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Fitorremediación en Aguas y Suelos Contaminados con Hidrocarburos del Petróleo

ENVIRONMENTAL & SANITARY ENGINEERING

Phytoremediation of Water and Soils Contaminated by Petroleum Hydrocarbons

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Resumen

Durante décadas, la producción, transporte, almacenamiento y comercialización de hidrocarburos del petróleo y sus derivados, han dado origen a una problemática ambiental debida a los grandes vertimientos de combustibles que se generan. El potencial contaminante y la compleja composición de los hidrocarburos, además de su facilidad de movilización en el medio y acumulación en el agua o suelo, ha incrementado el interés científico para encontrar soluciones que reduzcan el efecto de estos compuestos en los ecosistemas. Ante esta situación, se ha evaluado la fitorremediación como una solución que por su costo-efectividad y aporte paisajístico pueden ser usados para biorremediar aguas y suelos mezclados con combustibles, minimizando el riesgo de contaminación. El presente artículo de revisión resume los principios relacionados con la fitorremediación de suelos y aguas contaminadas con hidrocarburos como una alternativa ecotecnológica que puede ser aplicada mediante la interacción de microorganismos, plantas y procesos físicos, químicos y biológicos que ocurren en los sistemas naturales como los humedales. También se discuten algunas experiencias en la temática, los factores que inciden y los mecanismos que dominan la remoción de estos compuestos orgánicos.

Palabras claves: *hidrocarburos, humedales construidos, mecanismos de fitorremediación.*

Abstract

The production, transport, storage, and commercialization of petroleum hydrocarbons with their derivatives have become an environmental problem as a result of the large fuel spills frequently generated over the years. The contaminating potential and the complex composition of hydrocarbons and its derivatives, on top of their easiness of mobilization in the environment and their accumulation in water and soils, have increase the scientific interest in orderto find a solution to reduce their effect on the ecosystems. Therefore, researchers worldwide have focused on evaluating phytoremediation as a solution in view of its cost-effectiveness and landscaping contribution because it can be used to bioremediate water and soils mixed with fuels, minimizing the risk of pollution. This review article summarizes the principles related to phytoremediation of soils and water contaminated with hydrocarbons as an ecotechnological alternative that can be applied through the interactions between microorganism, plants and physical, chemical and biological processes that occur in natural systems like the wetlands. This paper also discusses some experiences about the subject, factors related and removal mechanisms that command the removal of the organic compounds.

Keywords: *constructed wetlands, hydrocarbons, phytoremediation mechanisms.*

1. Introduction

The increase in the demand for fuels, in combination with the opening of new gas stations in Colombia, has positioned the petroleum derivatives in the highest ranks of public interest for their environmental and public health consequences because of their toxic, mutagenic, and cancer producing effects, aside from their known recalcitrant and bioaccumulant characteristics (Haritash & Kaushik, 2009). The hydrocarbon derivatives (gasoline, kerosene, oils, fuels, paraffines, and asphalt among many others) are generally of common use in human activities that somehow allow their permeation into the environment because of the accidents in industrial, domestic, and transportation processes in combination with the spills and escapes as a result of drilling, pumping, conduction, and storage of the substances. The disposal of waters mixed with fuels as a result of the daily activities of the gas stations (through disposition or runoff) has not only impacted the surface layer of the soil and the surface water sources, but also has penetrated the ground waters.

The wastewater fuels are generally characterized by their contents of oils and greases, hydrocarbons, suspended solids and variable metal concentrations that on the soil block the atmospheric gas exchange, thus initiating a series of simultaneous physic-chemical processes, such as evaporation and penetration, that according to the type of hydrocarbon, temperature, humidity, soil texture, and amount disposed, may cause an increased resistance to their degradation. The hydrocarbons disposed of on the water tend to float because of the density difference and block the penetration of light and the gas exchange, thus promoting the solubilization of materials that affect the different populations: Plankton, microinvertebrate and benthos (macroinvertebrate) that live in the bottom of rivers and quagmires (Bento *et al.*, 2003).

The complexity of the hydrocarbons has forced the implementation of a variety of different treatment

technologies in-situ and ex-situ in order to assess their effectiveness when removing them. The use of phytochemical processes employing activated carbon, microorganisms, chemical substances, air and other compounds imply relative high investment and operation costs that make their application difficult (Susarla *et al.*, 2002; Sangabriel *et al.*, 2006). This is the reason why the interest has shifted to phytoremediation which represents a natural technique where the plants and their interaction with the microorganisms located on the rhizosphere can remove, abduce and/or degrade the organic contaminants into less toxic compounds or even to CO₂ y H₂O (Guendy, 2008). This technological alternative has limitations for its application on a large scale or when the contaminant is toxic for the plants (Glick, 2003), but the advantages when compared to other conventional technologies that include physical or chemical removal are evident because *i)* it represents a lower cost-effectiveness, *ii)* it captures the greenhouse gases, *iii)* improves the surroundings from a aesthetical perspective, and *iv)* its principal source of energy is the solar radiation (Guendy, 2008). In this review article the authors are focused on introducing the advantages of phytoremediation on the treatment and recovery of waters and contaminated soils by organic and inorganic compounds of complex degradation, specifically through constructed wetland systems.

2. Petroleum hydrocarbons

The hydrocarbons are classified according to the API degrees (density) that they possess and they have a characteristic look where some are of a clear appearance and easily evaporate, and some others are dense and obscure liquids that do not evaporate (ATSDR, 1999). The hydrocarbons are usually divided in three different groups: Acyclic with open chains, saturated cyclic with open chains, and non-saturated aromatic hydrocarbons (Kamath *et al.*, 2004), with the benzene ring as structural base like the BTEX (benzene, toluene, etilbenzene, and xylene that are monoaromatic) or the PAHs (Naphthalene, Phenanthrene, and Anthracene that are polyaromatic) (Gabriel *et al.*, 2004).

The BTEX are more soluble in water (low K_{ow} : 1.8-3.2) than the cyclic compounds of heavy molecular weight, this the reason for their easiness in displacement on aqueous environments and the easy biodegradation in aerobic conditions (USEPA, 1999); furthermore, they may be easily removed through volatilization due to their nature, highlighting the use of superficial flow wetlands as a good alternative for the task (Kadlec & Wallace, 2009). The PAHs belong to a wide group of hydrocarbons made up of 2 – 7 benzene rings that are characterized by their low solubility in water ($\log K_{ow} > 4$) and low volatility; these may achieve a mean life that goes from weeks to several years in the environment (Sverdrup *et al.*, 2003). Those with low molecular weight (2 -3 benzene rings) may be easily degraded through biological processes, but the ones with high molecular weight may be resistant to the microbial biodegradation (Sun *et al.*, 2010).

3. Phytoremediation mechanisms on waters and soils contaminated with hydrocarbons

Phytoremediation is defined as a low cost environmental friendly technological alternative developed to bring remedy to the affected resources with different types of contaminants (Khan *et al.*, 2013). This is based on the use of plants and their interaction with the microorganisms located in the rhizosphere in order to remove, isolate or degrade the contaminant substances present in the soil, sediments, surface waters, ground waters, and the air (Meagher, 2000; Susarla *et al.*, 2002; Ali *et al.*, 2012; Kabra *et al.*, 2012). This alternative may be used to remove metals, pesticides, solvents, explosives, oils derived from petroleum, hydrocarbons derived from petroleum, chlorinated compounds, lixiviated compounds, and volatile compounds in the air (Meagher, 2000; Newman & Reynolds, 2004; Imfeld *et al.*, 2009). The use of the phytoremediation depends on the type of affected resource, on the objectives of the remediation (type of contaminant), on the type of preferable outcome process: Stabilization, Isolation, Reduction, Degradation, Metabolization and/or Mineralization.

In agreement with some authors like Susarla *et al.* (2002) and Zhang *et al.* (2012), the plants play a major determinant role in the remediation of soils and contaminated waters through several processes that diminish the toxicity grade of the contaminant compounds by modifying the physicochemical properties of the contaminated system and the ratio of exudate – roots in order to increase the organic carbon and the ventilation of the radicular area.

Phytoremediation has been widely researched in the recent years in order to understand the sorption and metabolic processes of organic and inorganic compounds by the plants (Bock *et al.*, 2002). Peña *et al.* (2006) establish that the plants render an important function on the phytoremediation of organic compounds like the hydrocarbons because *i)* The rhizosphere improves the properties of the soil through the injection of air and the introduction of nutrients that encourage microbial diversity, *ii)* the interaction between the plant and the microorganisms promotes the cometabolism of the contaminants that forces the activation of several metabolic options, and *iii)* the transportation of water to the superior areas of the plant works in favor of the degradation or immobilization of the contaminant in order to produce a degradation in the interior and exterior of the plant.

It has been demonstrated that the plants can metabolize or immobilize the petroleum hydrocarbons through several processes, such as the metabolic oxidation or the co-oxidation, in agreement with the levels of concentration of the hydrocarbons. This is why upon low toxicity levels the rhizospheric system supplies favorable nutritional and ventilation conditions in order to increase the population and diversity of the flora, while on high toxicity levels the exudation of sugars, the growing factors, and the organic acids may be affected jointly with a break in the rhizospheric equilibrium, the decrease in microorganisms (fungi and bacteria), and the decrease of nitrogen assimilating and atmospheric nitrogen fixation bacteria (Pérez *et al.*, 2002).

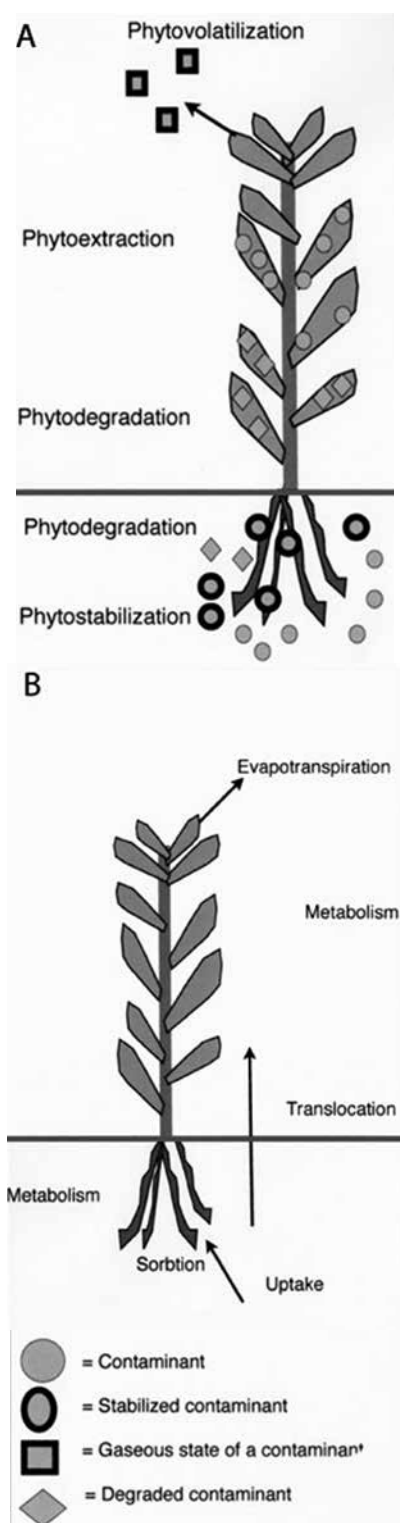


Figure 1. A. Layout of the different Phytoremediation techniques in the plant B. Physiological processes made by the plants during Phytoremediation
Source: Greipsson (2011)

3.1 Principal mechanisms of phytoremediation

In phytoremediation several mechanisms are present and they are classified according to the place where the process takes place (Figure 1): Phytoextraction, Rhizodegradation, Phytostabilization, Phytodegradation, and Phytovolatilization (Imfeld *et al.*, 2009; Jain *et al.*, 2011).

Phytoextraction This refers to the sorption of the contaminant by the root of the plant, also known as phytoaccumulation, because of its capacity to accumulate different compounds on its reaping parts, and tissues of leaves and stems (Glick, 2003; Carpena & Bernal, 2007), mainly when they are not completely or quickly degraded. This mechanism may be affected by the lipophilic nature of the compound, measured under the octanol-water partition coefficient (K_{ow}) (Kamath *et al.*, 2004). Several studies (Schnorr, 1997; O'Niell & Nzengung, 2004; Wallace & Kadlec, 2005; Boonsaner *et al.*, 2011) show that phytoaccumulation is an efficient mechanism in order to remove BTEX, chlorinated solvents, and aliphatic hydrocarbons of short chain because its K_{ow} varies between 1, 0-3, 5. The compounds that have a $K_{ow} > 4$ are hydrophobic compounds and, therefore, cannot be easily incorporated to the roots of the plant (Khan *et al.*, 2013), those that are soluble water have $\log K_{ow} < 1, 0$ values.

The plants destined to a Phytoextraction process are characterized for their high tolerance and effectiveness on accumulating the contaminant and they are also easy to harvest (Vangronsveld *et al.*, 2009). The principal advantage of this process lays on its low cost implementation if compared to other remediation techniques, and, among its disadvantages, it must be handled in low or moderated contaminant concentrations that require high accumulation times (Spaczyński *et al.*, 2012).

Rhizodegradation In this phytoremediation technique the degradation of the organic

contaminants takes place close to the roots of the plant through microorganisms (fungi and bacteria) that are stimulated by the liberated enzymes from the plant. This is the reason why it is also called phytoestimulation because the plants do not directly degrade the contaminant but in turn generate the proteins and enzymes that guarantee the growth of fungi and bacteria that degrade it (Van Deeps, 2006; Cameselle *et al.*, 2013; Khan *et al.*, 2013).

The Rhizodegradation in the case of soils, aside from having a low maintenance and investment cost if compared with conventional technologies as excavation, improves soil quality and texture, delivering stability and mitigating the erosion generated by the wind and water (Gerhard *et al.*, 2009). It, however, presents disadvantages in the face of traditional technologies because of the low rate of bioremediation and stressing environmental factors in temperature, precipitation, nutrients, pathogenic plants, herbivores, and the competence of weeds that may hinder or diminish the growth of the plants (Nedunuri *et al.*, 2000).

Phytostabilization This refers to the use of plants in order to reduce the bioavailability of the organic and inorganic contaminants by immobilizing them through the addition of amendments to the soil, the absorption or the roots of the plants or soil particles, and the precipitation in the area of the root in order to hinder their migration and the decrease of erosion, the runoff, and the lixiviation (Van Deeps, 2006; Kumpiene *et al.*, 2007). This mechanism is mainly applied to metallic contaminants because sometimes is advisable to immobilize the compound due to its difficult or incomplete biodegradation (Cameselle *et al.*, 2013). This phytoremediation technique, Schwitzguébel *et al.* (2011), promotes the restoration and the biodiversity of the ecosystems that represent ecological benefits for the production of industrial harvests. It is also advised the use of endemic plant species, adapted to the soils and weather of the areas to remedy, in order to avoid adaptation and invasion problems.

Phytodegradation This mechanism, also known as phytotransformation, allows the absorption of contaminants and transforms them into more simple molecules such as CO₂ y H₂O to later incorporate them to the plant tissues and help in its growth (Conesa *et al.*, 2012; Spaczyński *et al.*, 2012). This process is catalyzed by the enzymes and proteins from the plants in order to generate a break up in the contaminant molecules (de-Bashan *et al.*, 2012). The Phytodegradation takes place in three steps: *i*) conversion through oxidation-reduction reaction, *ii*) amino acid and sugar conjugation, and *iii*) the incorporation of the contaminant to the plant through its organelles (vacuole and cell wall) (Dietz & Schnoor, 2001). Spaczyński *et al.* (2012) point out that in spite that in the vegetal cells a complete degradation of organic compounds generally does not take place, the plants use the products of biotransformation in other forms such as the amino acid synthesis.

The Phytodegradation associated with certain microorganism has presented efficient results on the degradation of organic compounds such as the petroleum derivatives through a cooperation process named rhizo-phytodegradation, where the potential and biodiversity of the secondary metabolism of the plants is used (Vangronsveld *et al.*, 2009; Schwitzguébel *et al.*, 2011).

Phytovolatilization This phytoremediation process is based on the absorption of the contaminant compound that is generally of a low molecular weight on the part of the plants in order to achieve its posterior volatilization to the atmosphere through the leaves (Glick, 2003; O’Niell & Nzengung, 2004; Gerhardt *et al.*, 2009; Conesa *et al.*, 2012). The phytovolatilization has been mainly used for the elimination of heavy metals such as mercury which is transformed into its most elemental form that is less toxic than the organic or inorganic one, but this technique, however, has the disadvantage that the liberated metal into the atmosphere may return to the ecosystems through precipitation and be deposited again (Ghosh & Singh, 2005).

3.2 Environmental factors and nutritional needs in the phytoremediation of hydrocarbons

Among the determinant factors in the process of phytoremediation pointed by several authors (Frick *et al.*, 1999; Glick, 2003; Petenello & Feldman, 2012) the following are found: *i)* the concentration of microorganisms around the roots of the plants, *ii)* the regime of rains, *iii)* the type of roots, *iv)* the adaptation capacity of the plant to the contaminants, *v)* the temperature and solar radiation, *vi)* the concentration of the contaminant, and *vii)* the temperature. Aside from these, Gerhardt *et al.* (2009) indicate that relevant environmental factors for the phytoremediation on soils are: *i)* structure, *ii)* organic matter contained, *iii)* pH, *iv)* humidity contained, and *v)* microbial activity.

The increase in the concentration of carbon due to the hydrocarbons can create hydrogen and phosphorus deficiencies because of the immobilization caused by microbial processes and the nutritional requirements of the microorganisms and the plants for their metabolism and the remediation of the affected area (Kirkpatrick *et al.*, 2006; Guendy, 2008). Pardo *et al.* (2004) and Ramírez *et al.* (2009) indicate that the proportion C: N: P (100:10:1) must be adjusted through the addition of any type of fertilizer to stimulate the remediation when scarce nutrient availability is present. If, on the other hand, the content of nitrogen is excessive, it may become an inhibitory factor because of the toxic effect provoked by the accumulation of nitrates and nitrogen oxide generated by the processes of denitrification under anaerobic conditions and low pH values (Chaineau *et al.*, 2005; Ramírez *et al.*, 2009).

The assimilation of nutrients by the plants takes place thanks to the transformation of nitrogen in organic form to organic compounds that are good for cell formation and new tissue; this is why the potential of nutrient intake by the macrophytes is limited to its growth rate and the concentration of nutrients in their tissues (Vymazal, 2007). The capacity of nutrient intake by the emerging plants

is between 1000 to 2500 Kg N/Ha-year according to Vanier & Dahab (2001), and the ammonium ion found in the wetlands is the nitrogen form that can be taken by the plants through their radicular area or by the anaerobic microorganisms that turn it back into organic matter (Zhu *et al.*, 2010). These mechanisms are dependent on biotic and abiotic factors like pH, redox potential, availability and presence of microorganisms (Jones *et al.*, 2004).

4. Phytoremediation application on hydrocarbon contaminated waters through constructed wetlands

The constructed wetlands are engineering systems that have been designed and built in different parts of the world since the 1950's with the purpose of a controlled environment reproduction of the processes that take place in the natural wetlands, taking advantage of the interactions between the vegetation, the soils, and the microbial communities in order to treat wastewaters (Brix, 1994; Verhoeven & Meuleman, 1999; Vymazal, 2007; Haarstad *et al.*, 2012). The constructed wetlands may be classified in agreement with the type of growth or life form of the predominant macrophytes and with the flow regime (Brix, 1994; Mahmood *et al.*, 2013). The first classification is divided in systems based on macrophytes *i)* free floating, *ii)* submerged, and *iii)* emerging roots (Vymazal *et al.*, 1998). In the second classification, meanwhile, the constructed wetlands may be characterized as a function of the incoming water flow direction into the system; this can be in horizontal, surface, subsurface, or vertical flow (Kivaisi, 2001; Kuschik *et al.*, 2012).

The constructed wetlands have had different successful applications since their first implementations, from the most developed treatment of domestic wastewaters to the draining of mines, wastewater from swine farms, leachates, residues from the food industry, waters contaminated by pesticides, liquid residues from the textile industry, from the pulp and paper, sugar and distillation

Table 1. Research done on the use of constructed wetlands for the treatment of hydrocarbons in waters

Type of contaminant	Plant(s) Used	Configuration of the plantation	Findings	Ref
Subsurface water contaminated with gasoline-ethanol	<i>Salix babylonica</i>	HF	Reduction of ethanol and benzene >90%. Toxic compounds for macrophytes in concentrations over 2000 mg/L.	Corseuil & Moreno (2001)
Wastewaters contaminated with diesel	<i>Typha latifolia</i> – <i>Lemna minor</i> (Control)	HFSS	Removal efficiencies between 80, 78 y 72% on the surface, medium and bottom sections of the planted wetland.	Omari <i>et al.</i> (2003)
Subsurface waters with hydrocarbons and cyanide	<i>Ceratophyllum demersum</i> and <i>Potamogeton spp</i>	HFS	Removal of 67% of gasoline and diesel.	Gessner <i>et al.</i> (2005)
Effluents from BTEX refinery process	<i>Salix</i> , <i>Phragmites</i> , <i>Schoenoplectus</i> , <i>Juncus</i> and <i>Cornus</i> .	HFSS aired and non-aired	Research done on the pilot and real scales; the greatest removal efficiencies were found in aired wetlands; the removals of BTEX reached 94%.	Wallace & Kadlec (2005)
Subsurface waters with BTEX and diesel	<i>Salix</i> , <i>Phragmites</i> , <i>Scirpus</i> , <i>Juncus</i> , <i>Cornus</i>	Aired HFV	Removal of up to 88% of BTEX; benzene reduction between 13-21%.	Bedessem <i>et al.</i> (2007)
Waster waters contaminated with benzene	<i>Phragmites australis</i>	HFV	Benzene removal of 85%; in wetlands with biomass, the removal took half of the time to that of the wetlands without biomass; the predominant removal mechanism was Phytovolatilization.	Eke & Scholz (2008)
AR effluent of a primary treatment with PAHs and equilbenzene	<i>Phragmites australis</i> and <i>Arundo donax</i>	HFS, HFSS and gravel filter	The HFSS presented better efficiencies tan the other evaluated systems; the Phytodegradation mechanism was predominant.	Fountoulakis <i>et al.</i> (2009)
Subsurfacewaters contaminated with benzene and MTBE	<i>Phragmites australis</i>	HFHSS	Compared wetland systems with gravel and planted. The greatest removal efficiencies were on the planted wetland.	Seeger <i>et al.</i> (2011)
Runoff waters with hydrocarbons from vehicle exhaust pipesand heavy metals	<i>Phragmites australis</i>	HFV	Removalefficiencies of 90-95%. Widely satisfied the Dutch, European, and American standards for surface waters and shallow subsurface waters.	Tromp <i>et al.</i> (2012)
Subsurface waters contaminated with benzene and MTBE	<i>Phragmites australis</i> .	HF (1); HFSS (2) (planted & non-planted)	The HF jointly with the planted HFSS presented similar removal efficiencies.	Chen <i>et al.</i> (2012)
Synthetic wastewaters with diesel.	<i>Scirpus grossus</i>	HFSS	Toxic concentrations > 17400 mg/L of diesel; removal of 91,5%. Growth on the microbial concentration on the rhizosphere with the increase on the hydrocarbon concentrations.	Al-Baldawi <i>et al.</i> (2013)
Refinery effluents	<i>Ceratophyllum demersum</i>	----	The plant presented efficiencies> 80%. The principal removal mechanismwas Phytoextraction.	Alwan <i>et al.</i> (2013)

HFS: Wetland of Superficial flow; HFSS: Wetland of Subsurface Flow; HFHSS: Wetlands of Subsurface horizontal Flow; HFV: Wetland of Vertical Flow; HF: Floating Wetland

industries, dumping from the military and explosive industry (Haberl *et al.*, 2003; Paredes *et al.*, 2007; Rani *et al.*, 2011; Vymazal, 2011). The constructed wetlands have been used in some countries, like China, for the treatment of lakes and contaminated rivers (Zhang *et al.*, 2012). The principal steps for the removal of hydrocarbons through wetlands are the volatilization, the biological or microbial degradation, the photochemical oxidation, the sedimentation, the absorption, and the chemical filtration and precipitation (Kadlec & Wallace, 2009). Zhang *et al.* (2010) indicate, however, that these compounds may generate morphological damages in the plants, such as reduction in the growth of the roots and stems, deficiencies in the growth of radicular hair, and delays in floration and white dots appearance. At the cellular and tissue level, simultaneously, the plants may suffer an oxidant stress that reduces their effectiveness in the nutrient and water intake which inhibits the photosynthesis and the electron transportation. Table 1 presents a summary of the research where phytoremediation was used through constructed wetlands for the treatment of contaminated waters with different species of hydrocarbons.

This research confirms the advantages of the constructed wetlands for the treatment of hydrocarbons derivated from petroleum where removals from 67% to 90% and beyond are present. As a general rule, no evidence of predominant mechanisms of phytoremediation are present because the behavior chosen by the plants mainly lays on factors such as the partition coefficient of the contaminant hydrocarbon, volatility, the flow regime, and the type of plants used in the constructed wetlands. The studies present, regarding the use of plants, a vegetal species that is commonly used in research; the *Phragmites australis* has been the vegetal species largely used on the treatment of wastewaters and specifically on constructed wetlands because it has proven that the chemical demand for oxygen, the nutrients (dissolved and in particles), and some heavy metals are reduced when this type of plant is used in these waters (Chambers *et al.*, 1999), and, additionally, the hydraulic conductivity is improved on the beds

of the wetlands to insure the subsurface flow of the waters (Brix *et al.*, 2007). This is backed up with the use of the *P. australis* for the removal of compounds derivated from petroleum through studies where there is coincidence about the fact that the substances secreted by the roots stimulate the degradation of the studied compounds, and their interaction with microorganisms such as the *Mycobacterium* spp accelerate this degradation thus increasing its use possibilities on the treatment of compounds with high molecular weight (Jouanneau *et al.*, 2005; Toyama *et al.*, 2011). It is evident, however, that a great deal of the research is carried out on a pilot and lab scale, but there is the need for great scale studies to contribute to the establishment of implementation criteria on this type of systems in order to test their effectiveness on the treatment of great volumes of contaminated water by different hydrocarbons.

5. Phytoremediation used on the treatment of soils contaminated with hydrocarbons

Aside from its ecological and economic efficiency on the treatment for great soil areas and low contaminant concentration; other advantages offered to contaminated soils by the phytoremediation are the increase in microbial activity, render help in erosion reduction, and protection against the direct radiation of the sun (Cameselle *et al.*, 2013). Soil phytoremediation is generally based on planting selected vegetal species on contaminated soils where the action of the plants is initiated. Kathi & Khan (2011) introduce several studies with a wide selection of vegetal species for the treatment of contaminated soils by hydrocarbons, such as trees, plants, and shrubs among others. There are a wide number of experiences about the effectiveness of phytoremediation on contaminated locations by petroleum derivatives. Table 2 introduces a review on the research carried out on remediation of soils contaminated by hydrocarbons derivated from petroleum, and a summary of the principal findings is given with the species used for each case. There is a difference between the removal presented in the treatment of the wetland waters and the efficiency of plants that remove the hydrocarbon

Table 2. Research done on the use of constructed wetlands for the treatment of hydrocarbons on soils

Contaminant on the soil	Vegetal species used	Findings	Ref
Soil with HTP	<i>Lolium multiflorum</i>	Removal efficiencies > 97% in total hydrocarbons; greater presence of microorganisms if compared with soils unplanted.	Gunter <i>et al.</i> (1996)
PAHs	<i>Medicago sativa</i> <i>Panicum virgatum</i> <i>Schizachyrium scoparium</i>	These plantation showed removal efficiencies of 50% in six months	Prahand <i>et al.</i> (1998)
PAHs on marine sediment	<i>Spartina alterniflora</i>	The greatest concentration of contaminant was found in roots and stems in two and three order of magnitude respectively, below the concentration of the soil. Principally present adhered to the surface of the root.	Weatherly <i>et al.</i> (2006)
Accidental spill of fuel oil on the soil.	<i>Leguminous</i> (<i>Clitoria ternatea</i> , <i>Phaseolus coccineus</i> y <i>Cicer arietinum</i>) <i>Gramineae</i> (<i>Brachiaria</i> <i>hibrido</i> y <i>brizantha</i> y <i>Panicum maximum</i>)	The gramineae easily tolerated the compound The predominant mechanism was rhizovolatilization. The Brizhanta got the best compound degradation..	Sangabriel <i>et al.</i> (2006)
Hydrocarbons on soils	<i>Six gramineae</i> – <i>Principally, Medicago sativa</i>	Removals > 50% were obtained. The Alfalfa presented a dominant effect over the microorganisms, stimulating growth.	Phillips <i>et al.</i> (2006)
Phenanthrene and Pyrene	<i>Echinogalus</i> y <i>Astragalus membranaceus</i>	The studied compounds are not toxic for the mentioned leguminous. This degradation on the part of the plants is attributed to the increase of microorganism in the rhizosphere and their microbial activity.	Lee <i>et al.</i> (2008)
Hydrocarbons from petroleum fields	<i>Mirabilis jalapa L</i>	Removals between 40-60% and 19-37% in natural and greenhouse conditions respectively. Toxic for the plants from 10000 mg/Kg.	Peng <i>et al.</i> (2009)
Sediments from mangrove areas contaminated with total hydrocarbons	<i>Rizophora mangle</i> and <i>Avicennia schaueriana</i>	The phytoremediation presented greater efficiencies of contaminant removal (87%) than the bioremediation and the plants presented a greater growth in compared to the white units. The predominant removal mechanism was Rhizodegradation.	Moreira <i>et al.</i> (2011; 2012)
Soil contaminated with BTEX	<i>Canna generalis</i>	The plant can achieve removal of 1 80% of BTEX. Its predominant removal mechanism is Phytoextraction. Consideration to the soil water content must be taken because it affects the phytoremediation mechanism.	Boonsaner <i>et al.</i> (2011)
Soil with hydrocarbons and heavy metals	<i>Trees</i> (<i>P. nigra</i> and <i>P. tomentosa</i>) <i>Shrub</i> (<i>C. scoparius</i> .)	Real scale (10000m ²). The reduction of hydrocarbons reached 40% in three years. Increase of dehydrogenase indicating microbial activity.	Macci <i>et al.</i> (2013)
Soil contaminated with diesel oil	<i>Pinus densiflora</i> , <i>Populus tomentiglandulosa</i> <i>Thuja orientalis</i>	The evaluated species tolerated concentrations of 6000 mg/Kg. The microbial consortia and the addition of fertilizers improved the process efficiency..	Jagtap <i>et al.</i> (2014)

compounds on the soil, the later have an efficiency that varies in a wide range between 40-97% for the reported studies. A common vegetal species is neither present on the reported studies, there is a wide variety of used species on them. The authors, however, coincide in the fact that the mayor removals are introduced when grass and leguminous plants are present. It is more frequent to find real scale experiences for the removal of hydrocarbons on soils; however, the common denominator is that these experiences require at least three years to obtain adequate results (Macci *et al.*, 2013). The used vegetal species on soil phytoremediation generally present tolerance to hydrocarbonated compounds of up to 10000 mg/Kg, and, additionally, in some species the presence of contaminant compounds favor their growth and development.

6. Conclusions

This document confirms the potential of the wetland systems in the removal of the total petroleum hydrocarbons. This treatment alternative becomes a promising solution in order to reduce the effects caused by the contamination through these compounds with the clear application advantage that it may be used in or ex situ.

It is important to know the physiological and morphological characteristics of the plants to be used in order to remove the hydrocarbons from the wetlands. This will lead to the employment of macrophytes with a positive response towards the tolerance of the compounds in order to understand the involved removal and interaction processes between plants-environment-microorganisms that allow to transform and/or reduce the hydrocarbon concentration. It is also important to inquire about the microbial activity that takes place in the interior of the wetlands through biochemical and molecular tests that allow the identification of the associated microorganisms to the process of the hydrocarbon removal.

In spite of the different phytoremediation research projects done worldwide, several gaps still

remain that hinder the full understanding on how the technology functions because many of the experiments have taken place on a lab scale where a great deal of the factors have been controlled and this reduce the possibility to interpret the system effectiveness in real conditions where the weather conditions may also influence the degradation of the hydrocarbons. The application of phytoremediation must be evaluated on a real scale in order to estimate the efficiency of this technology in the application of specific organic compounds because the hydrocarbon family is very wide and their reactions with the water, soil, and plants change from one species to another.

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