BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXII No. 3A/2010	63 - 69	Seria Tehnică

Effects of Hydrocarbons Pollutants on Aquatic Organisms

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Abstract

Due to the growing consumption of petroleum products, oil pollution is increasingly frequent in aquatic ecosystems. Petroleum hydrocarbons are important pollutants for sea and marine organisms. Many researches about petroleum effects on aquatic systems regards the immediate and short-term toxic effects. The origin of hydrocarbons are either endogenic, which are synthetised by marine organisms or exogenic, due to oil pollution accumulated by marine organisms. This paper evaluates the results of research effects of petroleum hydrocarbons on some algae and plant organisms. The analsysis have been recorded by using total organic carbon (TOC) Fourier transform infrared spectroscopic measurements (FTIR), inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Key words: *Hydrocarbons, algae, photosynthesis, toxicity. petroleum biodégradation products.*

Introduction

Petroleum hydrocarbons are important pollutants of sea and marine organisms. The origin of hydrocarbons are either biogenic (endogenic) which are synthesised by marine organisms or exogenic due to oil pollution accumulated by marine organisms [1].

Different physical, chemical and biological parameters could influence the quality of oil, being important to evaluate the type of oil, oil dosage, physical environmental factors, prevailing weather conditions, seasonal factors, prior exposure of the area to oil, presence of other pollutants and type of remedial action [2].

The chemical properties of oil determine its effects. Some compounds are actively toxic, and are damaging to tissues, such as eyes, nasal cavities and other sensitive mucus membranes. Their properties are balanced by rapid dissipation and removal from the environment. The tar and weathered oil, which are not toxic but have greater potential for environmental impact because of their resistance to weathering [3].

Marine petroleum transportation and harbor throughput increase year after year, causing the frequency oil spill accident [1].

Ecotoxicity of hydrocarbons is highly variable, depending on their type and concentration, exposure time, state, environmental conditions and the sensitivity of affected species. The ecological impacts of oil on specific seaweed habitats has been studied by many authors, and clear differences are observed between sensitive taxa, such as Fucus, Ulva and Pelvetia, and resistant taxa, e.g. Laminaria, Chondrus and Ascophylum [4, 5].

Hydrocarbons from marine environment can be classified in two classes. Firstly biogenic hydrocarbons (biogeneous, autochthonous) synthesized by marine organisms as various fish, planktons, algae but these biogenic compounds are not particularly abundant. Secondly exogenic (anthropogenic, allochthonous) compounds enter to the sea from atmosphere, marine traffic, tanker accident, refinery, industrial and city sewage. Aromatic compounds especially polycyclic aromatic hydrocarbons (PAHs) are characteristic for petroleum. Marine organism do not synthesized these compounds. Anthropogenic hydrocarbons may cause changes in marine flora and fauna. Marine organisms are capable of accumulation oil hydrocarbons in their body [6].

Composition of a crude or refined petroleum governs its behavior and ultimate fate when spilled in the marine environment. It also affects the responses of marine organisms, including mammals, that might come in contact with spilled oil. The different chemical components of petroleum vary tremendously in their acute and chronic toxicity.

Acute toxicity of alkanes to aquatic organisms tends to increase with molecular weight. However, acutely toxic concentrations for all but lowest molecular weight alkanes are higher than their solubility, and therefore cannot occur naturally in aquatic environments. Low molecular weight cyclic alkanes (naphthene cyclohexane and several alkyl cyclohexanes) appear to be more toxic to aquatic organisms than n-alkanes and benzenes of similar molecular weight. Mixtures of higher molecular weight alkanes, such as paraffin oils, are considered inert. Low molecular weight alkanes (methane through octane) have mild anesthetic properties, and, because of their volatility, may occur in a form which can be inhaled. [3].

Aromatic hydrocarbons are the most toxic of the major classes of compounds in petroleum. The acute toxicity of crude and refined petroleums to aquatic organisms and mammals correlates directly with the concentration of light aromatic hydrocarbons (benzene through phenenthrene). Chronic effects of petroleum are attributed primarily to four- and five-ring aromatic and hetero-aromatic hydrocarbons, some of which are well-known carcinogens. Benzene, though a known carcinogen, is volatile and short-lived, and probably contributes more to acute than chronic toxicity [3].

Petroleum enters the marine environment from various sources. Natural sources such as marine oil seeps and erosion of oil-bearing rocks are the most difficult to estimate accurately. Tanker washing and accidents are responsable for most the oil contamination of marine water. The major source is from discharges of ballast water and tank washing water [3].

Algae are responsible for most of the primary productivity in some water bodies. They subsist on inorganic nutrients and produce organic matter from carbon dioxide by photosynthesis. In the absence of photosynthesis, the metabolic process consumes oxygen, causing oxygen depletion in the aquatic system [7]. Mono-species cultures of green algae contain protein (over 50% of dryweight), nutrients (nitrogen, phosphorus) and may contain various bioaccumulated toxic elements. This is an advantage from the viewpoint of tertiary sewage treatment but a disadvantage if the intent is to use waste-grown algae for fish or livestock feeding or composting [8].

Experimental details

Materials

Our experiments were performed to investigate the physiological responses of two algae. It was used a red alga from Coreea (*Porphyra umbilicalis*) (Fig. 1.) and a brown-green alga from China (*Fucus vesiculosus*) (Fig. 2.)

Fig. 1. Red alga *Porphyra umbilicalis*

Fig. 2. Brown-green alga *Fucus vesiculosus*

The algae were dried in a oven at 150°C for 5 hours. About 5 g of powder were taken in work. Probes were mixed with an artificial solution of water contaminated with petroleum ether, and were shaken very well for 12 hours at 20°C. Next step was to consider evidence from TOC, FTIR and ICP-AES.

Apparatus

FTIR is most useful for identifying chemicals that are either organic or inorganic. FTIR spectrometer Perkin Elmer SPECTRUM GX was used and was utilized ATR (Attenuated Total Reflectance) method for liquid samples.

The total organic carbon concentration (TOC) was determined on a TOC Analyser (Model Multi N/C Analytic Jena).The NPOC analysis measures was made using direct determination. The sample was acidified with 2 N HCl (pH = 2) outside the analyzer and the generated CO_2 was purged. Readily volatile organic compounds have been also purged with the carbon dioxide.

A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. A manual hydraulic press was used for the preparation of pressed pellets and a mixer for the blending of the materials. For the ICP-AES measurements, sub samples were cut off from the original sherds and were finely powdered in an agate mortar. The probes were put into a flask with the artificial solution and MRC (multielement standard solution). Multielement (1000 ppm), matrix matched standards were used for the quantitative determinations.

Results

Petroleum biodegradation is a naturally occurring process. Actually, it is considered as a tool against oil pollution in marine environment. The effects of compounds resulting from petroleum biogradation have been studied on two marine algae.

It was intensively studied the effects of petroleum on algae growth and was demonstrated that the toxicity of most petroleum is enhanced after intensive irradiation of petroleum. This has been attributed to photooxidation products of petroleum which are characterized by a higher polarity than the initial products [9]. Thus, the transformations of petroleum via physico-chemical or biological processes, have comparable effects *(in vitro)* on algae growth. High concentrations of petroleum degradation products may be more toxic to algae than the petroleum itself [7].

Estimation of Fourier transform infrared spectroscopic measurements (FTIR)

The spectra showed the characteristic absorption bands of petroleum ether obsorbed in algae (fig.3 a, b). The bands at 1462,91 cm^{-1} (aliphatics; aromatic ring stretch), 1366,08, 1377,97 and 1354,28 cm^{-1} (COO- stretch; CO of phenolic OH; aromatic ring stretch), 1309,26 cm^{-1} and 1276,76 cm^{-1} (aryl OH; COOH deformations; OH deformations), 1276,76 cm^{-1} and 1228,15 (aryl OH, COOH deformation), 1217,31 cm^{-1}, 1206,20 cm-1 and 1145,71 appear almost at the same band in petroleum ether and in algae impurificated with synthetic solution, that means the fact that algae incorporated ether [10, 11]. So we may conclude that this two algae *Porphyra umbilicalis* and *Fucus vesiculosus* have the power and the property to depollution the part of water when are they.

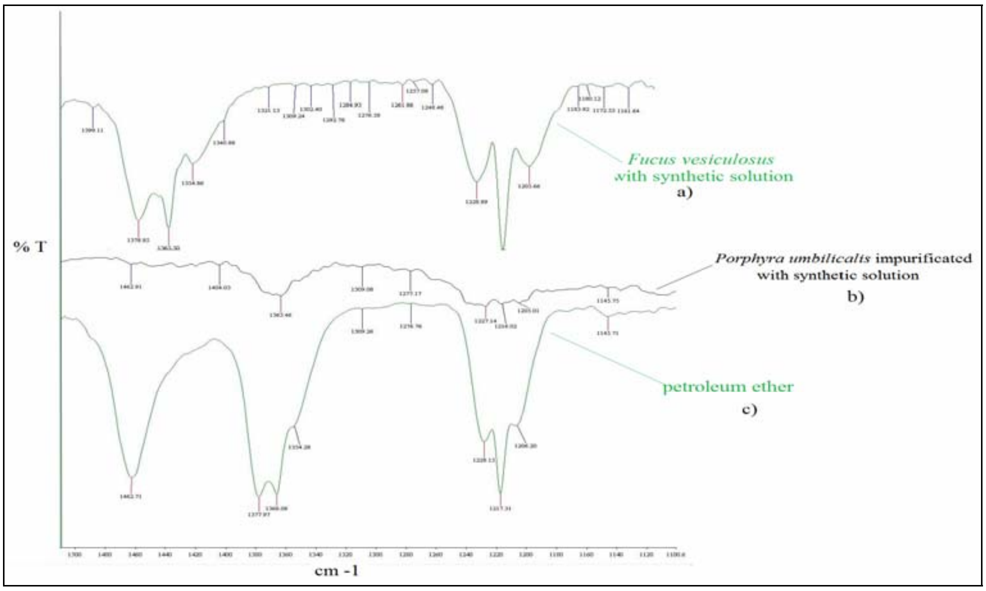


Fig. 3.FT-IR spectra comparation between a) *Fucus vesiculosus*, b)red alga *Porphyra umbilicalis* impurificated with synthetic solution (water and petroleum ether) and c)petroleum ether martor

Estimation of total organic carbon (TOC)

The basic principle of thermal oxidation method is the oxidation of the organic constituents of water using oxygen at temperature 950°C. The catalysts used for complete oxidation is Pt/Al_2O_3. The carbon dioxide produced from thermal oxidation is transported into the CO_2 measurement system with a carrier gas stream. A method of CO_2 measurement is infrared spectrometry, non-dispersive IR detectors (NDIR detectors). The carbon dioxide concentration is measured several times each second. An integral is derived from the signal sequence over time. The inregral is proportional to the concentration of the carbon in the measurement solution. The carbon content of the sample is calculated using a previously determined calibration function.

The result show the fact that algae are capable to reduce the pollution from water (table 1).

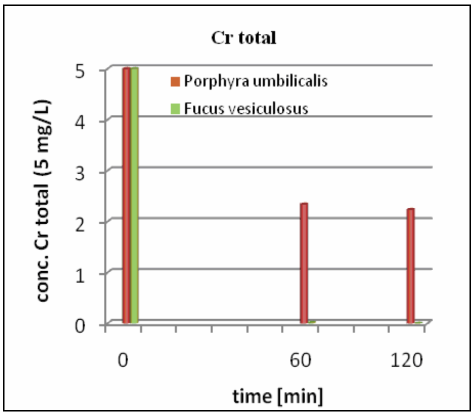
Table 1. TOC analysis show pollution reduction with different types of algae

Conc. of clean water (CO_2 mg/L)	Conc. of polluted water (with petroleum ether) (CO_2mg/L)	Conc. of polluted water with *Porphyra umbilicalis* (CO_2 mg/L)	Conc. of polluted water with *Fucus vesiculosus* (CO_2 mg/L)
0.00416	0.03124	0.01412	0.02101

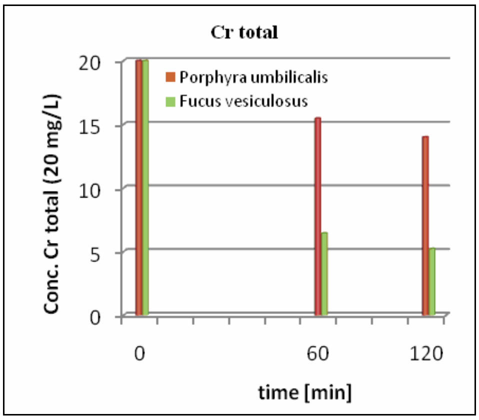
Estimation of Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

It is know the fact that seawaters are impurificated with heavy metals and they pollute.

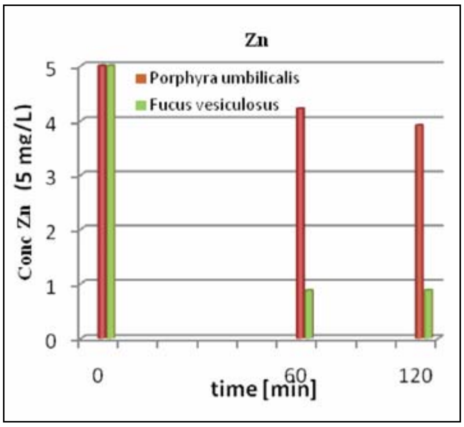
The samples were analysed at ICP-AES, after 60 and 120 minutes of continous agitation with a mechanic agitator for at room temperature and pH = 5.5.



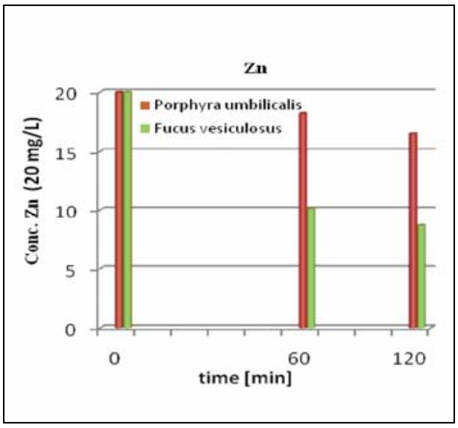
a)



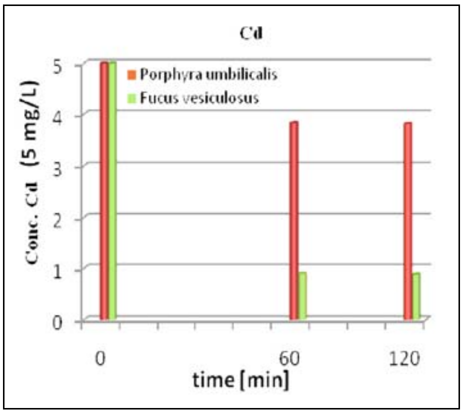
d)



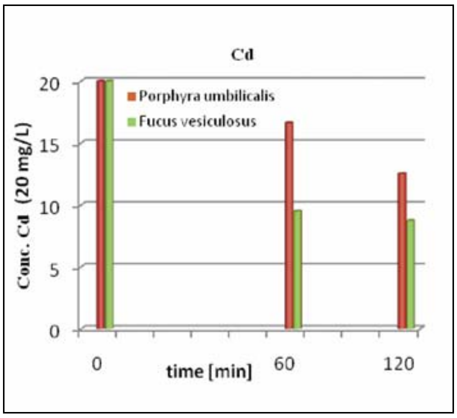
b)



e)



c)



f)

Fig. 5. Graphical presentation of evolution metal concentration on different types of algae at different times and concentrations. Fig. 5. a), b), c) at 5 mg/L conc.; fig. 5. d), e), f) at 20 mg/L conc.

Crude oil is a complex mixture of hydrocarbons, with four to 26 or more carbon atoms per molecule. The constituents may be straight, branched or cyclic chains, including aromatic compounds (i.e. with benzene rings). Some polycyclic aromatic hydrocarbons (PAH) are known to be potent carcinogens. Water-soluble components of crude oils include a variety of compounds that are toxic to a wide spectrum of marine plants and animals. Aromatic compounds are more toxic than aliphatic compounds, and middlemolecular-weight compounds are more toxic than high-molecular-weight compounds. Low-molecular- weight compounds are generally unimportant because they are volatile, and are rapidly lost to the atmosphere; however, they tend to be more water-soluble than other hydrocarbons. As well as being more toxic, aromatic compounds are generally more soluble in water than aliphatic compounds: for example, benzene has a water solubility of 1.8 g/l. The aromatic hydrocarbon fraction is, therefore, that which poses the greatest threat to fish and planktonic organisms [3].

Conclusions

In Fig. 5 it is presented the fact that at 5 mg/L concentration artificial solution, the decrease of heavy metal ions occurred like the same of 20 mg/L concentration. It is observed that *Fucus vesiculosus* decreases most rapidly, as happened at 20 mg/L concentration.

The algae *Porphyra umbilicalis* and *Fucus vesiculosus*, decreased rapidly in the first hour, for all metal ions concentrations (Cr, Zn, Cd), then they became almost constant during the entire experiment. Also, it is obvious that most effectively reduced metals is *Fucus vesiculosus*.

TOC determination shows satisfactory results in the process of CO_2 concentration.

FTIR determination showed the fact that brown algae *Fucus vesiculosus* is more is more efficient in the incorporation of hydrocarbons than red alga *Porphyra umbilicalis.*

The results of ICP-AES concluded that these algae (*Porphyra umbilicalis* and *Fucus vesiculosus*) can be used in removal recovery of heavy metal ions from industrial waste water. The difference between the initial and remaining metal concentration was assumed to be taken up by the biosorbent. Both algae can incorporate into their structure of petroleum products, in an amount greater or smaller, but long-term properties are destroyed.

Achnowledgments

Results were obtained in a project co-financed from European Social Fund through the POSDRU/88/1.5/S/63269 2009-2013.

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Efectele poluarii cu hidrocarburi asupra organismelor acvatice

Rezumat

Avand in vedere consumul in crestere de produse petroliere, poluarea cu petrol este din ce in ce mai frecventa in ecosistemele acvatice. Hidrocarburile petroliere sunt cei mai importanti poluanți pentru organismele marine si plantele marine. Numeroase studii au fost prezentate despre efectele toxice ale produselor petroliere asupra sistemelor acvatice pe termen lung sau scurt. Originea hidrocarburilor poate fi de endogena sau exogena. Aceasta lucrare evalueaza rezultatele efectelor hidrocarburilor petroliere asupra a doua tipuri de alge, din zone diferite. Au fost inregistrate rezultate cu ajutorul metodelor TOC (carbon organic total), spectrometrie in infrarosu cu transformata Fourier (FTIR), spectrometrie de emisie cu plasma cuplata (ICP-AES).