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# The role of algae in bioremediation of organic pollutants

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The accumulation of organic pollutants in the environment can cause serious problems, affecting negatively the stability of many aquatic ecosystems and can also cause adverse effects to human health and the environment. Organic pollutants are introduced into the aquatic ecosystems as a result of human activities involving agricultural uses, fuel use and industrial discharges, domestic effluents and agricultural runoff. The persistent organic pollutants are toxic substances for environment and human health. Recently, there has been increasing interest on using bacteria, fungi, plants and algae to remove, degrade, or render harmless organic pollutants in aquatic systems. The algae play an important role in controlling and biomonitoring of organic pollutants in aquatic ecosystems. The use of higher plants and bacteria for bioextraction and bioremediation of heavy metals and organic pollutants have been extensively studied. However, the application of microalgae in restoration of organic-polluted aquatic environment has just started. In this review we present an overview of the potential of microalgae species for phytoremediation of organic pollutants in aquatic ecosystems.

**Key words:** Algae, bioremediation, organic pollutants, biodegradation

## INTRODUCTION

The organic pollutants introduced into the environment through industrial discharges, agricultural uses, or improper waste disposal practices. The persistence of these chemicals in the environment poses a chronic threat to the health and safety of human and wildlife (Pavlostathis et al. 2001). Chemical contaminants present in the aquatic ecosystem may be immobilized and accumulated in sediments or may be subject to transformation and activation processes (Martínez-Jerónimo et al., 2008). Depending on biogeochemical processes, many organic pollutants like hydrocarbons are involved in adsorption, desorption and transformation processes and can be made available to benthic organisms as well as organisms in the water column through the sediment-water interface (Perelo 2010).

Hydrocarbons can become dangerous especially if they enter the food-chain, since several of the more persistent compounds, as PAHs and PCBs are carcinogenic (IARC 1983). According to the Stockholm Convention on

Persistent Organic Pollutants, 9 of the 21 persistent organic chemicals are pesticides. Classes of organic pesticides include organochlorine, organophosphate, organometallic, pyrethroids, and carbamates among others (Gilden et al. 2010, Stockholm convention 2011).

Relatively recently, there has been increasing interest on the use of bioremediation as the most desirable technology which uses plants (Phytoremediation) for removal of environmental pollutants or detoxification to make them harmless (Cunningham and Berti 1993). Methods for phytoremediation of contaminated soils, rivers and lakes are described in several reviews (Brooks 1998, Chaney et al. 1997, McIntyre and Lewis 1997, Flathman and Lanza 1998; Salt et al., 1998). Investigation on organic xenobiotics bioaccumulation/biodegradation in green algae is of great importance from environmental point of view because widespread distribution of these compounds in agricultural areas has become one of the major problems in aquatic ecosystem (Jin et al. 2012). The algae proved to be effective

in hyperaccumulation of heavy metals as well as degradation of xenobiotics (Suresh and Ravishankar 2004).

In recent years, the use of microalgae in bioremediation of colored wastewater has attracted great interest due to their central role in carbon dioxide fixation. In addition, the algae biomass generated has great potential as feedstock for biofuel production (Huang et al. 2010). These bioremediation capabilities of microalgae are useful for environmental sustainability (Ellis et al. 2012, Lim et al. 2010).

Worldwide, trees, grasses, herbs, and associated fungi and microorganisms are being used increasingly for cleaning polluted sites. Phytoremediation is "on the brink of commercialization" (Watanabe 1997), and is given a rapidly increasing market potential (Flathman and Lanza 1998). The phytoremediation market is still emerging in Europe, while in the US revenues are likely to exceed \$300 million in 2007 (Campos et al. 2008). In a recent study (Yamamoto et al. 2008), benthic microalgae have been used for the first time in the remediation of organically enriched sediments.

This review aims to give an overview over mechanisms used by microalgae for bioremediation of organic pollutants in aquatic ecosystems and the impact of genetically modified microalgae on xenobiotic degradation to minimize their impact on the environment.

### Bioremediation of petroleum hydrocarbons

The accumulation of petroleum hydrocarbons in the environment can cause serious problems, affecting negatively the stability of many aquatic ecosystems and can also cause difficulties for animals and human health. The amount of natural crude-oil seepage is currently estimated to be 600,000 metric tons per year, with a range of uncertainty of 200,000 to 2,000,000 metric tons per year (Kvenvolden and Cooper 2003).

The bioremediation technology offers a promising tool to treat aerobically oil-contaminated shorelines (Atlas 1991, Rosenberg et al. 1992, Venosa et al. 1992). This technique of decontamination of polluted areas gives much hope on the restoration of polluted mangrove swamps and is being utilized for the degradation of crude oil in soil matrix by using microorganisms, to transform the petroleum hydrocarbons into less toxic compounds (Davies and Westlake 1979, Orji et al. 2012a). This is achieved by the help of bacteria, fungi, algae that produce enzymes capable of degrading harmful organic compounds (Davies and Westlake 1979). In the presence of abundant hydrocarbon in the environment after a spill, microorganisms cannot effectively attack and utilise the hydrocarbon unless limiting nutrients such as nitrate, phosphate, even micro-elements are incorporated into the polluted medium (Van Hamme et al. 2003).

Microalgae and protozoa are the important members of the microbial community in both aquatic and terrestrial

ecosystems however only few reports are available regarding their involvement in hydrocarbon biodegradation (Jain and Bajpai 2012). On the other hand, introduction of hydrocarbon degrading bacteria in oil contaminated sites does not guarantee to remove all components of crude oil because some components still remain difficult to degrade, such as alkanes of shorter and longer chains (<C10 and C20–C40) and polycyclic aromatic hydrocarbons (PAHs) (Yuste et al. 2000).

Several microorganisms can metabolise the nonchlorinated aliphatic and aromatic hydrocarbons as sources of carbon, but due to their hydrophobicity they pass very slowly to the aqueous phase liquid where microorganisms are active (Brusseu 1998). Recently Orji et al. (2012b) reported that the Remediation by Enhanced Natural Attenuation (RENA) is currently being used as a cleanup technology in polluted environments with petroleum hydrocarbon in the Niger Delta including mangrove ecosystems. RENA is a full-scale bioremediation technology in which contaminated soils, sediments and sludge's, are periodically turned over or tilled into the soil to aerate the waste. This technique involves factors such as evaporation, dispersion, spreading, dissolution, oxidation, emulsification and spreading.

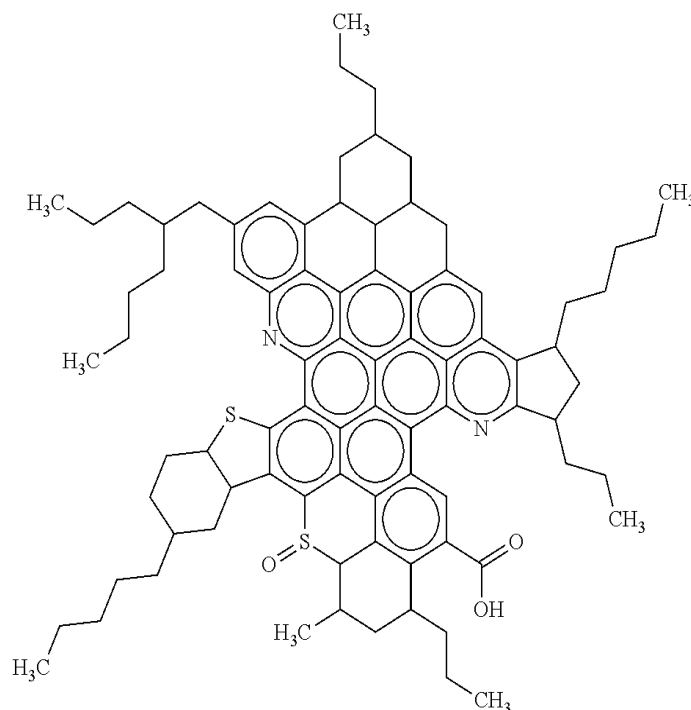
The asphaltenes (Figure 1), the most complex hydrocarbons of the petroleum, contain nitrogen, sulphur and oxygen (Mitra-Kirtley et al., 1993), and are very resistant to the microbial degradation (Guiliano et al. 2000). Pineda-Flores et al. (2001) found that a microbial consortium isolated from crude oil was able to take faster and greater oxygen consumption when it was mixed to asphaltenes as the only source of carbon and energy, and is able to degrade the crude oil too. Some microalgae produce enzymes capable of degrading harmful organic compounds to transform the petroleum hydrocarbons into less toxic compounds (Davies and Westlake 1979).

The microalgae *Scenedesmus obliquus* GH2 (Table 1), is used to construct an artificial microalgal-bacterial consortium for crude-oil degradation (Tang et al. 2010). Addition of the bacterial consortium in different amendments significantly enhanced degradation efficiency of both aliphatic and aromatic hydrocarbons of crude oil. Another consortium of pre-isolated oil-degrading bacteria in association with three species of plants effectively remediated contaminated silt-loam soil more than silt, loam and sandy loam with an average 80% reduction of total petroleum hydrocarbon (Ghosh and Syed 2001).

The presence of the *Rhodococcus* genus, which has been associated with the biodegradation of n-alkanes up to C36, and the high content of heavy alkanes in the Prestige fuel could indicate that *Rhodococcus* has a role in the degradation of fuel (Jiménez et al. 2007).

### Bioremediation of polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls, PCBs (Figure 2), are among the



**Figure 1:** Chemical structure of Asphaltenes from traditional heavy crudes

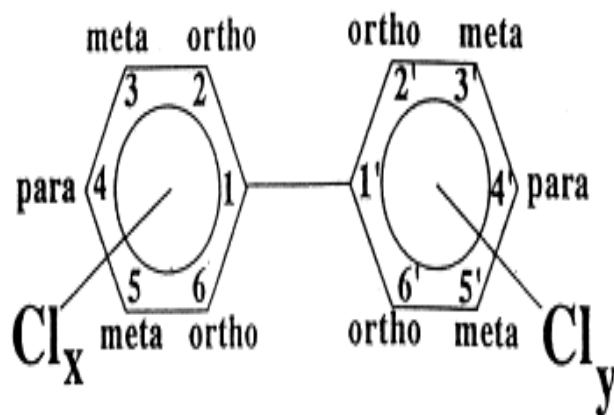
**Table 1:** Organic pollutants accumulation by algal species

Species	Organic pollutant	References
<i>Monoraphidium braunii</i>	bisphenol	Gattullo et al. 2012
<i>Agmenellum quadruplicatum</i>	bisphenol	Cerniglia et al. 1979
<i>Selenastrum capricornutum</i>	Benzene, toluene, naphthalene, phenanthrene, pyrene	Gavrilescu 2010
<i>Scenedesmus obliquus</i> GH2	crude-oil degradation	Tang et al. 2010
consortium of <i>Chlorella sorokiniana</i> and <i>Pseudomonas migulae</i>	Phenanthrene	Muñoz et al. 2003
<i>Scenedesmus quadricauda</i>	Fungicides (dimethomorph and pyrimethanil) and herbicide (isoproturon).	Olette et al. 2010
<i>Phytoplankton</i>	chlorinated hydrocarbons	Harding and Phillips 1978
<i>Chlamydomonas reinhardtii</i>	Herbicide (prometryne)	Jin et al. 2012
<i>Chlamydomonas reinhardtii</i>	Herbicide (fluroxypyr)	Zhang et al. 2011
<i>Monoraphidium braunii</i>	bisphenol	Gattullo et al. 2012
<i>Pediastrum tetras</i> , <i>Ankistrodesmus fusiformis</i>	Herbicide (mesotrione)	Moro et al. 2012
<i>Amphora coffeaeformis</i>		

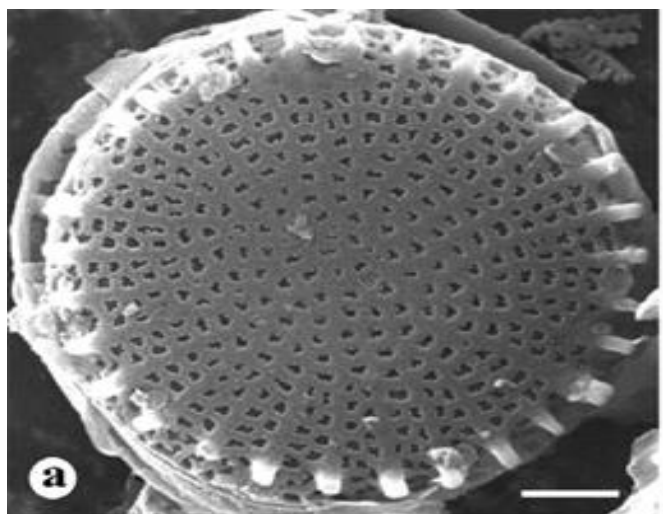
worst pollutants because of their toxicity, carcinogenicity, wide distribution and slow biodegradation in the environment (Perelo 2010, Meagher 2000). Some monohydroxylated PCBs are potent endocrine disruptors (Figure 1C), and some PCB metabolites with a hydroxy group in the meta or para position have been reported to be involved in developmental neurotoxicity (Maltseva et al. 1999).

PCBs were used extensively in a variety of industrial

applications due to their thermal stability and persist in aquatic sediments (Dhankher et al. 2012). Some microorganisms can degrade PCBs aerobically or anaerobically under a variety of conditions (Borja et al. 1999, Pieper and Seeger 2008). PCB degradation is complex as there are many different forms and it has been shown that orthochlorinated PCBs inhibit and inactivate a key enzyme in the degradation pathway, dehydroxybiphenyl oxygenase (Dai et al. 2002). Aerobic



**Figure 2:** Structures of PCBs (numbers 2-6 (2'-6') indicate the possible positions of the chlorine atoms at ortho(o), meta(m) and para(p) positions)



**Figure 3:** *Stephanodiscus minutulus* according to Cruces et al. (2010)

degradation of lower chlorinated PCBs is via co-metabolism by dioxygenases, resulting in ring cleavage and possibly complete mineralization (Dhankher et al., 2012).

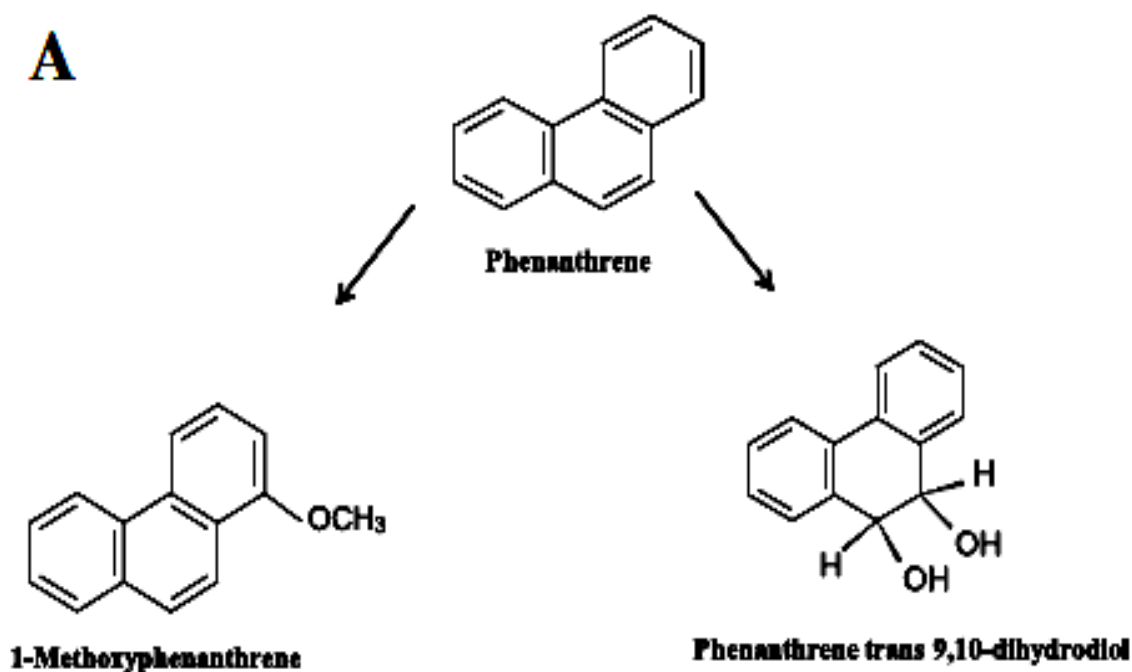
Phytoplankton plays a critical role in controlling the fate of persistent organic pollutants (POPs), such as PCBs in the water column because they are high in lipids and they serve as the base of both the pelagic and benthic food chains (Lynn et al., 2007).

Benthic microalgae have been used for the first time for in situ remediation of the organically enriched sediments (Yamamoto et al. 2008). Previously Harding and Phillips (1978) suggested that marine organisms including phytoplankton can uptake and accumulate several chlorinated hydrocarbons decreasing their concentrations in the media. Lynn et al. (2007) analysed the effect of different nutrient treatments on the uptake of PCB

congener 2,2',6,6'-tetrachlorobiphenyl by the diatom *Stephanodiscus minutulus* (Figure 3) and transfer to a zooplankton (*Daphnia pulex*), and they found that the uptake of PCB by phytoplankton can be significantly altered by nutrient availability which subsequently affects transfer to zooplankton, potentially through such responses as grazing rate and lipid assimilation.

The association of PCBs and live algal cells in rivers was studied by Fitzgerald and Steuer (2006), suggesting a positive relations between particle-associated PCBs and both chlorophyll-a and algal carbon concentrations indicated that live algal cells were a significant sorption phase for dissolved PCBs.

Previously Lara et al. (1989) reported the ability of brown algae *Caepidium antarcticum* and *Desmarestia* sp. to associate their exudates with hydrophobic pollutants such



**Figure 4.** The degradation pathway of Phenanthrene, a PAH compound by the cyanobacteria *Agmenellum quadruplicatum* PR-6 (Narro et al. 1992).

as polychlorinated biphenyls (PCBs). Organic macromolecules in seawater samples and exudates from brown algae *Ascophyllum nodosum* and *Fucus* sp. are able to incorporate organic compounds like amino acids, sugars and fatty acids. PCBs are generally deposited in the lipid stores of organisms and Berglund et al. (2001) found that lipid content explained most of the variation of PCB concentration in phytoplankton in 19 southern Swedish lakes.

Recently Chun et al. (2013) reported that a common limitation is the lack of an effective method of providing electron donors and acceptors to promote in situ PCB biodegradation, and the application of an electric potential to soil/sediment could be an effective means of providing electron-donors/-acceptors to PCB dechlorinating and degrading microorganisms, suggesting that this approach could be a cost-effective, environmentally sustainable strategy to remediate PCBs in situ.

#### **Bioremediation of polycyclic aromatic hydrocarbons (PAHs)**

Polycyclic aromatic hydrocarbons, PAHs, are ubiquitous pollutants in aquatic ecosystems (Figure 4). PAHs naturally occur in fossil fuels such as coal and petroleum, but are also formed during the incomplete combustion of organic materials such as coal, diesel, wood and vegetation

(Freeman and Cattell 1990, Lim et al. 1999). PAHs are a class of organic compounds that consist of two or more fused benzene rings and/or pentacyclic molecules that are arranged in various structural configurations (Bamforth and Singleton 2005). They are highly recalcitrant molecules that can persist in the environment due to their hydrophobicity and low water solubility (Cerniglia 1992). PAHs are produced primarily during fuel combustion and share many properties with PCBs: elevated boiling points, very low solubility in water, high stability and toxicity (Lima et al. 2005).

The phytoremediation of PAHs have limited success due to the high toxicity of this class of pollutants (Dhankher et al. 2012). The accumulation and biodegradation of two typical polycyclic aromatic hydrocarbons (PAHs), phenanthrene (PHE) and fluoranthene (FLA), by the diatoms was studied by Hong et al. (2008), using two algal species *Skeletonema costatum* (Figure 5) and *Nitzschia* sp (Figure 4). The authors found that the accumulation and degradation abilities of *Nitzschia* sp. were higher than those of *S. costatum*. Degradation of FLA by the two algal species was slower, indicating that FLA was a more recalcitrant PAH compound. The microalgal species also showed comparable or higher efficiency in the removal of the PHE-FLA mixture compared with PHE or FLA alone, suggesting that the presence of one PAH stimulated the degradation of the other.

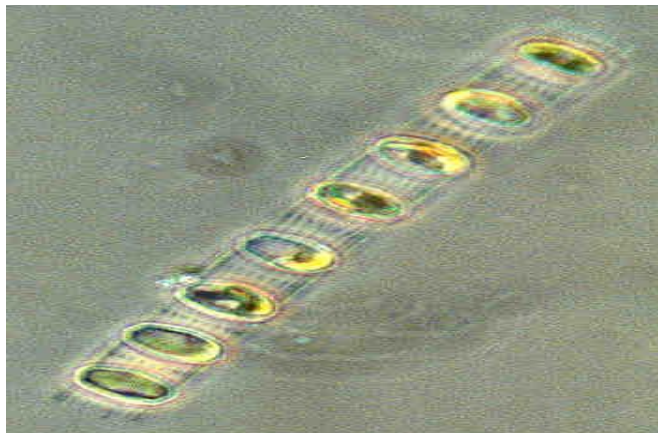


Figure 5: *Skeletonema costatum* according to Hasle and Syvertsen (1996)

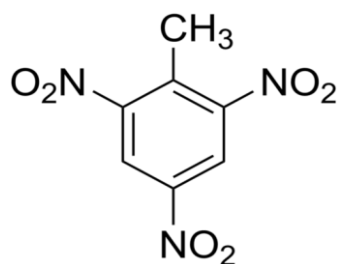


Figure 6: Trinitrotoluene

Muñoz et al. (2006) suggested that it is possible to use microalgae to produce the  $O_2$  required by acclimatized bacteria to biodegrade hazardous pollutants such as polycyclic aromatic hydrocarbons, phenolics, and organic solvents. When PAHs are taken up by microorganisms, they activated in aerobic metabolism by insertion of two oxygen atoms by bacteria and green algae to produce either cis-dihydrodiols or phenols (Al-Turki 2009).

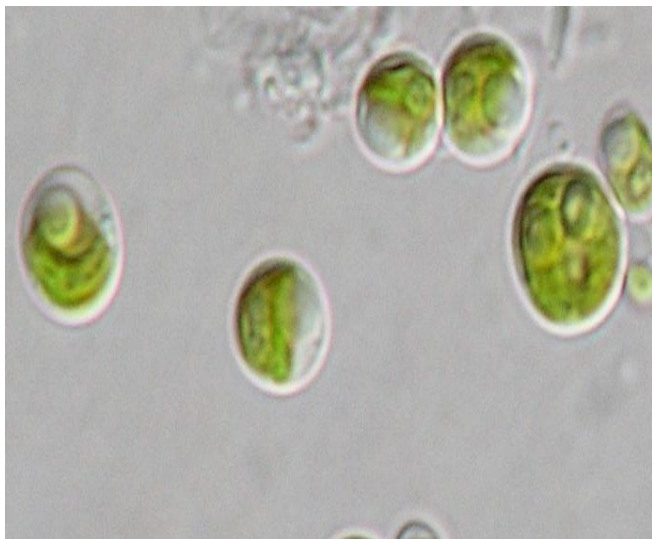
Cerniglia et al. (1980) studied the oxidation of naphthalene by cyanobacteria and microalgae. They found that nine cyanobacteria, five green algae, one red alga, one brown alga, and two diatoms could oxidize naphthalene under photoautotrophic conditions, suggesting that the ability to oxidize naphthalene is widely distributed amongst the algae.

The PAH phenanthrene (PHEN) is a highly toxic pollutant, commonly found in aquatic environments, the effects of which on aquatic plants have not been studied in depth (Burritt 2008). An algal-bacterial consortium formed by *Chlorella sorokiniana* (Figure 7) and a phenanthrene-degrading *Pseudomonas migulae* strain was able to biodegrade 200-500 mg/l of phenanthrene dissolved in silicone oil or tetradecane under photosynthetic conditions and without any external supply of oxygen (Muñoz et al. 2003), suggesting that the microalgae release biosurfactants that could further enhance phenanthrene degradation (Table 1).

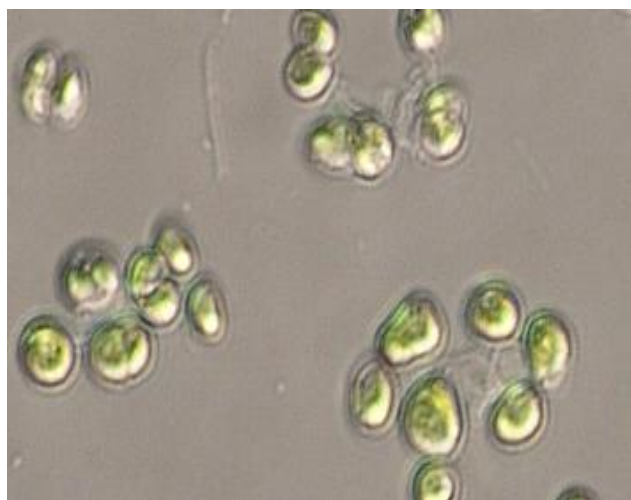
There are many factors that can influence the bioremediation of PAHs, these includes: temperature, oxygen, pH, bioavailability and Toxicity of end-products. Temperature has a considerable effect on the ability of the *in situ* microorganisms to degrade PAHs and, in general, most contaminated sites will not be at the optimum temperature for bioremediation during every season of the year (Bamforth and Singleton 2005). The solubility of PAHs increases with an increase in temperature (Margesin and Schinner 2001), which increases the bioavailability of the PAH molecules. Another factor that can influence PAH degradation is pH of contaminated sites. Phenanthrene degradation in liquid culture has been investigated at a range of pH values (pH 5.5-7.5) with *Burkholderia cocovenenas*, an organism isolated from a petroleum-contaminated soil (Wong et al. 2002). It has also been reported that oxygen play a key role in bioremediation of organic contaminants such as PAHs, and this process can proceed under aerobic and anaerobic conditions (Bamforth and Singleton 2005).

### Bioremediation of explosives (TNT)

Trinitrotoluene (TNT) (Figure 6), used for decades as an explosive, is a pervasive contaminant at many military sites around the world (Glass 2005). To treat-contaminated areas, *in situ* technologies like bioremediation using plants



**Figure 7:** *Chlorella sorokiniana* according to Hasle and Syvertsen (1996)



**Figure 8:** *Dictyosphaerium chlorelloides* according to Hasle and Syvertsen (1996)

and algae are being investigated, and a number of naturally-occurring plants have been shown to have the ability to degrade TNT and other nitroaromatic compounds through the activity of enzymes such as nitrate reductases (Subramanian and Shanks 2003, Wolfe and Hoehamer 2003).

Nitroaromatics form an important group of recalcitrant xenobiotics. Only few aromatic compounds, bearing one nitro group as a substituent of the aromatic ring, are produced as secondary metabolites by microorganisms (Snellinx et al. 2002). The compounds 2,4,6-TNT and 1,3,5-trinitrobenzene are the most toxic substances followed by 3,5-dinitrophenol, 3,5-dinitroaniline and 4-amino-2-nitrotoluene (Neuwoehner et al. 2007).

The nitroaromatic explosive 2,4,6-trinitrotoluene (TNT),

which is relatively soluble in water (Ro et al. 1996), and is generally recalcitrant to biological degradation relative to other xenobiotic compounds (Spain 1995, Esteve-Núñez et al. 2001). TNT dissolved in seawater or adsorbed in marine sediment is toxic to a variety of marine organisms (Won et al. 1976, Green et al. 1999, Nipper et al. 2001).

Previously, Cruz-Uribe and Rorrer (2006) suggested that the marine red alga *Portieria hornemannii* has the capacity to remove TNT from the seawater. The pentaerythritol tetranitrate (PETN) reductase gene from *Enterobacter cloacae* strain PB2 encodes an enzyme that removes nitrate from TNT, allowing the bacteria to use TNT as a nitrogen source (Dhankher et al. 2012).

Some plant species are able to tolerate relatively low levels of TNT, transforming it to an aminodinitrotoluene that is then conjugated to sugars or glutathione, and then probably stored in the vacuole or cell walls, or secreted (Dhankher et al. 2012). Microarray and other gene expression assays have revealed several important classes of enzymes involved in the plant responses to nitroaromatics (Dhankher et al., 2012, Gandia-Herrero et al. 2008). A new genetic approach was developed by Altamirano et al. (2004) to detect TNT in the media. The proposed specific algal biosensor for TNT is based on the use of two different genotypes of the green microalga *Dictyosphaerium chlorelloides* (Figure 8): a sensitive and a resistant strain. The inhibition of chlorophyll *a* fluorescence of PSII by TNT was used as the biological signal. Resistant mutants always exhibited higher value of maximum fluorescence of light-acclimated thylakoids (*F'm*) in the presence of TNT than sensitive wild-type cells.

The plants contain many enzymes that can degrade organic pollutants, among these are nitroreductase, useful for degrading TNT and other nitroaromatics, dehalogenases, for degradation of chlorinated solvents and pesticides, and laccases, for metabolism of anilines (e.g., triaminotoluene) (Schnoor et al. 1995, Boyajian and Carreira 1997). Some plant species are able to tolerate relatively low levels of TNT, transforming it to an aminodinitrotoluene that is then conjugated to sugars or glutathione, and then probably stored in the vacuole or cell walls, or secreted (Dhankher et al. 2012).

Investigating the evolutionary adaptation of a microalgae to increasing concentrations of the contaminant 2,4,6-trinitrotoluene (TNT), García-Villada et al. (2002) suggested that rare spontaneous preselective mutants seem to be enough to ensure the survival of microalgae after a catastrophic environmental change resulting from water contamination by TNT and reselected microalgae will have no problem proliferating in a polluted biosphere.

Using axenic plantlets derived from three species of marine macroalgae, the green alga *Acrosiphonia coalita* and the red algae *Porphyra yezoensis* and *Portieria hornemannii*, Cruz-Uribe et al. (2007) found that all algal species possessed a similar metabolic route to remove the

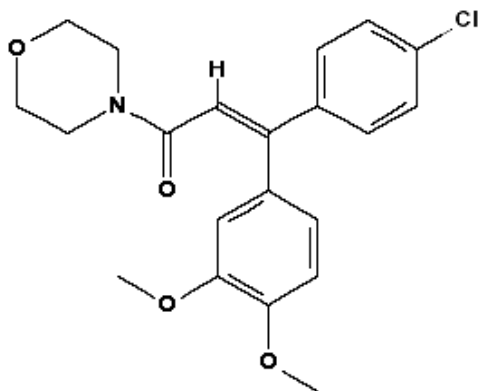


Figure 9: Dimethomorph (fungicide)

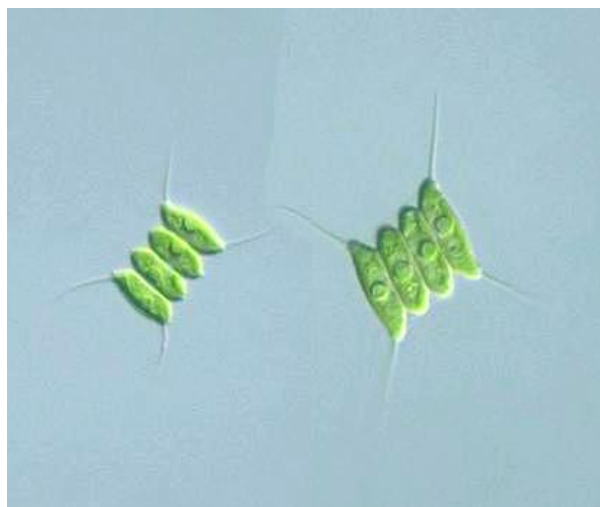


Figure 10: *Scenedesmus quadricauda* (The Japanese Fresh-water Algae)

explosive compound 2,4,6-trinitrotoluene (TNT) from seawater and all species reduced TNT to 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, but these products never accounted for more than 20% of the initial TNT.

### Bioremediation of Pesticides

The Aquatic systems contamination by pesticides is one of the most serious problems that might face the environment and organisms as a whole. The intensively cultivated agricultural areas are significant sources of surface water contamination by pesticides via spray drift and/or run-off (Kloepfel et al. 1997; Shultz 2001; Olette et al. 2010). Extensive use of herbicides in agriculture is accompanied by the risk of environmental contamination of aquatic ecosystems (Moro et al. 2012). Once in the aquatic environment, these chemicals have the potential to induce adverse effects on ecosystem health (Moore et al. 2007).



Figure 11: *Chlamydomonas reinhardtii* according to Shao et al. (2008)

Organochlorine pesticides are ubiquitous environmental pollutants in the global ecosystem and, due to their lipophilicity and persistency; they accumulate along the food chain (Loganathan and Kannan, 1991, Voldner and Li 1995). In developing countries, pesticides are the cause of up to one million cases of intoxication and up to 20,000 deaths a year (Duran-Nah and Colli-Quintal 2000).

Multiple methods including incineration and land filling have been used to remove this class of pollutants; however, these physical methods are expensive and inefficient. Bioremediation using microorganisms capable of degrading the polluting pesticide and enhanced phytoremediation of pesticides using transgenic plants are emerging as more effective solutions (Hussain et al. 2009).

Olette et al. (2008) have studied the capacity of aquatic plants, *Lemna minor*, *Elodea canadensis* and *Cabomba aquatic*, to remove and assimilate three pesticides: copper sulphate (fungicide), flazasulfuron (herbicide) and dimethomorph (fungicide) (Figure 9). The authors found that *Lemna minor* had the most efficient uptake capacity, followed by *Elodea Canadensis* and then *Cabomba aquatic*. Recently, Olette et al. (2010) demonstrated that the microalgae *Scenedesmus quadricauda* (Figure 10) was more effective in the removal of two fungicides (dimethomorph and pyrimethanil) and one herbicide (isoproturon) from their medium (Table 1).

The green alga *Chlamydomonas reinhardtii* (Figure 11) showed a great ability to accumulate and degrade the herbicide prometryne (Jin et al. 2012). Such uptake and catabolism of prometryne led to the rapid removal of the substance from the media and this process of degradation can be interpreted as an internal tolerance mechanism, suggesting that the green algae is useful in bioremediation of prometryne-contaminated aquatic ecosystems (Table 1).



The same species were found to accumulate the herbicide fluroxypyr (Table 1). The accumulated fluroxypyr could be rapidly degraded in the cells suggesting that the accumulation and degradation of fluroxypyr occurred simultaneously (Zhang et al. 2011). *Monoraphidium braunii*, green algae, appeared to be a promising species for the phytoremediation of waters from bisphenol A and also at high levels of contamination found in surface waters (Gattullo et al. 2012). Recently, it has been reported that freshwater microalgae converted bisphenol A into its mono-glucoside (Nakajima et al., 2004).

Moro et al. (2012) studied the effect of the herbicides chlortoluron and mesotrione on three microalgae species: two chlorophyceae (*Pediastrum tetras*, *Ankistrodesmus fusiformis*) and one diatom (*Amphora coffeaeformis*). Chlortoluron showed a significant inhibitory effect on the growth of *A. coffeaeformis*, whereas mesotrione induced an increase in cellular density in *A. fusiformis* (Table 1).

The role of algae *Chlorococcum* sp. and *Scenedesmus* sp in  $\alpha$ -endosulfan (a cyclodiene insecticide) degradation was convincingly demonstrated when these algae degraded  $\alpha$ -endosulfan to endosulfan sulfate, the major metabolite, and endosulfan ether, a minor metabolite, in a defined liquid medium (Sethunathan et al. 2004). When a high density of the algal inoculum was used, both metabolites appeared to undergo further degradation as evident from their accumulation only in small amounts and the appearance of an endosulfan-derived aldehyde

However, in freshwater systems located in urban or agricultural areas, microalgae are exposed to a multitude of toxicologically different pesticides (Junghans et al. 2006) and, therefore, it could be hypothesized that the appearance of resistant mutants can simultaneously determine the arising of new morphological populations driven by algacide-resistant clones (López-Rodas et al. 2006).

### The roles biosurfactants in bioremediation

Biosurfactants are surfactants that are produced extracellularly or as part of the cell membrane by several microorganisms and their applications in the environmental industries are promising due to their biodegradability, low toxicity and effectiveness enhancing biodegradation and solubilization of low solubility compounds (Mulligan 2005).

All biosurfactants are amphiphiles and tend to accumulate at interfaces, form micelles, lower the surface tension and thereby enhance the solubility and bioavailability of hydrophobic pollutants in water (Rosenberg 1993, Schippers et al. 2000).

Biosurfactants are a unique class of compounds that have been shown to have a variety of potential applications in the remediation of organic- and metal-contaminated sites, in the enhanced transport of bacteria, in enhanced oil recovery, as cosmetic additives, and in biological control

(Bodour et al. 2003). Biosurfactant-producing microorganisms may play an important role in the accelerated bioremediation of hydrocarbon-contaminated sites (Rosenberg and Ron 1999, Del Arco and Franca 2001, Rahman et al. 2002). The biosurfactants can enhance hydrocarbon bioremediation by two mechanisms. The first includes the increase of substrate bioavailability for microorganisms, while the other involves interaction with the cell surface which increases the hydrophobicity of the surface allowing hydrophobic substrates to associate more easily with bacterial cells (Mulligan and Gibbs 2004).

Application of biosurfactants or microorganism produced biosurfactants in *in situ* co-contaminated sites bioremediation seems to be more environmentally compatible and more economical than using modified clay complexes or metal chelators (Plociniczak et al. 2011).

Biodegradative properties of biosurfactant producing *Brevibacterium* sp. PDM-3 strain were tested by Reddy et al. (2010). They reported that this strain could degrade 93.92% of the phenanthrene and also had ability to degrade other polyaromatic hydrocarbons such as anthracene and fluorene.

Moldes et al. (2011) found that biosurfactant from *Lactobacillus pentosus*, grown on synthetic media, reduced the concentration of octane in the soil to 58.6% and 62.8%, for soil charged with 700 and 70,000 mg.Kg<sup>-1</sup> of hydrocarbon, respectively. Many surfactants of different kinds have been so far investigated for their possible applications in increasing bioavailability and solubility of PAHs in the aqueous phase (Makkar and Rockne, 2003). Washing with surfactant solutions has been shown to be effective for the removal of hydrophobic organic contaminants (HOCs) such as PAHs, hydrocarbons, polychlorinated biphenyls, or chlorinated solvents, such as trichloroethylene, from soil (Underwood et al. 1993, Fountain et al., 1996).

The biodegradation rates of both naphthalene and phenanthrene were increased significantly by surfactant addition, indicating that the PAH dissolution rates were increased by the surfactant and the increase in phenanthrene dissolution rate was most responsible for phenanthrene degradation rate enhancement (Makkar and Rockne 2003). In another study, Pastewski et al. (2006) found that the solubilization of *o*-dichlorobenzene and tetrachloroethylene compounds was more effective in solutions of biosurfactant rhamnolipid JBR 425 than in solutions of non-ionic surfactants. However, at the currently high costs of biosurfactants production, their use in bioremediation will be profitable only under special circumstances. For example, when other technologies are either not applicable or inefficient (Medrzycka et al. 2009)

### Role of genetic engineering in developing microalgae for phytoremediation of organic pollutants

The combination of microbiological and ecological

knowledge, biochemical mechanisms, and field engineering designs are essential elements for successful *in situ* bioremediation using genetically modified bacteria and microalgae (Das and Chandran 2011, Subashchandrabose et al. 2013).

Recently the genetic engineering has also been used to improve the bioremediation of organic pollutants. The transgenic approach for engineering the plants either with bacterial or animal xenobiotic degrading genes has been successfully tried for *in situ* bioremediation and accumulation of heavy metal as well as degradation of various xenobiotics like explosives and hydrocarbons (French et al. 1999, Suresh and Ravishankar 2004).

Transgenic plants and associated bacteria constitute a new generation of genetically modified organisms for efficient and environment-friendly treatment of soil and water contaminated with organic pollutants like PCBs (Aken et al. 2010). The genetic engineering can create genetically modified organism which can potentially degrades various types of poly cyclic hydrocarbons (PAHs) and the modern biotechnology could be applied for the removal of various toxic compounds (Jain and Bajpai 2012). Genetically modified organisms have been developed to degrade or modify many different compounds including carbozole, a petroleum component that inhibits catalysts used in refining (Riddle et al. 2003), pesticides (Qiao et al. 2003), explosives (Duque et al. 1993), aromatic compounds (Lorenzo et al. 2003; Watanabe et al. 2003).

Mixotrophy in cyanobacteria and microalgae can provide many competitive advantages over bacteria and fungi in degrading organic pollutants and Molecular methods and metabolic and genomic information will help not only in identification and selection of mixotrophic species of cyanobacteria and microalgae with capabilities to degrade organic pollutants but also in monitoring the efficiency of remediation efforts under the field condition (Subashchandrabose et al. 2013).

Recently Sivakumar et al. (2012) reported that microalgae are capable of producing lipids and hydrocarbons quickly and their photosynthetic abilities make them a promising candidate for wastewater treatment (bioremediation) and can be used as an alternative energy source (Biodiesel). Some microorganisms could be used in biomonitoring of organic pollution by constructing these organisms using bioluminescence genes (Horsburgh et al. 2002).

The expression of the catabolic genes of PCB-degrading microorganisms is a key factor for PCB biodegradation in contaminated soils (Seeger et al. 2010). Transgenic plants expressing the bacterial xenobiotic degradation genes combine the advantages of both the systems, i.e. the greater ability of biodegradation by bacteria and the high biomass and stability of the plants to have an ideal system for *in situ* bioremediation of contaminants (French et al. 1999). However, the strict regulations for the introduction of genetically engineered organisms in the environment

limit their use for bioremediation technologies.

## Conclusions

From this review, we can conclude that the application of microalgae in biomonitoring and restoration of aquatic systems favour the phytoextraction and biodegradation of many organic pollutants; however there are still some persistent organic pollutants that are difficult to break down by the microalgae. The genetic engineering can solve this problem and offers a promising tool to improve the absorption and bioremediation of many organic pollutants and increase microalgal tolerance to these pollutants. It is also necessary to study and to control different parameters of aquatic ecosystems such as temperature, pH, nutrient availability and other environmental parameters to increase the absorption, accumulation and biodegradation of different pollutants by microalgae, thus accelerating the bioremediation process and reducing the time of decontamination of an aquatic ecosystem.

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