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Phytoremediation of Industrial Wastewater from Oil and Gas Fields using Native Plants: The Research Perspectives in the State of Qatar

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ABSTRACT

The producing oil and gas countries are keen, eager and anxious to look at the impact of the industrial wastewater (IWW) spilled during the production and processing on various aspects of life including the public health, economy, agriculture and wild life. Arab Gulf States, including Qatar, have enacted laws and regulations by which Environmental Impact Assessment (EIA) should be implemented for any plan to conduct projects by oil and gas companies that might change the natural habitats. This review aimed to clarify the objectives and principles that should be considered and implemented for any future studies concerning the use of IWW in various aspects of agriculture after removing the contaminants. Therefore, any investigations, studies and researches in the State of Qatar concerning the impact of IWW in soils and waters should cover the following aspects: (1) recognize the native plants and the associated microbes, like bacteria and fungi, that prove efficient in phytoremediation and bioremediation, (2) analyze IWW periodically to monitor the changes in its chemical contents (organic and inorganic) such as petroleum hydrocarbons, nutrient elements, heavy metals as well as other compounds that might be added during the extraction and processing, (3) set up systems of soil, sand and water cultures suitable for the local plants in Qatar to conduct successful experiments about the phytoremediation techniques, (4) study the physiological and biochemical parameters that might be affected in plants proved efficient in phytoremediation. The outcomes of such studies can be used latter on in more advanced investigations, and (5) implement ambitious advanced plans to use modern technology to develop genetically modified plants that are efficiently remove, degrade, metabolize various types of pollutants.

Key Words: Bioremediation, Phytoremediation, Industrial Wastewater, Native Plants, Microorganisms, Heavy metals, Petroleum Hydrocarbons

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INTRODUCTION

The Problem

The value of life on Earth is closely associated with the quality of the environment, as the environment is clean and free of contaminants; that would encourage human development, creativity and production optimization. There is no doubt that mankind is facing serious problems and challenges concerning the food and health security, these problems can be summarized as follows: (1) the population of the world is increasing steadily; on 31st October 2011 the population of the world became 7 billion. The United Nations (UN), Food and Agriculture Organization (FAO) estimate the population on the Earth in the fourth decade of the current century to be 12 Billion people, (2) global food production reached plateau, (3) 70 % of the surface of earth is covered with salt water, and 43 % of the land is arid or semi-arid lands, and half of these lands is highly saline soil [1, 2]. FAO data have estimated that at least 40% of the world is affected by salinization [3], (4) irrigation of crops in those regions faces serious challenges because of limited water supply of good quality suitable for irrigation, especially in areas where agriculture is dependent on surface irrigation, (5) increasing pollution problems in the environment including water, soil and air as a result of industrial development and human activities. The accumulation of petroleum products and heavy metals in soils and water started with the beginning of production of oil and gas, causing a lot of threats in many sectors of economy; agriculture, health and wild life, (6) lack of financial support for the applied research in the field of agriculture, especially in the poor and developing countries, (7) the pattern of distribution of food and the economic policies of rich nations are additional problems facing mankind.

The Produced Water during the Extraction of Gas and Oil:

During the extraction and processing of natural gas or crude oil, the trapped water in the underground is produced in huge volume and brought to the surface, such water often considered as waste, however there are some indications that such water may be useful and can be considered as potential profit stream [4]. Billions of barrels of wastewater are produced annually from the oil and gas fields in the producing countries around the world. In reports of [5] and the American Petroleum Institute (API) about 18 billion barrels, bbl (bbl = 42 U.S. gallons) of produced water was generated by U. S. onshore operations in 1995 [6], and additional large volume was generated at U. S. offshore wells. Moreover, it was estimated that an average of 210 million bbl of water was produced each day worldwide. The produced water is separated from gas during the production process, other components are produced like monocyclic aromatics such as benzene, toluene, ethyl benzene, and xylene (BTEX), and these are more toxic than the produced waters from oil production. Studies indicate that the produced waters discharged from gas/condensate platforms are about 10 times more toxic than the produced waters discharged from oil platforms [5, 7]. The management of the produced water presents great challenges and costs to the companies and the producing countries [5]. Some authors [4] have suggested five options for managing the produced water: (1) avoid production of water onto the surface, and this can be done by using polymer gels that prevent the leakage of water from fractures or using some agents to separate water from oil and gas streams and re-inject water into suitable formation, (2) inject the produced water, and this can be done either with or without treatment, (3) discharge the produced water, and this can be done by treating water to meet the international standards and regulations, (4) reuse in oil and gas operations after treatment to meet the quality required for drilling, stimulation, and work over operations, and (5) consume in beneficial use. Wastewater may need some treatments to meet the required standards of irrigation, rangeland restoration, livestock consumption and drinking water.

In fact, such wastewater may contain various components of hydrocarbons, and these are of two major types: (1) aliphatics which include alkanes (e.g., methane, ethane, propane), alkenes, alkynes and cycloalkanes, and these compounds contain chains of carbon atoms strung together, and (2) aromatics which include mono-aromatics (e.g. benzene, toluene, ethylbenzene, and xylene, collectively known as BTEX) and polycyclic aromatic hydrocarbons (PAHs; e.g., naphthalene, phenanthrene, anthracene, benzo-α-pyrene), and these compounds contain one or more benzene rings bonded together [8]. Aromatic compounds are more toxic and dangerous than aliphatic ones, since the former especially PAHs are carcinogenic [9].

Also, wastewater may contain considerable amount of trace metals such as Cd, Cr, Cu, Hg, Pb, Zn and may be others, and these may be toxic to plants, animals and humans. Thus, pollution that has resulted from various industrial activities including mining and smelting of metalliferous ores, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and generation of municipal represent a great challenge to the local authorities [10]. In fact, the accumulation of petroleum hydrocarbons and heavy metals in soils and waters as a result of industrial activities of the extraction and production gas and oil may cause serious threats to many sectors of human's life including health, agriculture and economy.

Effect of wastewater on growth and development of plants:

The inorganic components of industrial wastewater include mainly inorganic heavy metals. Some of these heavy metals are essential or being considered as essential for plant life, while others are not essential [11]. Crude oil is rich of heavy metals like Ni, V, Cu, Cd, and Pb [12], while some other heavy metals associated with crude gas like Hg and As as well as other elements and compounds containing sulfur, halogen compounds (containing chlorine and fluorine), nitrogen compounds like amines, ammonia and nitrogen oxides [13]. Their impact on the growth and development has been studied extensively in many native plants. Authors like [14] have stated that the negative impact of those heavy metals is reflected primarily in numerous changes at different levels of biological system organizations. They are exerted their toxic effects in relatively low concentrations, and they are categorized as very dangerous environmental pollutants. Increased concentrations of heavy metals in waters and sediments have harmful effects to plants and animals due to their toxic properties, and they are also affect humans through food chain. [15]. On the other hand, many reports have discussed the impact of spills of petroleum hydrocarbons during oil and gas production and processing in the soil and water on plants and the associated microbes (bacteria). For example, [16] have conducted pilot experiments to analyse the effect of different environmental factors on the rhizoremediation of petroleum contaminated soil using different plant species (cotton, ryegrass, tall fescue and alfalfa). High TPH (Total Petroleum Hydrocarbon) content inhibited the bioremediation process likely because of the toxicity of TPH to the plant and bacteria. Some plants are sensitive to oil pollution, and plant growth may be greatly reduced in a high-TPH soil. [17] have found that 5 % TPH content gave the best degradation in soil planted with ryegrass, and they come to the conclusion that plants differ in their effectiveness in the process phytoremediation; tall fescue (*Festuca arundinacea*) > ryegrass (*Lolium perenne* L.) > alfalfa (*Medicago sativa*) > cotton (*Gossypium hirsutum Linn*). A high TPH content is toxic to plant growth and inhibits the degradation of petroleum hydrocarbons, and the degradation rate of TPH increased with increased addition of fertilizer. [18] have discussed the impact of organic pollutant on plant metabolism which could have great impact on plant growth and development, these compounds cause great influence on the uptake of nutrients and possibly other chemical components across plasma membranes since they are lipophilic and covalently bound to the soil components. These compounds either limit the uptake or cause accumulation in the partly suberized root cortex. Before the pollutant is translocated by the transpiration stream in the xylem into other tissues, it enters the symplast of the root endodermis where detoxification and metabolism occur [19]. [20] concluded that TPH content of 1.5% is considered as a critical value for plant growth and living of earthworm and 0.5% will affect the activity of luminescent bacteria.They found that, TPH pollution in the soil inhibited seed germination in some crop plants like wheat and maize when the concentration of petroleum was higher than 0.1%. [21] have found that the germination rate was significantly reduced in *Schinus terebinthifolius* Raddi, in soil affected by diesel oil at a rate of 92.4 ml per Kg, and the toxic effect contaminant decreased over time. [22] have found that addition of oil field wastewater to the soil increased bacterial populations in the wastewater – contaminated soils above those of the uncontaminated soils.

PHYTOREMEDIATION

The current attention is being paid and concentrated to remove pollutants of various kinds from water, soil, and air to make the environment clean and healthy. Many methods have been used, the conventional methods of remediation in the soil include digging through the contaminated soil and remove the contaminants mechanically and transfer the pollutants to another sites. These methods have some drawbacks including the financial cost and the ethic commitment and potential liability [23], and are not guaranteed success and pollution can be transferred to other sites. Moreover, the traditional methods may destroy the ecosystem at the site [9, 24]. On the other hand, new modern approaches have been adopted which include complete degradation of the pollutants or transfer them to innocuous substances. In this regard, bioremediation methods have been used worldwide using microorganisms to degrade the environmental contaminants mainly organic wastes in to less toxic concentrations [23, 25]. Bioremediation seemed a good alternative to conventional technologies in many countries across the world because it is cheap and easy to implement. It was first concentrated on the degradation of the most toxic environmental pollutants into less toxic forms and to levels below the concentration limits established by local authorities. In the modern era, the process of bioremediation was devised in the 1960's by George M. Robinson and not applied until 1972 when fuel holding tanks were cleaned up, and since then it has become a main method of cleaning up spills of gasoline, diesel, heavy metals and other easily degraded petroleum products [26]. However, these methods are not applicable to heavy metals, since heavy metals cannot be degraded and many of them are toxic at high concentrations. Therefore, phytoremediation techniques have been developed and seemed as good choice and have the potential as effective techniques to clean-up soils and water contaminated with toxic compounds, some plants can be used especially those proved efficient and widely used to remove heavy metals or petroleum hydrocarbons from soil and water [8, 10, 27, 28]. Phytoremediation has been considered as innovative bioremediation processes, non-destructive and clean in situ technology that uses green plants and the associated microbes to remove, transfer, stabilize, metabolize, degrade, or volatilize contaminants in soil and ground water for environmental cleanup [29]. Green plants were used to mitigate contaminants of various types, organic and inorganic, without the need to excavate and dispose them elsewhere, and this technique was described as phytoremediation. The term phytoremediation was derived from two syllables: (a) Ancient Greek, Phyto means plant, and (b) Latin remedium means restoring balance or remediation. Plants used for phytoremediation should be appropriate for the environmental conditions and have the ability to tolerate stress imposed by contaminants [30, 31]. [32] have confirmed in their report on; Phytoremediation of Petroleum-Contaminated Soils in the Tropics, that phytoremediation is a non-destructive and economic technology that uses plants to clean up soil and water from contaminants. Moreover, plants may stimulate some microbes to degrade petroleum products in the rhizosphere. Also, aquatic plants, algae, fungi and lichens can be used to clean soil and wastewater from various types of pollutants and is widely used in many countries across the world [33]. There are many techniques using various types of living organisms and have been used successfully to remove contaminants from the soil and water [9, 34, 35]: **(1) Rhizosphere biodegradation:** in this process natural substances (exudates) released by plant roots to supply nutrients to the microorganisms at the rhizosphere area to enhance their ability to degrade organic pollutants, **(2) Phyto-stabilization:** in this process the substances released by the plant roots immobilize the contaminants mainly heavy metals. Roots of plants may prevent water erosion and immobilize the pollutants by adsorption or precipitation and at the end stabilize them. Moreover, stabilization can be achieved by addition of some chemicals like organic matter, phosphates, alkalizing agents and bio-solids to the soil, **(3) Phyto-accumulation,** and also called **Phyto-extraction:** in this process, plant roots adsorb the contaminants, nutrients and water. Then, the plant absorbs these contaminants and accumulates them in the roots, rhizomes, stalks, and leaves. This method is used mainly to remove heavy metals from soil and water. At the end of the season, plant parts are harvested and either smelted for potential metal recycling or can be disposed as a hazardous waste. As far as bioavailability of metals is concerned, there are three types of metals: (a) readily bioavailable metals which include: Cd, Ni, Zn, As, Se and Cu, (b) moderately bioavailable metals which include: Co, Mn and Fe, and (c) not very bioavailable metals which include Pb, Cr and U. Pb can be made available by addition of chelating agents to the soil, while ammonium nitrate enhances the availability of uranium, **(4) Rhizo-filtration:** this method is similar to the phyto-accumulation method, but the plants used to cleanup wastewater are growing either in hydroponic system or in sand culture. The groundwater containing contaminants is pumped to the surface to irrigate plants growing in water culture, sand culture, or in any artificial soil media like perlite or vermiculite. When the roots of plants are saturated with contaminants, they can be harvested and disposed of, or the accumulated metals in various parts of the plant can be extracted and utilized in industry, **(5) Phyto-volatilization:** in this method some plants can be utilized to absorb organic contaminants which are water soluble and convert or modify them to volatilized components and released them into the air through stomata of their leaves as they transpire the water. Many examples of phyto-volatilization can be reported in various plants. During the last decade, researchers have been working on various native plants or genetically modified plants that are able to absorb some contaminants, organic or metals, from the soil and convert them to gaseous species within the plant, and release them into the atmosphere. This method has been used successfully in case of Hg and As ions and selenium [29, 36, 37, 38]. Moreover, some plants proved efficient in metabolizing selenium into volatile forms to clean Se contaminated environments [39], **(6) Phyto-degradation or Phyto-transformation**: in this method plants absorb organic contaminants and metabolize and destroy them within the plant tissues, or such degradation could be taken place externally, i.e. Ex plants metabolic processes hydrolyze organic compounds into smaller units that can be absorbed by the plant. Plant exudates may breakdown organic contaminants into small units, and when absorbed they become part of the plant metabolism as it grows and at the end they become incorporated into the plant tissues, and **(7) Hydraulic Control:** in this method trees are used and act as natural pumps and their roots reach down towards the water table. Roots of trees establish a dense mass to take large quantities of water by which the movement of ground water and soil water is controlled. Thus, water infiltration or leaching may be contained, reduced or prevented, and on the other hand, water upward flow may be induced. There are some examples of the magnitudes of water uptake reported by [34] by which this method was adopted using some trees like polar tree, willow tree, alfalfa, tamarisk and eucalyptus.

HISTORICAL BACKGROUND

It is believed that bioremediation was first used during Roman's era (about 600 BC) to treat waste water. However, phytoremediation as a bioremediation process is not a new technique to remove heavy metals or organic compounds from wastewater or contaminated soil. About 300 years ago some plants like *Thlaspi caerulescens* and *Viola calaminaria* were reported to accumulate high concentrations of heavy metals [10, 40, 41]. In the twentieth century, these efforts continued to add more plants that have the potential in removing toxic metals and organic compounds from soil and water. For example, [42] reported that *Astragalus* accumulated considerable amount of Se in the top of plant, [43] found that *Alyssum bertolonii* Desv. accumulated about 1 % Ni in the shoot system, [44] reported that *Thlaspi caerulescens* proved tolerant to high concentrations of Zn. Finally large number of publications in the last decade of the twentieth century and the first decade of the current century increased the list of plants that are efficient in removing toxic elements and organic compounds from the environment, and improving the phytoremediation techniques. [45] working with 30 plant species, using water culture technique, found that some *Brassica* species accumulated substantial amounts of Zn and Cd. The list of plants now includes hundreds of species as metal hyperaccumulators of various plant groups; however, *Thlaspi*, *Brassica, Sedum alfredii* H., and *Arabidopsis* species have proved efficient in removing heavy metals from soil and water [25, 46, 47]. [48] reported some tropical plants that have the ability to accumulate heavy metals like Co, Cu, Pb, Ni and Se. [49] reported in their review that some trees such as willow (*Salix* spp.) can be used for the phytoremediation of heavy metal-contaminated land. [50] working with hydroponic system found that *Leersia hexandra* accumulated Cr in all plant parts. [51] analyzed the evolutionary origin of Ni accumulation in some species of *Stackhousia*. Only *S. tryonii* accumulated Ni above the hyperaccumulation threshold (1000 ppm), containing between 2500 and 41000 ppm by dry weight. [14] have concluded that macrophytes (aquatic plants) such as *Typha latifolia*, *Phragmites communis*, *Nuphar lutea*, *Ceratophyllum demersum*, *Salvinia natans* and *Hydrocharis morsus-ranae*are good indicators of heavy metal pollution (like Cd, Zn, Cu, Pb, Fe, Mn and Ni) and might have remedying properties. On the other hand, phytoremediation techniques have also been used for petroleum contaminated soils. [8] have listed some plants that are efficient in phytoremediation of soil polluted with petroleum compounds. These plants included some wild plants like *Panicum virgatum*, *Medicago sativa* L. and *Phragmites australis*, and many crop plants. In a study from Nigeria [31], the problem of contamination emerged with the continued production of oil since the fifties of last century, the petroleum products were accumulated in the agricultural lands and fishing waters which left those lands unsuitable for agriculture and water free of fish. Researchers using the soya bean (*Glycine max* L.), which succeeded in ridding the soil of the toxicity of petroleum products. [16] found that *Mirabilis jalapa* L. was tolerant to petroleum contaminated soil and effectively promote degradation of total petroleum hydrocarbons (TPHs). [52] used *Phragmites australis* as a phytoremediating species to test how petroleum contamination affects the ecophysiological parameters, the availability of essential elements and microbe biology. The outcomes of this study proved that this species was excellent choice to breakdown petroleum compounds. Moreover, useful information was obtained about the effect of petroleum pollution on the plant-microbe interaction and the role of these interactions in the phytoremediation of petroleum polluted soil.

In Qatar, there are no reports about the accumulation of trace metals in wild plants and crops near the oil and gas fields; however, some studies in other parts of Qatar have shown that the concentrations of these elements were at acceptable range recommended for normal plant growth [53, 54]. Fe was found at higher concentrations in most plant species and locations, followed by Ni, Cu, Zn, Cr, Co and Cd. Such topic should be addressed to look at the accumulation of heavy metals in the native plants living around the gas and oil fields.

List of Plants Involved in Phytoremediation:

During the last three centuries the number of plants that have been recognized as active and efficient in removing, degrading, metabolizing or immobilizing contaminants (organic and inorganic) increased tremendously. The literature have listed many native plants or crops that can be used in phytoremediation. For example, [8] have listed some plants that have been used in the phytoremediation of hydrocarbons: *Agropyron smithii*, *Andropogon gerardi*, *Bouteloua curtipendula*, *Bouteloua gracilis*, *Buchloe dactyloides*, *Buchloe dactyloides* var. Prairie, *Chloris gayana*, *Cynodon dactylon* L., *Daucus carota*, *Elymus canadensis*, *Festuca arundinacea* Schreb., *Festuca rubra* var. Arctared, *Glycine max Lemna gibba*, *Lolium multiflorum*, *Lolium perenne* L., *Medicago sativa* L., *Panicum coloratum* var. Verde, *Panicum virgatum*, *Phaseolus vulgaris* L., *Populus deltoides x nigra*, *Secale cereale* L., *Schizachyrium scoparius*, *Sorghastrum nutans*, *Sorghum bicolor*, and *Zoysia japonica* var. Meyer. [29] have found that four aquatic plants: *Typha domingensis*, *Lemna obscura*, *Hydrilla verticillata*, and *Crinum americanum* are active in removing Se from aqueous solutions. [55] have studied the physiological and biochemical aspects of Cd toxicity in two aquatic plants *Phragmites australis* and *Typha latifolia*. [56] have found that seven subspecies of the genus *Amaranthus* are able to accumulate heavy metals in their organs. [37] have discovered that *Pteris vittata* proved efficient as arsenic hyper-accumulating plant and this plant uses two phytoremediation methods, namely phytoextraction and phytovolatilization. [31] used *Glycine max* as a phytoremediator plant in soil contaminated with crude oil. The ability of *G. max* to reduce the level of crude oil in oil polluted soil can help to restore polluted soils back for agricultural use. The high acceptability of *G. max* due to its high nutritional value, high adaptability and ease of propagation will make it an easy tool for remediation of soil contaminated with crude oil. However, this study has not shown the accumulation of heavy metals in this plant during its growth in such soils. [14] have studied the accumulation of many heavy metals (Cd, Zn, Cu, Pb, Fe, Mn and Ni) in some aquatic macrophytes in aquatic ecosystems in the Republic of Serbia, these plants include: *Typha latifolia*, *Phragmites communis*, *Nuphar lutea*, *Ceratophyllum demersum*, *Salvinia natans* and *Hydrocharis morsus-ranae*. [28] have studied the Mn accumulation and tolerance in six species: *Phytolacca Americana* L., *Poa annua* L., *Comnyza canadensis* L., *Cynodon dactylon* L., *Polygonum hydropiper* L., and *Polygonum perfoliatum* L. They found that these species have different abilities to accumulate Mn in different plant organs. [57] have discussed the phytoremediation of heavy metal polluted soils using various plant species. Heavy metals included in this study are: As, Cd, Co, Cu, Ni, Zn, Pb and Cr, and over

400 hyperaccumulator plants have been reported and include members of the Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae, and Euphobiaceae. In Egypt, [58] used *Typha domingensis* in the phytoremediation of industrial wastewater ponds in El-Sadat city.

Bioremediation and the Role of Soil Microorganisms:
Bioremediation has been considered as cost effective clean-up technique using microorganisms to achieve partial or complete degradation of organic contaminants; with little long–term damage to the environment. Some microorganisms can degrade or immobilize these contaminants apart of the intervention of living plants [8]. However, such activities might be accelerated with the presence of plants, since the secretion of some substances including enzymes and / or readily degradable substances by plant roots may facilitate co-metabolic transformation of hazardous petroleum hydrocarbons. Moreover, it is necessary that bacteria and the contaminants are in contact with each other, this is not easy to take place since microbes and contaminants are not uniformly spread in the soil. However, some bacteria are mobile and exhibit some kind of chemical affinity toward the contaminants. Also, mobilization of the contaminants can be accelerated using some surfactants like sodium dodecyl sulphate to bring bacteria and contaminants together [23]. The literature have listed large number of microorganisms which are active in the degradation petroleum hydrocarbons. These microorganisms included bacteria, fungi, protozoa and algae. The following is a brief review of the general roles of microorganisms in the degradation of petroleum hydrocarbons and the mechanisms of such degradation. [59] have concluded that bioremediation takes place by synergistic action of microbial community rather than a single species, [23] has discussed all possible bioremediation technologies using various types of microorganisms including: (1) aerobic bacteria, there are some examples include those active in the degradation of aliphatic and aromatic hydrocarbons, (2) anaerobic bacteria, these are not frequently used, and these microorganisms can be used for bioremediation of polychlorinated biphenyl (PCBs), dechlorination of the solvent trichloroethylene (TCE) and chloroform, (3) ligninolytic fungi, these include white rot fungus *Phanaerochaete chrysosporium* which has the ability to degrade extreme toxic pollutants, (4) methylotrphs, these are aerobic bacteria that are able to grow utilizing methane for carbon and energy. These microorganisms have some enzymes like methane monooxygenase. These microorganisms are active against a wide range of compounds including aliphatic trichloroethylene and 1,2 dichloroethane, [60] have concluded that the rate of diesel degradation was better with the present bacterial consortium rather than individual bacteria, and present bacterial consortium can be better choice for faster and complete remediation of contaminated hydrocarbon soils, [61] has stated some important issues concerning the role of microorganisms: (1) types of microorganisms involved in phytoremediation, (2) reasons for microbial degradation, (3) differences in the degradation by various microorganisms, (4) characteristics of microbial communities involved in the degradation, (5) role of microorganisms in reducing phytotoxicity to plants, [62] have discussed in their review the degradation of petroleum hydrocarbons contaminants, the microorganisms involved and the enzymes catalyzing the reactions. They reported the main types of petroleum hydrocarbons and the microorganisms involved in their degradation. For example, they listed six microorganisms namely: *Arthrobacter*, *Burkholderina*, *Mycobacterium*, *Pseudomonas*, *Sphingomonas* and *Rhodococcus* were found to be involved for alkylaromatic degradation. A study from Nigeria [63] revealed and isolated some bacterial strains from soils contaminated with crude oil. These bacteria include: *Pseudomonas*, *P. aeruginosa*, *Bacillus subtilis*, *Bacillus* sp., *Alcaligenes* sp., *Acinetobacter lowffi*, *Flavobacterium* sp., *Micrococcus roseus*, and *Corynebacterium* sp. Another study [64] identified some tropical aerobic hydrocarbon degrading microorganisms from petroleum contaminated soil. These bacteria including *Gordonia*, *Brevibacterium*, *Aeromicrobium*, *Dietzia*, Burk*holderia*, and *Mycobacterium*, however, *Sphingomonas* were found active in sites contaminated with polyaromatic hydrocarbons [65]. Fungi genera were found in considerable number in petroleum hydrocarbons contaminated soil. For example, [66] and [67] have listed 31 genera of hydrocarbon degrading fungi which were isolated from marine environments. In the last decade, some fungal genera were isolated from petroleum contaminated soil namely: *Amorphoteca*, *Neosartorya*, *Talaromyces*, *Graphium*, *Aspergillus*, *Cephalosporium* and *Pencillium* [64, 68]. Yeast genera were also isolated from the similar sites, and these genera included: *Candid*a, *C. lipolytica*, *Rhodotorula mucilaginosa*, *Geotrichum* sp, *Trichsporon mucoides*, *Yarrowia*, and *Pichia* [62, 69].

Algae and protozoa have also been reported to remediate and degrade petroleum hydrocarbons. However, studies are scanty regarding their involvement in the biodegradation of petroleum hydrocarbons [62]. [70] isolated an alga, *Prototheca zopfi* which is capable to degrade various types of hydrocarbons of crude oil; aliphatic and aromatic compounds. [71] have shown that many autotrophic simple organisms are capable of oxidizing naphthalene, and these organisms include nine cyanobacteria, five green algae, one red algae, one brown algae, and two diatoms. [72] have reported large number of enzymes from microorganisms like bacteria and fungi, and higher green plants to be involved in the bioremediation of toxic organic pollutants. The main microbial enzymes in bioremediation belong to the main groups, these are oxidoreductases and hydrolases. The oxidoreductases include: microbial oxidoreductases, microbial oxygenases, microbial monooxygenases, dioxygenases, laccases, and microbial peroxidases. The latter group includes many secondary groups like microbial lignin peroxidases, microbial manganese peroxidases and microbial versatile peroxidase. On the other hand, hydrolases include three enzymes: lipase, cellulase and protease.

Soil microorganisms are adapted to a wide range of environmental conditions of salinity, drought, temperature, oxygen, and various levels of petroleum hydrocarbons and hazardous compounds. Plants are normally colonized by various types of microorganisms like bacteria, fungi, algae or protozoa, and these plants offer a wide diversity of habitats including (a) phyllosphere (aerial parts), (b) rhizosphere (the zone of root system and its surrounding), (c) endosphere (internal transport system). Such relationships may be detrimental or beneficial for either the microorganisms or the plant, and can be classified as neutralism, commensalism, synergism, mutualism, amensalism (a symbiotic relationship between organisms in which one species is harmed or inhibited and the other species is unaffected), competition or parasitism [73, 74]. However, a great deal of attention has been paid to bacteria, fungi, and algae in the degradation of petroleum hydrocarbons in soils and waters in many countries. These microorganisms can destroy or immobilize organic contaminants by a bioremediation process. The list of these microorganisms includes at least 25 bacterial genera: *Acidovorax*, *Alcaligenes*, *Arthrobacter*, *Mycobacterium*, *Pseudomonas*, *Rhodococcus*, *Sphingomonas*, *Xanthomonas*, *Achromobacter*, *Micrococcus*, *Acinetobacter*, *Norcardia*, *Bacillus*, *Proteus*, *Brevibacterium*, *Sarcina*, *Chromobacterium*, *Serratia*, *Corynebacterium*, *Spirillum*, *Cytophaga*, *Streptomyces*, *Erwinia*, *Vibrio*, and *Flavobacterium* [8]. The fungi include at least 38 genera: *Cunninghamella*, *Fusarium*, *Penicillium*, *Phanerochaete*, *Acremonium*, *Monilia*, *Aspergillus*, *Mortierella*, *Aureobasidium*, *Paecilomyces*, *Beauveria*, *Phoma*, *Botrytis*, *Rhodotorula*, *Candida*, *Saccharamyces*, *Chrysosporium*, *Scolerobasidium*, *Cladosporium*, *Sporobolomyces*, *Cochliobolus*, *Sprotrichum*, *Cylindrocarpon*, *Spicaria*, *Debaryomyces*, *Syncephalastrum*, *Geotrichum*, *Tolypocladium*, *Gliocladium*, *Torulopsis*, *Graphium*, *Trichoderma*, *Humicola*, and *Verticillum* [61]. Some of these genera are found among the flora of Qatari soils [75, 76, 77, 78, 79]. Moreover, algae can be used as phytoremediators to clean contaminated waters with various types of heavy metals and petroleum hydrocarbons in various parts of the world including oceans and lakes [80**,** 81, 82]. In fact, algae have been recognized as important living groups to control metal concentration in lakes, ponds, rivers, oceans as well as wetland habitats. *Chlorella* is a good example of an alga capable of accumulating heavy metals [83]. In fact, algae play an important role in controlling metal concentrations and possibly organic contaminants in lakes, ponds … etc. For example, [84] have investigated the ability of algae to remediate As and B in some springs from Sang-E- Noghreh area, Iran. The results showed many living organisms from four major divisions like chlorophyta, cyanophyta, euglenophyta and heterokontophyta can be used to remediate these metals efficiently. It is believed that algal flora have absorbed and accumulated these elements from their environment into their bodies.

Evaluation of Phytoremediation:

Any remediation method of any adverse factor could have advantages and disadvantages during the mitigation processes. Phytoremediation process is not exception of this rule. Looking at the available literature the following are the advantages of phytoremediation: (1) it is a natural process, less invasive and destructive, and cheap technology, (2) the bio-degraded products are either immobilized in the soil or metabolized in the plant. Thus, the dangerous compounds especially the organic ones are transformed to harmless products, avoiding any future contamination, (3) the complete destruction of contaminants is possible, (4) it promotes biodiversity and helps accelerate the restoration of processes, (5) It can improve the aesthetics of the contaminated sites and may promote better air or water quality of the contaminated site, (6) the growing plants in the phytoremediation site may reduce erosion, and these plants may provide shade to building and serve as a carbon sink to help sequester carbon emitted from other sources, and (7) it avoids the dramatic landscape disruption and preserve the ecosystem [9, 10, 23]. However, there are some possible disadvantages of phytoremediation which have been reported in the literature [23, 35]: (1) not all compounds can be degraded and absorbed completely or substantially, (2) some degraded products are more toxic than the original compounds, (3) the biodegradation by microorganisms is a specific processes, and not all sites have the appropriate bacteria or fungi for complete degradation of petroleum hydrocarbons. Some sites might not have appropriate levels of growth condition for active microbial metabolism, (4) some biodegradation processes of plants and the associated microbes are too slow and take very long time for complete degradation [35]. In fact, there is a limited knowledge of the basic remedial methods that are used by a particular plant species [10], (5) plants used for the remediation process in some soils should be selected carefully, some plants have morphological and structural characteristics not suitable for all sites [35], (6) determination of the final endpoints of phytoremediation treatments is another concern; there is no acceptable performance, (7) it is difficult to extrapolate all the outcomes of academic experiments to the field., (8) the biomass of the harvested plants might be another problem of pollution. Contaminants may enter the food chain through animals that eat the harvested biomass unless it is disposed properly or finding suitable industry to extract the accumulated chemicals especially heavy metals and (9) In the field, the interaction between soil, contaminants, microbes and plants is a complex one; it is affected by a variety of climatic and soil factors. It is difficult to make a generalization of the outcomes of each trial; it is a site-specific as far as the phytoremediation practices are concerned [10].

NATIVE PLANTS IN QATAR

Concerning the plant species inhabiting the land across the State of Qatar that have been used in many studies of phytoremediation of pollutants from soils and waters elsewhere of the world included: **(1)** *Typha domingensis* Pers.: this plant has been used in phytoremediation studies to remove heavy metals from industrial wastewater and solution cultures [29, 58]. In a previous study, [55] have shown that *Typha latifolia* L was capable to accumulate and translocate cadmium ion (Cd^{2+}) from roots to shoots and their defense mechanisms induced by Cd^{2+} at the levels of thiol metabolism and antioxidant enzyme activity, **(2)** *Phragmites australis*: this species has been used in the phytoremediation of petroleum-polluted soils in China [8, 52]. Also, this plant has been tested as a good choice to accumulate Cd^{2+} in various organs with the defense mechanism induced by Cd^{2+} at the levels of thiol metabolism and antioxidant enzyme activity [55]. They concluded that such wetland species were useful for the cleaning of eutrophic lakes and waste waters, as well as contaminated soils. The above plants and other wetland plant species like *Typha latifolia*, *Phragmites communis*, *Nuphar lutea*, *Ceratophyllum demersum*, *Salvinia natans* and *Hydrocharis morsus-ranae* that grow in some fish ponds proved efficient in accumulating heavy metals including Cd, Zn, Cu, Pb, Fe, Mn and Ni [14]. Other aquatic plants (Cattail: *Typha domingensis*, duckweed: *Lemna obscura*, hydrilla: *Hydrilla verticillata* Royle, and swamp lily: *Crinum americanum*) were used to remove Se from aqueous solutions. Some authors [8] have listed various plant species that are able to tolerate high concentrations of petroleum hydrocarbons and those that are used in the cleaning oil-contaminated soils. Among these plants are species belong to the genera of *Typha* and *Phragmites*. In 2011 *Typha domingensis* was used to remediate contaminants of heavy metals from industrial wastewater, soil and sediments from ponds, El-Sadat city, Egypt [58]. In this study, the ability of *Typha domingensis* to absorb heavy metals (aluminum, iron, zinc and lead) as well as its potential application for phytoremediation was assessed. This plant proved capable of accumulating these elements in different plant organs especially in roots and old leaves. Rhizofiltration mechanism was found to be the best method to explain the capability of *Typha domingensis* in phytoremediation. Such plant seemed to have two secondary avoidance mechanisms to deal with high concentrations of heavy metals. The first one is operating between root system and shoot system, while the second mechanism is operating in the shoot systems; extra ions are excluded to the old leaves to avoid any disturbances in the plant metabolism in the active sites of the shoot system. Such plant might shed of old salt-saturated leaves to avoid the damage caused by extra salt accumulation [85]. In another study, [52] have examined how plant ecophysiological traits, soil nutrients and microbial activities were influenced by petroleum pollution in a phytoremediating species of *Phragmites australis*. The outcomes of this study can be summarized as follows: (a) petroleum pollution reduced plant performance especially at the early stages of plant growth; (b) petroleum compounds had negative effects on the net accumulation of inorganic nitrogen from its organic forms by decreasing the inorganic nitrogen available to the plants; (c) quantification of hydrocarbon-degrading bacterial traits based on their catabolic genes, and it was found that the plant's ability of phytoremediating different components of petroleum hydrocarbons might vary during the plant life cycle. Therefore, they have come to the conclusion that phytoremediation was most effective during the vegetative growth stages as greater abundances of hydrocarbon-degrading bacteria containing genes that code some traits for such degradation. Also, the effects of wastewater; which was rich in nitrogen and have high levels of salinity-alkalinity, were studied on some photosynthetic parameters of *Phragmites australis* [86]. These parameters included photosynthesis rate, chlorophyll fluorescence characteristics, and chlorophyll content were reduced in this plant under these conditions. They concluded that such agricultural wastewater may be helpful in restoration of *Phragmites*-dominated salinized wetland, **(3)** *Chloris gayana* (Poaceae) is known by its common name as Rhodes grass. It is native plant and can be cultivated in many parts of the world including the Middle East as livestock feed and ground cover to reduce erosion and to re-cultivate denuded soil. Browsing the available literature, little information has been reported concerning the phytoremediation of soil contaminated with petroleum hydrocarbons using this grass. However, this plant can tolerate moderately saline and alkaline soils and could be efficient in removing toxic elements from soils; it was used to remove some heavy metals from contaminated soil especially As, Pb, and Zn [87]. Rhodes grass proved efficient in the metalliferous mined land re-vegetation program in many parts of the world especially in the subtropical and tropical areas. However, [88] using hydroponic system showed clearly that Rhodes grass was sensitive to Cu which caused some damages to plant roots at a concentration of < 1 µM, **(4)** *Medicago* spp. (Fabaceae): legumes have an advantage over other plant groups in phytoremediation because of their ability to fix nitrogen under condition of oil-contaminated soils [8, 89]. In fact, the interaction between the nitrogen fixing bacteria such as rhizobia and the legume plants such as *Medicago* spp. forms a symbiotic association called nodules, which are able to fix atmospheric nitrogen as ammonia, and after a few reactions in the plant tissues, ammonia enters the metabolic pathways that end in amino acids and proteins. Such association has proved successful in remediating PHCs (Petroleum Hydrocarbons) and heavy metal contaminated soils [90]. In the flora of Qatar two main species namely *Medicago laciniata* and *medicago polymorpha* are native plants, and can be tested as option in the phytoremediation, however, *Medicago sativa* has been cultivated and used as fodder in the State of Qatar and this species has been proved efficient in the phytoremediation of soil polluted with petroleum compounds [8]. The study of [91] on twenty genotypes of *Medicago sativa* showed that the overall agronomic performance is reduced in soil contaminated with crude oil, but variability exists among these genotypes in their growth and phytoremediation capabilities of contaminated soils. Another study [92] on three plant species namely: alfalfa (*Medicago sativa*), switch grass (*Panicum virgatum*), and little bluestem grass (*Schizachyrium scoparium*), to assess the potential of phytoremediation of soil of manufactured gas plant contaminated with PAHs (Polynuclear Aromatic Hydrocarbons). The study of [93] showed that *Medicago sativa* could be used as effective and low-cost remediation option for TNT (Trinitrotoluene) and PCBs (Polychlorinated Biphenyls) contaminated soil of low organic matter content. [94] conducted a study using alfalfa to remediate soil contaminated with heavy metals like Cd, Ni, and Pb, and providing nutrients like Mg, Fe, Zn, Mn and Cu, vermicompost was added to support the remediation processes. Finally, the study of [95] showed clearly that *Medicago sativa* was efficient to remediate soil contaminated with PCBs (Polychlorinated Biphenyls) especially when RAMEB (Randomly Methylated Beta-cyclodextrins) mixture was added. RAMEB is a complex compound enhances aerobic biodegradation of PCBs by increasing pollutant bioavailability in soil microcosms, **(5)** Barley plant (*Hordeum vulgare*) is a crop plant; tolerant to salinity and drought [96, 97, 98, 99, 100, 101], and proved efficient in removing salts from soils and might be good option in phytoremediation programs [102]. The data of [25] showed clearly that this plant could be used to remove some heavy metals from soil. In fact, the success of phytoextraction as a mechanism of phytoremediation carried out by crop plants depends on four main characteristics: (a) the ability of plants to produce large amount of biomass, (b) the tolerance mechanism of plants to heavy metals, (c) the efficiency of plants to translocate metals from the root system to the shoot system, and (d) the metal species and its site in the cell organelles [103]. Many crop plants including sweet sorghum, oat, barley, maize, and sunflower proved efficient in accumulating toxic metals, **(6)** Brassicaceae: members of this family are very good choice in phytoremediation of heavy metals [25, 45, 104]. The wild mustards (*Sinapis arvensis* L.) was used as a test plant in soil contaminated with toxic metals [105], **(7)** *Juncus rigidus* Desf. members of the family Juncaceae might be used in phytoremediation [106], **(8)** *Tamarix* spp., species of this genus had been used to produce wood by growing them in arid lands and irrigated them with salty effluent from desalinization plants or with recycled sewage [107], **(9)** *Prosopis Juliflora*: this tree can be used in phytoremediation of heavy metals [108, 109], and **(10)** *Glycine max* has been successfully used in removing toxic petroleum products from the contaminated soil [31].

Most of the above plants have been found in ponds of wastewaters in Doha like Abu Nakhla wetland, this pond contains some aquatic plants like *Phragmites australis*, *Typha domingensis*, *Rumex dentatis*, *Sporobolus arabicus* and *Juncus rigidus*. Moreover, *Tamarix ramosissima* and *Tetraena qatarense* as terrestrial plant species can be found in such wetland area as well [75, 110].

METABOLISM OF PETROLEUM HYDROCARBONS

As a result of the great industrial and human activities, and urbanization in many parts of the world especially in the oil and gas producing countries, organic contaminants accumulate causing a lot of disturbances and damages to many sectors of life including economy, health and agriculture [8, 18, 23, 31, 61, 93, 111]. The analysis of data during the last two decades revealed the essential role of living organisms in cleaning the contaminated environment. [112] has stated that phytotechnologies are now offering efficient tools and environmentally friendly solutions for the cleanup of soils and water contaminated by organic pollutants. In addition to the accumulation of heavy metals, plants are able to carry out degradation processes leading to complete or partial decomposition of organic contaminants. In fact, it is very essential to understand how plants can accumulate, detoxify and metabolize organic contaminants [111] Thus, from the techniques of phytoremediation discussed in the introduction of this report, there are at least four methods can be used by plants and the associated microorganisms to remediate soil and wastewater contaminated with petroleum hydrocarbons: (1) phyto-degradation or phyto-transformation, (2) phyto-extraction, (3) phyto-volatilization, and (4) rhizosphere biodegradation [113, 114]:

(1) Phyto-degradation (phyto-transformation): it is the breakdown of organic pollutants by external and/or internal metabolic processes driven by plants. *Ex planta* metabolic processes hydrolyze organic compounds into small units that can be absorbed by the plant. Such activities can be controlled and catalyzed by extracellular enzymes and / or membrane bound enzymes. Extracellular enzymes are secreted by root cells to the outside of cells; these are used for degrading large molecules into small ones [115]. Also, some organic contaminants may be absorbed and broken down by the internal enzymes. The penetration of petroleum hydrocarbons into roots occurs mainly by simple diffusion through unsuberized cell walls, and it seems that there are no specific transporters for these compounds in the plasma membranes, thus the movement of these compounds depends largely on their physicochemical properties. The absorbed substances diffuse in the free spaces of the root, some of which adsorbed at the apoplastic system, such substances may be excreted to the outside of the cell [114]. However, the main substances that enter the cells distribute and accumulate in the tissues. Modification of these compounds takes place through series of reactions like oxidation, reduction and / or hydrolysis followed by conjugation with some cellular components such as glutathione (GSH), sugars or organic acids [116]. Such reactions and activities may end in decreasing the toxicity of these organic components and / or contributing in the metabolism what is called Green Liver Model [117, 116]. Thus, the organic small units resulted from the above activities can be used as metabolites by the plant as it grows and are incorporated into plant cells and tissues [114]. The phytotransformation of organic contaminants following their uptake by plant cells can be categorized into different fates and phases. [118] have reported three phases: (a) phase 1 is the conversion of these compounds by enzymatic transformation including oxidation, reduction, hydrolysis, … etc., (b) phase 2 is the conjugation of compounds produced from phase 1 with some important biological molecules like glutathione, sugars, amino acids, … etc., and (c) phase 3 is the compartmentation of the conjugates and / or the molecules that are produced from further conjugation in the vacuoles or bound to cell wall components [115]. However, some other workers have identified different fates of organic contaminants following their uptake by plant roots [9, 61,111, 116]: (1) translocation to other plant tissues and may be volatilized, (2) undergo partial or complete degradation, (3) transformation of toxic organic components into less toxic compounds and bound in plant tissues to non available forms. [114] have discussed the different processes that taking place in plants to deal with these organic contaminants. Some organic pollutants are excreted outside the plant cell when they are not undergoing any transformation, such secretion is rather rare, and if it happens, it does so at very high concentrations and of highly mobile compounds. However, according to Sandermann's green liver concept, substantial amounts of contaminants undergo enzymatic transformations [117] which can be summarized as follows: (a) functionalization: it is the addition of functional groups like hydroxyl, carboxyl, or amino, to the organic contaminants, thereby increasing their affinity to enzymes and become liable of transformation, (b) conjugation: this might take place either on parent organic contaminants and / or on the functionalized organic contaminants. These compounds can be conjugated with some cell components including proteins, peptides, amino acids, organic acids, mono-, oligo-polysaccharides, lignin, … etc by covalent bonds like peptide, ether, ester, thioether, … etc. Many enzymes are involved in the conjugation processes including: transferases: Glutathione S-transferase (GST), glucuronozyl-O-transferase, malonyl-O-transferase, glucosyl-O-transferase, … etc. (c) comparmentation: there are two main cell organelles can accommodate the conjugated compounds; vacuoles and cell wall components. Normally soluble conjugates toxic compounds can be stored in vacuoles avoiding the active metabolic sites of the cell; cytoplasm and other cell organelles, while the insoluble compounds can be coupled with cell wall components to be excreted outside the cell by exocytosis mechanism [114]. Such system is almost analogous to that found in mammalian liver; then such system in plants was termed Green Liver Model [117], (d) deep oxidation: it has been considered as the most advantageous pathway of organic contaminants transformation in plants. There are many enzymes involved in the deep oxidation like: cytochrome P450-containing monooxygenese, peroxidase and phenoloxidase. With the presence of atmospheric oxygen, super oxide anion radical (O^{2-}) and hydroxyl radical (**.**OH) are formed and with further oxidation reactions, benzene and phenolic compounds are produced as well as water and carbon dioxide [114],

(2) Phyto-extraction (Phyto-accumulation): it is the containment method that plants can bind or neutralize contaminants, and thus organic components are not necessarily degraded when they enter the plant cell [61], instead may be sequestered in the vacuole,

(3) Phyto-volatilization: many plants have the ability to volatilize organic contaminants that have been taken up through its roots as a natural air-stripping pump system [61,119], and

(4) Rhizosphere biodegradation: the direct or indirect role of plants to degrade the organic compounds will end to simple components, less harmful and less persistent like alcohol, acids, carbon dioxide and water [61]. Although little information are available about the direct degradation of petroleum hydrocarbons, Fig-1 shows the possible pathway has been found in some plants like corn seedlings, tea and poplar shoots [120].

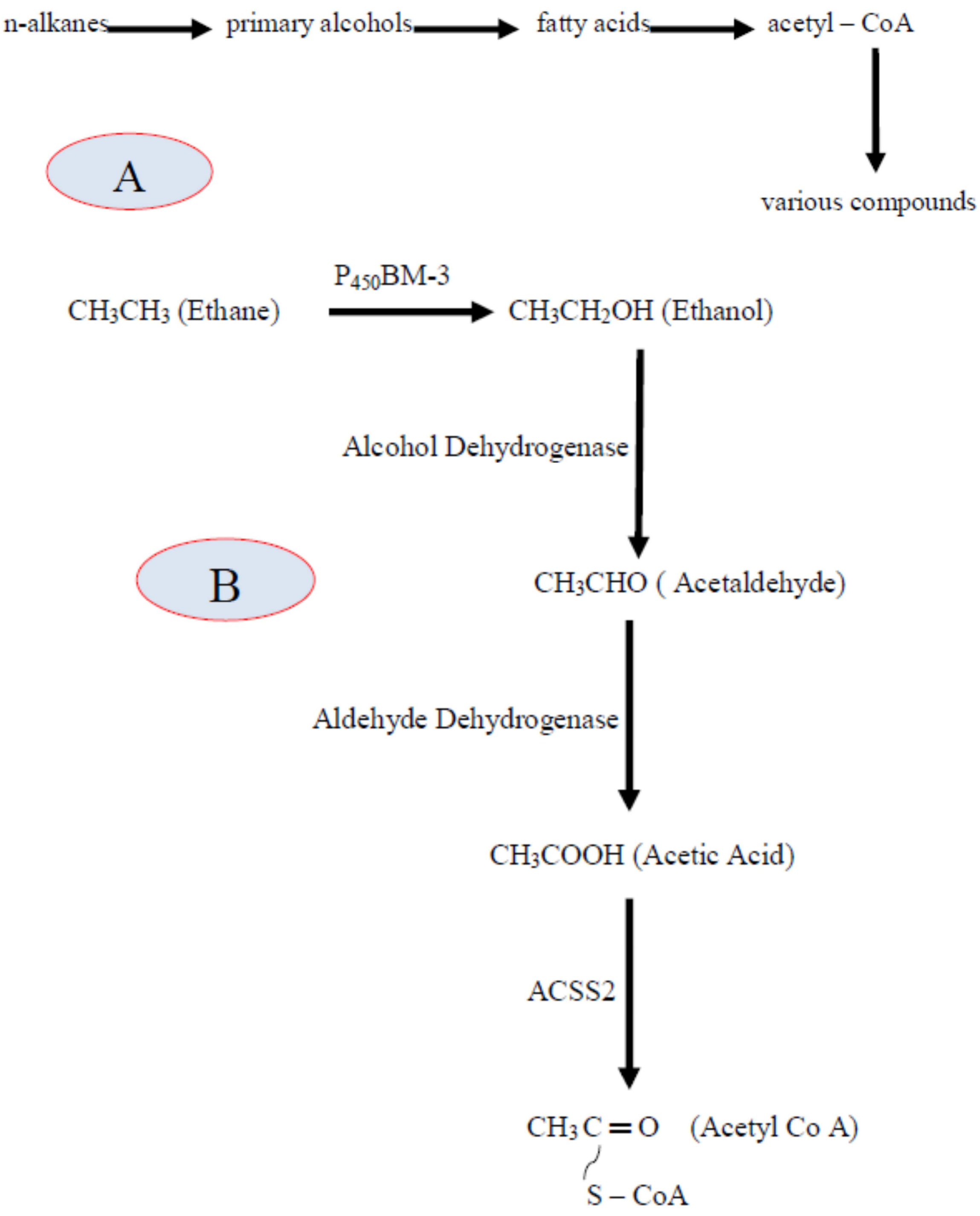

Fig: 1, Possible direct pathway of the degradation of petroleum hydrocarbons (Diagram, A) and (Reactions, B) inside plant tissues leading to acetyl Co A.

Thus, the degradation of aliphatic hydrocarbons may lead to the biosynthesis of many key compounds of the central intermediary metabolism. For example, acetyl Co A is a precursor for many key metabolites of Krebs cycle and the biosynthesis of fatty acids [11]. Also, aromatic hydrocarbons can be degraded which leads to the formation of phenolic compounds like catechol and muconic acid, and further reactions may lead to fumaric acid (Fig- 2) and other tricarboxylic acid cycle intermediates [62,114].

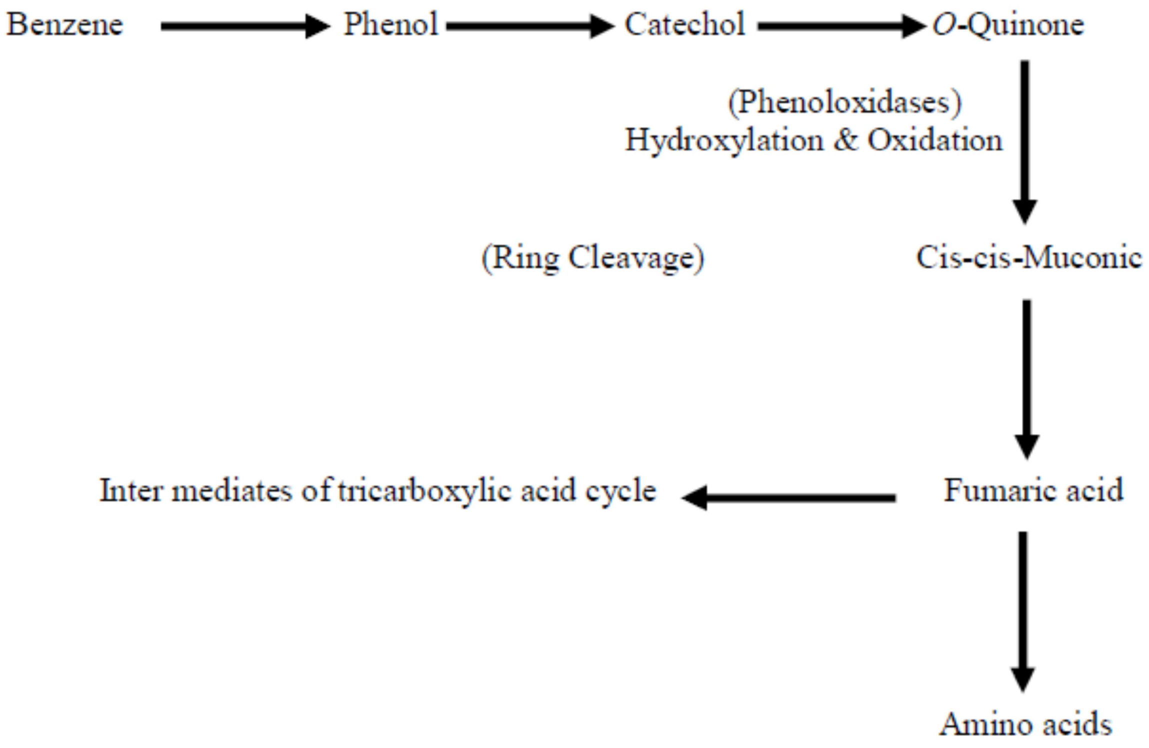

Fig: 2, Degradation of aromatic hydrocarbons inside the plant tissues may lead to fumaric acid and other metabolites.

Indirect degradation, on the other hand, has gained a great deal of attention and there have been huge information in the literature about the different methods that plants and their root system can use to degrade organic components. For example, root exudates can be considered as a link between plants and their associated microorganisms, which might enhance co-metabolic degradation. Co-metabolism is a process that a compound can be modified with the presence of another growth supporting substrate. For example, plant exudates were served as co-metabolites during the biodegradation of (^{14}C) pyrene in the rhizosphere of crested wheat grass [121]. Another indirect role of plants, the root associated enzymes may help transform organic pollutants; many enzymes are possible catalyzing agents like: dehalogenase, nitroreductase, peroxidase, laccase and nitrilase. Moreover, soil conditions may change as a result of physical and chemical effects of plants and their root system [122, 61]. Moreover, the role of micro-organisms should be considered here apart of their roles in the absence of plants. Many aspects are of concern including the types of micro-organisms and their communities, the aim of degradation and the different pathways to achieve it, and the roles they play in reducing phytotoxicity to plants [8, 61]. [123] have shown that total petroleum hydrocarbon (TPH) disappeared from rhizosphere soil using winter wheat faster than the non-rhizosphere soil. It seems that such plant promoted the degradation of petroleum components by microorganisms which were associated with increased catalase activity at the rhizosphere.

HEAVY METAL ACCUMULATION IN PLANTS

Industrial wastewater could have negative impact on various sectors of human life; not only because of their content of organic pollutants but its content of inorganic components mainly heavy metals may cause great disruptive influence on the biological systems as well as disturbing the environment and ecosystem [49, 55, 57, 124]. Looking at the heavy metals, as mentioned above, some of these heavy metals are essential for plant life like Fe, Mn, Zn, Cu, Mo and Ni, while others either are not essential such as Cd, Al, V, Cr, Pb and Hg, or are being considered as essential like Co and Se [11]. Most plants are able to accumulate heavy metals from soil and water, but these heavy metals become toxic when their concentrations exceed certain limits [10, 125]. Remediation of inorganic elements from soil, water and air is impossible because they are unlike organic pollutants cannot be degraded. Thus, the best way to remediate soil or water contaminated with heavy metals is to use algae or plants that are able to absorb them by phytoremediation; this process is called metaphorically as phytomining [126, 127, 128]. Crude oil is rich of heavy metals like Ni, V, Cu, Cd, and Pb [12], while some other heavy metals associated with crude gas like Hg, As and possibly other elements and compounds containing sulfur, halogen compounds (containing chlorine and fluorine), nitrogen compounds like amines, ammonia and nitrogen oxides [13]. Looking at the available literature, the following are some results, conclusions, plants involved, and the pattern of heavy metal accumulation in different plant organs. [29] were trying to assess the ability of some aquatic plants like Cattail (*Typha domingensis*), duckweed (*Lemna obscura*), hydrilla (*Hydrilla verticillata* Royle), and swamp lily (*Crinum americanum*) to remove Se from aqueous solutions. The potential of these plants as phytoremediating agents depends upon the concentration of Se in solution media. At concentrations of 100 ppm or less, these plants proved good to excellent in removing this element, about 65 to 100% of the total Se was removed, depending on the plant species. Exposure to concentrations greater than 100 ppm had an inhibitory effect on plant growth. Willow (*Salix* spp.) was tested to remediate soil contaminated with heavy metals that are normally associated with crude oil and gas [49]. These researchers found that heavy metals have different patterns of behavior and mobility within the trees. Pb, Cr and Cu tend to be held in the root system, while Cd, Ni and Zn are translocated to the shoot system. [37] found that *Petris vittata* was effective in volatilizing As, since it removed about 90 % of the total uptake of As from soil. [124] used unicellular green alga *Dunaliella salina* to remediate Lake Mariut, Alexandria, Egypt, from some heavy metals including Cu, Co, Cd and Zn. This organism showed high tendency to accumulate Zn followed by Cu and Co, the lowest tendency was for Cd. [129] has concluded that modification of the rhizosphere environment may improve the bioavailability of pollutants, and increasing the mobilization of metals, thereby enhancing their uptake, sequestration and / or metabolism. [14] working on some aquatic plants like *Phragmites communis* growing in Ecka fish pond in the republic of Serbia, they found that most heavy metals accumulated in the rhizomes and stalks. [130] have stated that toxic elements such as Hg, As, Cd, Pb, Cu, and Zn, are not involved in all biochemical reactions; thereby remain in the environment causing a lot of disturbances to the biological system. The heavy metals remain in various ecosystems would seep into surface water, groundwater or even channel into the food chain by crops growing on such a soil. These heavy metals may adversely affect many aspects of human life like agricultural product, and water quality as well as the human health [131].

GENETIC APPROACH

Genetic engineering techniques have been considered as a promising approach to improve the growth and development of many crops under various severe environmental conditions like drought, salinity, and in response to biotic factors that causing diseases including plants, animals, bacteria, fungi… etc [132, 133, 134]. Such modern techniques have covered other aspects of plant life, for example the process of phytoremediation can be improved by manipulation and analysis of biochemical processes and gene regulations of desired plants [130]. In fact, these techniques to transfer genes into plants to improve the remediation potential have been suggested by many authors. Genetic engineering approach can facilitate the alteration of the biological functions of plants through modification in the main metabolism activities and by adding new phenotypic and genotypic characters to plants to improve the phytoremediation properties [135].

Various plant groups including legumes, grasses, and various families such as Poaceae, Cyperaceae, Juncaceae, and Typhaceae are very important natural remediators of environmental contaminants, and could be considered as possible experimental material to deal with gene technology. The genetic improvement has been considered as important effort since the introduction of some key genes to plants can improve the remediation potential. For example, [106] have shown that the transfer of key genes for Hg phytoremediation into *Spartina alterniflora* and may be other plants living in various habitats is possible, which could improve the capability of that plant to remediate Hg contaminated wetland in spite of the fact that transferring many genes to a plant to deal with one trait is not easy task. [27] have suggested that breeding plants having high biomass could lead to superior phytoremediation potential in these plants. However, the difficulty of achieving such goal is that the productivity is not controlled by one gene. [136] used chloroplast transformation to enhance the capacity of tobacco (*Nicotiana tabacum*) plant for Hg phytoremediation. [137] have concluded that transgenic plants and associated bacteria bring hope for a broader and more efficient application of phytoremediation for the treatment of organic compounds like polychlorinated biophenyls (PCBs). Thus genetic modification of plants may improve some phytoremediation mechanisms like phytoextraction, phytotransformation, etc, and also improve the bacterial efficiency in biodegradation of those organic compounds (rhizoremediation). The application of gene manipulation and the use of native plants that are metal tolerant and /or efficient in absorption and degradation of organic compounds should be accelerated and transferred from the experimental level to the field [57].

OBJECTIVES AND CURRENT STATUS

During the last three decades, the environment in many oil and gas producing countries become heavily polluted by various contaminants, organic and inorganic, which could cause a great deal of danger for many life aspects including general health of plant, animals and humans, agriculture, economy, and wild life. In Qatar, the University of Qatar (QU) has signed contracts with some energy, gas and oil companies to deal with industrial wastewater, for example in October 2012 and in December 2013 QU signed contracts with Exxonmobil Research Qatar and Maersk Oil Qatar respectively to address the industrial wastewater extracted in the production of oil and gas. These projects aim either to use native plants and the associated microbes or using new technologies for water cleaning and purification [138, 139]. The application of phytoremediation processes could save the ecosystem from further deterioration and can be considered as first steps in the restoration programs of endangered habitats [74]. Therefore, the main objective of any future project in Qatar is to recognize native plants and the associated microbes which have the ability to absorb and degrade the contaminants. In fact, if these contaminants involved in the metabolism of these plants, this would solve the problem of the possible future pollution of soil, water and air in the whole region of Arabian Gulf. To begin with there are some steps should be taken to achieve the above objective bearing in mind that such research efforts have not been done before in the State of Qatar. The following executive objectives should be considered: (1) Set up an appropriate system of culture techniques using wastewater from oil and gas fields, (2) Identify wild or cultivated plants that are efficient in removing metals and organic compounds from industrial wastewater and soils, (3) Analyze organic and inorganic components in different plant organs of various plant species and areas around Qatar especially those near the gas and oil fields, and (4) Identify some microorganisms that can play active role in the bioremediation processes.

So far, a Joint project between some energy companies and Qatar University is being carried out to investigate the abilities of native and/or cultivated plant species and the associated microbes to improve the quality of industrial wastewater (IWW) produced during the production and processing of oil and gas through phytoremediation. Some Qatari plants including native aquatic plants like cattail **(***Typha domingensis*) Pers common reed (*Phragmites australis*) and alfalfa (*Medicago laciniata* and *medicago polymorpha*) and cultivated ones (*Medicago sativa*) are tested using this process especially those proved efficient and worldwide used to remove heavy metals and/or to degrade, remove and metabolize petroleum hydrocarbons. There are some good signs that at least some of these plants are able to cope with soil contaminated with IWW, and these plants included: common reed (*Phragmites australis*), and possibly others are able to cope with soil contaminated with petroleum hydrocarbons or other organic pollutants that are normally added during the processing of gas and oil production [140].

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