambientales: investigación, desarrollo y práctica,* 1-10.

Pinkus-Rendón MJ y Contreras-Sáncez A. (2012). Impacto socioambiental de la industria petrolera en Tabasco: el caso de la Chontalapa. Revista LiminaR Estudios Sociales y Humanisticos 10 (2), 122-144.

Plohl, K. and Leskovsek, H. (2002) Biological Degradation of Motor Oil in Water. Acta Chimica Slovenica, 49, 279- 289

Pramauro, E. y Pelizzetti, E. (1996). Surfactants in Analytical Chemistry. Applications of Organized Amphiphilic Media, *Wilson and wilson's Comprehensive Analytical Chemestry* 31. SG Weber (Ed) Elsevier, Netherlands

RESENDIZ-VEGA, Marisol & GARCÍA-MELO, José Alberto. Effectiveness of Humic Acids, Fulvic Acids and lechuguilla extract (Agave lechuguilla), as biosurfactants in the Remediation of soils contaminated with Hydrocarbons. Journal of Environmental Sciences and Natural Resources. 2019, 5-16: 17-25

Rieger, MM, Rhein, EL y Dekker, M. (1997). Surfactants in Cosmetics. 2nd ed, Marcel Dekker, Nueva York.

Salager, JL (2002). Surfactantes tipos y usos, Cuaderno FIRP 300, Laboratorio FIRP, Universidad de los Andes. Mérida, Venezuela.

Riveroll-Larios J., Escalante-Espinosa E., Fócil-Monterru- bio RL y Díaz-Ramírez IJ (2015). Biological activ- ity asessment in mexican tropical soil with different hydrocarbon contamination histories. Water, Air, Soil Poll. 226 (10), 353-362.

Roberts, D. (2000). Aquatic toxicity—Are surfactant properties relevant. *J Surfactants Deterg* 3, 309-315

Rosen, MJ (2004). *Surfactants and Interfacial Phenomena*, 3rd ed. Edited by John Wiley and Sons, Inc., New York. pp. 1-10.

ISSN-On line: 2414-8830

Rzewdowski, Jerzy y Graciela Calderón de Rzedowski. 1988. Dos nuevas localidades de *Larrea tridentata*

Saldívar, Ricardo HL (2003). Estado actual del conocimiento sobre las propiedades biocidas de la gobernadora [*Larrea tridentata*(DC) Coville]. Revista Mexicana de Fitopatología, 21(2), 214-222.

Salager JL y Fernández A. (2004). Surfactantes-Parte 3. Aniónicos. Cuaderno FIRP S302PP, Laboratorio FIRP, Universidad de los Andes. Mérida, Venezuela.

Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT), 2012, Norma Oficial Mexicana que establece los límites máximos permisibles de hidrocarburos en suelos y las especificaciones para su caracterización y remediación (NOM-138-SEMARNAT/SS-2012). México, DF Diario Oficial de la Federación, 10 de septiembre de 2013, 21 Recuperado de http://www.dof.gob.mx/nota_detalle.php?codigo=5313544&fecha=10/09/2013

Subsecretaría de recursos naturales (junio, 2020), Especies Forestales Maderables y No Maderables Sujetas a Aprovechamiento,Sistema Integral de Información ambiental del Estado de Coahuila, http://www.sema.gob.mx/SRN-SIIAEC-SFE-USOS-ESPECIES-GOBERNADORA.php

Tejada, A. (2014). Hidrocarburos aromáticos policíclicos. *Revista de ciencias de la Universidad Pablo de Olavide*, 104, 86-88.

Uphues, G. (1998). Chemistry of amphoteric surfactants. *Lipid/Fett* 100, 490-497

Van Hamme, JD, Singh, A. y Ward, OP (2006). Physiological aspects. Part 1 in a series of papers devoted to surfactants in microbiology and biotechnology. *Biotechnol Adv* 24, 604-620

Velasco, JA, & Volke, TS (2002). *Tecnologías de remediación para suelos contaminados.* México: INE...