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SUMMARY AND CONCLUSION

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This work was designed to evaluate the petroleum contaminations in some soil samples. The physical properties of the studied samples were investigated. The mechanical analysis shows that the distribution of different components of the soil samples as follow:

- 1- Coarse sand 1.12 – 7.04% except samples no.12 and 13 (46.74 and 51.93% respectively).
- 2- Fine sand 26.98 - 39.05% except sample no.13 (12.94%).
- 3- Clay 30.12 - 39.52% except samples no.12 and 13 (8.28 and 17.81% respectively).
- 4- Silt 17.72 - 32.51% except sample no.12 (8.72 %).

Data obtained reveal that the texture classes are either Loam or Clay loam except for samples no.12 or 13 (Loamy sand and Sandy loam respectively). Values for the moisture content of the surface samples are lower than the values obtained for the subsurface samples and it can be attributed to the differences in the rate of evaporation. The bulk densities of surface samples are lower than the subsurface samples and this can be attributed to the differences in organic matter content and compaction.

The chemical properties of the samples show that the ECs are affected by the concentrations of the soluble cations and anions. The pH values obtained indicate that the samples are ranging between neutral to moderately alkaline. The CEC values are found to be related to the clay content of the samples.

Data obtained for the heavy metals concentrations, show that for iron, there is no significant trend. The values are fluctuated between road, side road, and subsurface samples along the 32 km in the first location. For manganese, the valued of the road surface values of the samples are lower than those of the side surface. Cadmium is not detected at the first and second locations, but detected only in samples no.13 and 14 in the third location. Nickel concentrations decrease from the road to side samples in the first and second stages in the first location. The presence of Pb in soil may be due to accumulation process from traffic sources during the past years. The studied locations have some what different values

of copper content where Cu can be introduced to soil by Cu-containing pesticides.

The first step in assessing the environmental pollution study is to determine the magnitude and concentration of the total petroleum hydrocarbons (TPH). Data obtained show that the (TPH) contents of the samples are between 647 and 1560 ppm except for samples no.12 and 13. The first one (sample no.12) has nil value, since it was collected from a virgin area and where the sources of contaminations are rare, while the other sample (sample no.13) has 62,120ppm, which is logic, since it was taken from an oil field production area. The concentrations obtained are considered to affect the agriculture soil in one way or another as they are higher than the alarming level.

The second step in assessing the environmental pollution study is to identify the source and type of the (TPH) using gas chromatographic technique. For the surface samples in the first location, the origin of contamination is mainly petrogenic for samples no.1 and 7, while samples no.3 and 11, reveal that the origin of contamination is mixed petrogenic with biogenic due to the predominance of n-C₂₅. For the side samples of the same location (samples no.2, 4 and 8) show that the origin of contamination is mainly petrogenic. The subsurface samples (samples no.5, 6, 9 and 10) are characterized by a mixed petrogenic with biogenic origin of contamination. For the third location, sample no.13 has the characteristic feature of petroleum origin, while samples no.14, 15, 16, and 17, have the characteristic feature of mixed petrogenic with biogenic. GC fingerprint of the studied samples reveal that the type of contamination is mainly petroleum hydrocarbons and / or a combination of terrestrial plant waxes and petroleum sources. Some GC parameters were applied in order to identify the origin, source, and degree of weathering.

The effect of some heavy metals (HM) namely, Cu, Mn, Ni and Zn, individually and in a mixture on the biodegradation of phenantherene as a model for polyaromatic petroleum hydrocarbons was studied. The results obtained show that the heavy metal resistance of *Cellulomonas hominis* N2 is widespread. N2 shows high biodegradation potentials on phenanthrene even in presence of heavy metals, although their presence decreases its

biodegradation potentials. *Cellulomonas hominis* N2 is found to have the ability to produce a biosurfactant which may help to overcome toxicity of such heavy metals.

The results also show that the effects of heavy metals are complex and suggest that many factors could be in operation. This may explain why in spite of the high HM concentration in the collected PCS, the natural bacterial clean-up of crude oil spill in biostimulation experiment still takes place.

Natural oil biodegradation by the indigenous microbial populations (natural attenuation process) is taking place at the oil contaminated site. However, the rate is slow. The low rate of hydrocarbon biodegradation at the site is due to insufficient nutrient level in the soil, low population diversity in the microbial community, high oil content, and other environmental conditions unfavorable for aerobic microbial metabolism. Biodegradation of oil contaminants at the site can be accelerated and enhanced through additions of inorganic nutrients (biostimulation process).

In conclusion, results from this work have clearly demonstrated the potential of naturally occurring microorganisms in soil systems in Egyptian polluted sites for aerobic biodegradation of petroleum hydrocarbons and tolerance to heavy metals found in polluted sites.

Further work is recommended to study the type of the produced biosurfactant and its effect on the kinetics of biodegradation process in presence and absence of heavy metals.

At the end we must move to protect this area and more efforts are still needed in order to prevent or minimize such oil pollution as we have not inherited the environment from our parents, but we have borrowed it from our children.

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REFERENCES

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Abalos, A. ; Vinas, M. ; Sabate, J. ; Manresa, M. and Solanas, A., Enhanced biodegradation of casablanca crude oil by a microbial consortium in presence of a rhamnolipid produced by *Pseudomonas Aeruginosa* AT10. *Biodeg.*; **15(4)**, 249-260 (2004).

Abbondanzi, F. ; Bruzzi, L. ; Campisi, T. ; Frezzati, A. ; Guerra, R. and Iacondini, A., Biotreatability of polycyclic aromatic hydrocarbons in brackish sediments: preliminary studies of an integrated monitoring. *Int. Biodet. Biodeg.*; **57**, 214-221(2006).

Acher, A. J. ; Boderie, P. and Yaron, M., Soil pollution by petroleum products I. Multi-phase migration of kerosene components in soil columns. *J. of Contam. Hydrology*; **4**, 333-345 (1989).

Adeniyi, A. A. and Afolabi, J. A., Determination of total petroleum hydrocarbons and heavy metals in soils within the vicinity of facilities handling refined petroleum products in Lagos metropolis. *Environ. International*; **28**, 79–82 (2002).

Admon, S. ; Green, M., and Avinimelech, Y., Bioremediation kinetics of hydrocarbons in soil during land treatment of oily sludge. *Bioremediation J.*; **5**, 214-221(2001).

Aislabie, J. M. ; Saul, D. J. and Foght, J . M., Bioremediation of hydrocarbon-contaminated polar soils. *Extremophiles*; **10**, 171-179 (2006).

Aleksandrowicz, J. and Duda, H., Uprogu Medycyny Jutra. PZWL, Warsaw, p.150(1988).

Alexander, M., Biodegradation and bioremediation. Academic Press, San Diego. U.S.A. (1999).

Alexander, M., Biodegradation and bioremediation. Alexander, M. London: Academic Press (1994).

Ali, M. A. and Dzombak, D. A., Interactions of copper, organic acids, and sulfate in goethite suspensions. *Geochim. Cosmochim. Acta*; **60(24)**, 5045-5053 (1996).

Allen, J. P. and Torres, I. G., Physical separation techniques for contaminated sediment, in recent developments in separation science, N.N. Li, Ed., CRC Press, West Palm Beach, FL, Vol V. author, Dept. Soils, Univ. of Wisconsin, Madison, WI. (1991).

Amadi, A. ; Samuel, D. A. and Anthny, N. M., Chronic effects of oil on soil properties and microflora of a rain forest ecosystem in Nigeria. *Water, Air and Soil Pollution*; **86**, 1-11(1996).

Amellal, N. ; Portal, J. M. and Berthelin, J., Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbon within aggregates of a contaminated soil. *Appl. Geochem*; **16**, 1611-1619 (2001).

Amit, M. and Ajay, T., Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. *Chemosphere*; **65**, 449-456 (2006).

Amor, L. ; Kennes, C. and Veiga, M. C., Kinetic of biodegradation of monoaromatic hydrocarbons in presence of heavy metals. *Bioresour. Technol*; **78**, 181-185 (2001).

Anxiang, L. ; Shuzhen, Z. and Xiao-quan, S., Time effect on the fractionation of heavy metals in soils. *Geoderma*; **125**, 225-234 (2005).

Arzahanova, V. S. and Yelpat, Y., Migration of micronutrients in brown mountain forest soils. *Soviet. Soil Sci.*; **11**, 51-60 (1980).

ASTM., Standard test method for determination of water (moisture) content of soil by the microwave oven method. **D4643**, 743-746 (1993).

ASTM., Standard test method for pH of soils. **D4972**, 27-29 (1995a).

Atagana, H. I., Biodegradation of polycyclic aromatic hydrocarbons in contaminated soil by biostimulation and bioaugmentation in the presence of copper (II) ions. *World J. microbiol. Biotechnol*; **22**, 1145-1153 (2006).

Atlas, R. M., Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiol. Revk*; **45(1)**,180-209 (1981).

Bachoon, A. ; Molina, M. and Hodson, R., Microbial community dynamics and evaluation of bioremediation strategies in oil-impacted salt marsh sediment microcosms. *J. Ind. Microbiol. Biotechnol*; **27**, 72-79 (2001).

Baldrian, P. ; Der Wiesche, C. I. ; Gabriel, J. ; Nerund, E. and Zadrazil, F., Influence of cadmium and mercury on activities of ligninolytic enzymes and degradation of polyaromatic hydrocarbons by *Pleurotus Ostreatus* in soil. *Appl. Environ. Microbiol*; **66**, 2471- 2478 (2000).

Banat, I. M. ; Makkar, R. S. and Cameotra, S. S., Potential commercial applications of microbial surfactants. *Appl. Microbiol. Biotechnol*; **53(5)**, 495-508 (2000).

Barakat, A. O. ; Moustafa, A. R. ; Qian, Y. and Kennicutt, M. C., Application of petroleum hydrocarbon chemical fingerprinting in oil spill investigations — Gulf of Suez, Egypt. *Spill Sci. and Technol. Bulletin*; **7(5,6)**, 229-239 (2002).

Bariller-Boyer, A. ; Bariller, L. ; Massé, H. ; Razet, D. and Héral, M., Correction for particulate organic matter as estimated by loss on ignition in estuarine ecosystem. *Estuarine Coastal and Shelf Sci.*; **58**, 147-153 (2003).

Barry, D. A. and Sposito, G., Application of the convection–dispersion model to solute transport in finite soil columns. *Soil Sci. Soc. of Am. J.*; **52**, 3-9 (1988).

Bartlett, R. J. and James, B. R., Mobility and bioavailability of chromium in soils and chromium in the natural environment; Nriagu, J. O. and Nieboer, E. Ed.; John Wiley & Sons: N. Y. 267-304 (1988).

Battaglia, A. ; Calace, N. ; Nardi, E. ; Petronio, B. M. and Pietroletti, M., Reduction of Pb and Zn bioavailable forms in metal polluted soils due to paper mill sludge addition effects on Pb and Zn transferability to barley. *Bioresour. Technol.*; **98(16)**, 2993-2999 (2007).

Benka-Cocker, M. O and Ekundayo, J. A., Effect of heavy metals on growth of species of *Micrococcus* and *Pseudomonas* in a crude oil/mineral salts medium. *Bioresour. Technol.*; **66**, 241-245 (1998).

Bento, F. M. ; Camargo, F. A. ; Okeke, B. C. and Frankenberger, W. T., Comparative bioremediation of soils contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation. *Bioresour. Technol.*; **96(9)**, 1049-1055 (2005).

Bhide, J. V. ; Dhakephalkar, P. K. and Paknikar, K. M., Microbiological process for the removal of Cr(VI) from chromate-bearing cooling tower effluent. *Biotechnol. Lett*; **18**, 667-672 (1996).

Bishop, P. ; Gress, D. and Olafsson, J., Cement sabilization of heavy metals: leaching rate assessment, industrial wastes-proceedings of the 14th mid-atlantic industrial waste conference, Technomics, Lancaster, PA.(1982).

Black, C. A., Methods of soil analysis, Agronomy, manual No.9, part 1. American Society of Agronomy Madison Wisconsin, U.S.A. (1965).

Black, C. A., Methods of soil analysis. Soil Science Society of American Inc. Publisher, Madison Wisconsin U.S.A. (1982).

Bodek, I. ; Lyman, W. J. ; Reehl, W. F. and Rosenblatt, D. H., Environmental inorganic chemistry: properties, processes and estimation methods, Pergamon Press, Elmsford, N.Y. (1988).

Boehm, P. D. ; Douglas, G. S. ; Burns, W. A. ; Mankiewicz, P. ; Page, D. S. and Bence, A. E., Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques

after the Exxon Valdez oil spill. *Marine Pollution Bulletin*; **34(8)**, 599-613 (1997).

Bohn, H. L. ; McNeal, B. L. and O'Connor, G. A., Soil Chemistry. Wiley, N. Y. (1979).

Bolan, N. S. and Duraisamy, V. P., Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. *Australian J. of Soil Research*; **41**, 533– 555 (2003).

Bolton, J., Liming effect on the toxicity perennial ryegrass of sewage sludge contamination with Zn, Ni, Cu and Cr. *Environ. Pollution*; **9**, 295-299(1975).

Bopp, L. ; Chakrabarty, A. and Ehrlich, H. L., Chromate resistance plasmid in *Pseudomonas fluorescens*. *J. Bacteriol*; **155**, 1105-1109 (1983).

Bouloubassi, I. and Saliot, A., Dissolved, particulate and sedimentary naturally derived polycyclic aromatic hydrocarbons in a coastal environment: geochemical significance. *Marine Chemistry*; **22(2)**, 127-143 (1993).

Braddock, J. F. ; Walworth, J. L. ; Kathleen, A. and McCarthy, K. A., Biodegradation of aliphatic vs. aromatic hydrocarbons in fertilized arctic soils. *Bioremediation J.*; **3(2)**, 105–116(1999).

Bradl, H., Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid Interf. Sci.*; **277**, 1–18 (2004).

Brady, N. C. The nature and properties of soils. Macmillan Publ. Co, N.Y. (1990).

Brown, E. J. ; Resnick, S. M. ; Rebstock, C. ; Luong, H. V. and Lindstorm, J. E., UAF radio respirmetric protocol for assessing hydrocarbon mineralization potential in environmental samples. *Biodeg.*; **2**, 121-127 (1991).

Buelt, J. L. and Thompson, L. E., The in situ vitrification integrated program: focusing on an innovative solution on

environmental restoration needs, Battelle Pacific Northwest Laboratory, Richland, WA (1992).

Burgos, P. ; Madejo'n T, E. ; Pe´rez-de-Mora, A. and Cabrera, F., Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation. *Geoderma*; **130**, 157–175 (2006).

Burns, K. A. and Kanp, A. H., The Bahia Las Minas oil spill hydrocarbon uptake by reef building corals. *Marine Pollution Bulletin*; **20(8)**, 391-398 (1989).

Callahan, M. A. ; Slimak, M. W. and Gabel, N. W., Water-related environmental fate of 129 priority pollutants, vol. 1, introduction and technical background, metals and organics, pesticides and PCBs. Report to U.S. EPA, Office of Water Planning and Standards, Washington, D.C. (1979).

Camobreco, V. J. ; Richards, B. K. ; Stenhuis, T. and McBride, M. B., Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Sci.*; **29**, 697-750 (1996).

Caravaca, F. and Roldan, A., Assessing changes in physical and biological properties in a soil contaminated by oil sludges under semiarid Mediterranean conditions. *Geoderma*; **117**, 53–61 (2003).

Castro-Silva, A. ; Lima, A. O. S. ; Gerchenski, A. V. ; Jaques, B. ; Rodrigues, L. ; De-Souza, L. and Rorig, L., Heavy metals resistance of microorganisms isolated from coal mining environments of Santa Catarina. *Brazilian J. of microbial*; **34**, 45-47 (2003).

Chaerun, S. K. ; Tazaki, K. ; Asada, R. and Kogure, K., Alkane-degrading bacteria and heavy metal from and Nakhodka oil spill-polluted seashores in the sea of Japan after five years of bioremediation. *The Science Report of Kanazawa University*; **49**, 1-2 (2004).

Chaillan, F. ; Le Fleche, A. ; Bury, E. ; Phantavong, Y H. ; Grimont, P. ; Saliot, A. and Oudot, J., Biodegradation of

mixtures of polycyclic aromatic hydrocarbons under aerobic and nitrate-reducing conditions. *Res. in Microbiol*; **55**, 587-595 (2004).

Chaineau, C. H. ; Rougeux, G. ; Yepremain, C. and Oudot, J., Effect of nutrient on the biodegradation of crude oil and associated microbial populations in the soil. *Soil Biol. Biochem*; **37**, 1490-1497 (2005).

Chen, R. B. ; Kokal, S. L. ; Al-Ghamdi, M. A. ; Gwathney, W. J. ; Al-hajji, A. A. and Dajani, N., Bioremediation of petroleum hydrocarbon-contaminated soil: A laboratory enhancement study, 2nd Specialty Conference on Environmental Progress in the Petrochemical Industries. Saudi Arabian Section-air and waste management association and Bahrain society of engineers, 17-19 November (1997).

Chosson, P. ; Lanau, C. ; Cannan, P. and Dessort, D., Biodegradation of refractory hydrocarbon biomarkers from petroleum under laboratory conditions. *Nature*; **351**, 640-642 (1991).

Christensen, T. H., Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH and calcium. *Water, Air and Soil Pollution*; **21**, 105– 114 (1984).

Chrotowski, P. ; Durda, J. L. and Edelman, K. G., The use of natural processes for the control of chromium migration. *Remediation*; **2**, 341-351(1991).

Chung, M. K. ; Hu, B. R. ; Cheung, K. C. and Wong, M. H. Pollutants in Hong Kong soils polycyclic aromatic hydrocarbons. *Chemosphere*; **67**, 464–473 (2007).

Coleman, E. A. and Hendrix, T. M., Fiberglass electrical soil-moisture instrument. *Soil Sci.*; **67**, 425-438 (1949).

Collard, J. ; Corbisier, P. ; Diels, L. ; Dong, Q. ; Jeanthon, C. ; Mergeay, M. ; Taghavi, S. ; Der-Lelie, V. ; Wilmotte, A. and Wuertz, S., Plasmids for heavy metal resistance in *Alcaligenes eutrophus* CH34: Mechanism and Applications. *FEMS Microbiol. Rev*; **14**(4), 405-414 (1994).

Conner, J. R., Chemical fixation and solidification of hazardous wastes, Van Nostrand Reinhold, N. Y. (1990).

Corwin, D. L. and Lesch, S. M., Apparent soil electrical conductivity measurements in agriculture. *Computers and Electronics in Agriculture*; **46**,11–43 (2005).

Cybulski, Z. ; Dziurla, E. ; Kaczorek, E. and Olszanowski, A., The influence of emulsifiers on hydrocarbon biodegradation by *Pseudomonadacea* and *Bacillaceae* strains. *Spill Sci. Technol. Bull*; **8**, 503-507(2003).

Damondy, R. G. ; Foss, J. E. ; McIntosh, M. and Wolf, D. C., Municipal sludge compst. Amended soils: some temporal treatment effects. *J. Environ. Qual.*; **12**, 231-236 (1983).

Das, K. and Mukherjee, A. K., Crude petroleum-oil biodegradation efficiency of *Bacillus subtilis* and *Pseudomonas aeruginosa* strains isolated from a petroleum-oil contaminated soil from north-east India. *Bioresour. Technol.*; **98**, 1339-1345 (2007).

Davis, J. A., Complexation of trace metals by adsorbed natural organic matter. *Geochim. Cosmochim. Acta.*; **48**, 679-691(1984).

Davydova, S., Heavy metals as toxicants in big cities. *Microchemical J.*; **79**,133– 136 (2005).

Dawis, J. and Freites, F., Physical and chemical methods of soil& water analysis. FAO. Rome. *Soil Bulletin* No.10 (1970).

Deenik, J. L. and Yost, R. S., Chemical properties of atoll soils in the Marshall Islands and constraints to crop production. *Geoderma*; **136**, 666-681(2006).

Deighton, N. and Goodman, B. A., The speciation of metals in biological systems. In *Chemical Speciation in Environmental* ed. Ure, A.M. and Davidson, C.M. London: Blackie Academic and Professional; 307-334 (1995).

De-Oteyza, T. G. and Grimalt, J. O., GC and GC–MS characterization of crude oil transformation in sediments and

microbial mat samples after the 1991 oil spill in the Saudi Arabian Gulf coast. *Environ. Pollution*; **139(3)**, 523-531(2006).

Dibble, J. T. and Bartha, R., Effect of environmental parameters on the biodegradation of oil sludge. *Appl. Environ. Microbiol*; **37**, 729-739 (1979).

Doong, R. and lin, Y., Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. *Water Research*; **38**,1733-1744 (2004).

Dowdy, R ; Latterell, J. J. ; Hinesly, T. D. ; Grossman, R. B. and Sullivan, D. L., Trace metal movement in an Aerobic Ochraqual following 14 years of annual sludge application. *J. Environ. Qual.*; **20**, 119-123 (1991).

Duarte, G. F. ; Rosado, A. S. ; De-Araujo, L. S. W. and Van, E. J. D., Analysis of bacterial community structure in sulfurous-oil-containing soils and detection of species carrying dibenzothiophene desulfurization (dsz) gene. *Appl. Environ. Microbiol*; **67(3)**, 1052-1062 (2001).

Dudka, S. and Domy, C. A., Environmental impacts of metal ore mining and processing: a review. *J. Environ. Qual.*; **26**, 590–602 (1997).

Dzombak, D. A. ; Rosetti, P. K. ; Evanko, C. R. and DeLisio, R. F., Treatment of fine particles in soil washing processes, in proceedings of the specialty conference on innovative solutions for contaminated site management. Water Environment Federation, Alexandria, VA, 473-484 (1994).

Dzombak, D. A. and Morel, F. M., Adsorption of inorganic pollutants in aquatic systems. *J. Hydraulic Eng.*; **113**, 430-475 (1987).

Dzombak, D. A. and Morel, F. M., Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons, N. Y. (1990).

Edgehill, R. U., Effect of copper-chromate-arsenate (CCA) components on PCP degradation by *Arthrobacter* strain ATCC 33790. *Bulletin Environ. Contam. Toxicol.*; **57**, 258-263 (1996).

El-Gendi, S. A. ; Badawy, S. H. and Helal, M. I. D., Mobility of some heavy metals nutrients in sandy soil irrigated with sewage sludge effluents. *J. Agric. Sci.*; **22 (10)**, 3535-3552 (1997).

El-Gendi, S. A., Fractionation and mobility of some heavy metals in soil amended with sewage sludge. *J. Agric. Sci.*; **18**, 95-114 (2003).

El-Leboudi, A. ; Yousry, M. and Khatar, A., Effect of sulphur and petroleum byproducts on soil characteristics. Availability of certain nutrients in alluvial soils. *Egypt J. Soil Sci.*; **25**, 21-27 (1985).

Ellis, W. D. and Fogg, T., Interim report: Treatment of soils contaminated by heavy metals, hazardous waste engineering research laboratory. Office of Research and Development, U.S. EPA, Cincinnati, Ohio. (1985).

El-Tokhi, M. M. and Mostafa, Y. M., Heavy metals and petroleum hydrocarbons contamination of bottom sediments of El-Sukhna area, Gulf of Suez. *Egypt Petroleum Sci. and Technol.*; **19(5&6)**, 481- 494 (2001).

Emmerich, W. E. ; Lund, I. J. ; Page, A. L. ; Chang, A. L. and Chang, A. C. Predicted solution phase of heavy metals in sewage sludge- treated soils. *J. Environ. Qual.*; **11**, 182-186 (1982).

Evans, L. J., Chemistry of metal retention by soils. *Environ. Sci. Tech.*; **23**,1046-1056 (1989).

Farrington, J. W. and Tripp, B. W., Hydrocarbons in western North Atlantic surface sediments. *Geochim. Cosmochim. Acta.*; **41(11)**,1627-1641(1977).

Fingas, M., A literature review of the physics and predictive modeling of oil spill evaporation. *Hazard. Mater*; **42**, 157-175 (1995).

Fleck, L. C. ; Bicca, F. C. and Ayub, M. A., Physiological aspects of hydrocarbon emulsification, metal resistance and DNA profile of biodegrading bacteria isolated from oil polluted sites. *Biotechnol. Lett*; **22**, 285-289 (2000).

Franke, H. C. and Clark, F. E., Disposal of oil wastes by microbial assimilation report 1934. U.S. Atomic Energy commission, Washington, DC. (1974).

Frey, B. ; Stemmer, M. ; Widmer, F. ; Luster, J. and Sperisen, C., Microbial activity and community structure of soil after heavy metal contamination in forest ecosystem. *Soil Biol. Biochem.*; **38**, 1745-1756 (2006).

Friis, N. and Myers-Keith, P., Biosorption of uranium and lead by *Streptomyces longwoodensis*. *Biotechnol. Bioeng.*; **28**, 21-28 (1986).

Gao, Y. Z. ; Xiong, W. ; Ling, W. T. and Xu, J., Sorption of phenanthrene by soils contaminated with heavy metals. *Chemosphere*; **65**, 1355-1361 (2006).

Gao, Y. Z. ; Zhu, L. Z. and Ling, W. T., Application of the partition limited model for plant uptake of organic chemicals from soil and water. *Sci. Total Environ.*; **336**, 171-182 (2005).

García-Orenes, F. ; Guerrero, C. ; Mataix-Solera, J. ; Navarro-Pedrenño, J. ; Gómez, I. and Mataix-Beneyto, J., Factors controlling the aggregate stability and bulk density in two different degraded soils amended with biosolids. *Soil & Tillage Research*; **82**, 65-76 (2005).

Gassmann, G. Chromatographic separation of diastereomeric isoprenoids for the identification of fossil oil contamination. *Marine Pollution Bulletin*; **12(3)**, 78-84 (1981).

Gee, G. W. and Bauder, J. W., Particle-size analysis. In: Klute, A. (Ed.), *Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods*, 2nd ed. *American Society of Agronomy, Madison, WI*, p. 383-411 (1986).

Geller, J. T. ; Holman, H. Y. ; Su, G. ; Conrad, M. E. ; Pruess, K. and Hunter-Cevara, J. C., Flow dynamics and potentials for biodegradation of organic contaminant in fractured rock vadose zones. *J. Contam. Hydrol.*; **43**, 63–90 (2000).

Gerber, M. A. ; Freeman, H. D. ; Baker, E. G. and Riemath, W. F., Soil washing: A preliminary assessment of its applicability to Hanford, prepared for U.S. Department of Energy by Battelle Pacific Northwest Laboratory, Richland, Washington. Report No. PNL- 7787; UC 902, (1991).

Ghazali, F. M. ; Abdul Rahman, R. N. ; Salleh, A. and Basri, M., Biodegradation of hydrocarbons in soils by microbial consortium. *Int. Biodet. Biodeg.*; **54**, 61-67 (2005).

Gogoi, B. K. ; Dutta, N. N. ; Goswami, P. and Krishna, T. R., A case study of bioremediation of petroleum-hydrocarbon contaminated soil at a crude oil spill site. *Advances in Environ. Research*; **7**, 767-782 (2003).

Golgolev, A. and Wilke, B. M., Combination effects of heavy metals and fluoranthene on soil bacteria. *Biol. Fertil. Soils*; **25**, 274-278 (1997).

Gong, Z. ; Wilke, B. M. ; Alef, K. ; Li, P. and Zhou, Q., Removal of polycyclic aromatic hydrocarbons from manufactured gas plant-contaminated soils using sunflower oil: laboratory column experiments. *Chemosphere*; **62**, 780–787(2006).

Gong, Z. ; Wilke, B. M. ; Alef, K. and Li, P., Activated carbon adsorption of PAHs from vegetable oil used in soil remediation. *J. of Hazardous Materials*; **143**, 372-378 (2007).

Gough, M. A. and Rowland, S. J., Characterization of unresolved complex mixtures of hydrocarbons in petroleum. *Nature*; **344**, 648-654 (1990).

Guo, C. L. ; Zhou, H. W. ; Wong, Y. S. and Tam, N. F., Isolation of PAH-degrading bacteria from mangrove sediments and their biodegradation potential. *Marine Pollution Bulletin*; **51(8-12)**, 1054-1061 (2005).

Haapea, P. and Tuhkanen, T., Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment. *J. of Hazardous Materials*; **136**, 244–250 (2006).

Hatch, A. C. and Burton, G. A., Photo-induced toxicity of PAHs to *Hyalella azteca* and *Chironomus tentans*: effects of mixtures and behavior. *Environ. Pollution*; **106**, 157-167 (1999).

Hesse, P. R., A Textbook of soil chemical analysis. Chem. Publ. Co., Inc. N.Y. (1972).

Horckmans, L. ; Swennen, R. and Deckers, J., Retention and release of Zn and Cd in spodic horizons as determined by single extractions. *Sci. of the Total Environ.*; **376**, 86-99 (2007).

Huesemann, M. H., Guideline for land-treating petroleum hydrocarbon contaminated soil. *J. Soil Contam.*; **3(3)**, 299-318(1994).

Hurst, C. J. ; Knudsen, G. R. ; McInerney, M. V. ; Stetzenbach, L. D. and Wailer, M. V. Manual of environmental microbiology. Washington DC: American Society for Microbiology Press (1997).

Jackson, M. L., Soil chemical analysis advanced course. Published by Author, Dept. of soils. Univ. of Wisconsin U.S.A. (1969).

Jackson, M. L., Soil chemical analysis. Prentice Hall. Englewood Cliffs, N.Y. (1973).

Jamrah, A. ; El-Futaisi, A. ; Hassan, H. and Al-Oraimi, S., Petroleum contaminated soil in Oman: Evaluation of bioremediation treatment and potential for reuse in hot asphalt mix concrete. *Environ. Monit. Assess*; **124**, 331-341(2007).

Jeng, W. L. and Huh, C., A comparison of sedimentary aliphatic hydrocarbon distribution between the southern Okinawa Trough and a nearby river with high sediment discharge. *Estuarine, Coastal and Shelf Sci.*; **66(1-2)**, 217-224 (2006).

Johnson, C. R. and Scow, K. M., Effect of nitrogen and phosphorus addition on phenanthrene biodegradation in four soils. *Bioidegradation*; **10(1)**, 43-50 (1999).

Jullien, A. and François, D., Soil indicators used in road environmental impact assessments. *Resources, Conservation and Recycling*; **48**, 101–124 (2006).

Kaplan, C. W and Kitts, C. L., Bacterial succession in a petroleum land treatment unit. *Environ. Microbiol.*; **70**, 1777-1786 (2004).

Karin, L. ; Olle, S. ; Erasmus, O. and Marika, B., Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry*; **21**,1613–1624 (2006).

Kathryn, A. B., Analytical methods used in oil spill studies. *Marine Pollution Bulletin*; **26 (2)** 68-72 (1993).

Kelly, J. J. and Tate, R. L., Effects of heavy metals contamination and remediation on soil microbial communities in the vicinity of a Zn smelter. *J. Environ Qual*; **27**, 609–617(1998).

Kim, H., Soil sampling, preparation, and analysis, second edition (2005).

King, A. J. ; Readman, J. W. and Zhou, J. L., Dynamic behaviour of polycyclic aromatic hydrocarbons in Brighton Marina, UK. *Marine Pollution Bulletin*; **48(3-4)**, 229-239 (2004).

Kirimura, K. ; Furuya, T. ; Nishii, Y. ; Yoshitaka, I. ; Kino, K. and Usami, S., Biodesulfurization of dibenzothiophene and its derivatives through the selective cleavage of carbon-sulfur bonds by a moderately thermophilic bacterium *Bacillus subtilis* WU-S2B. *J. Biosci. Bioeng*; **91(3)**, 262-266 (2001).

Koomen, I. ; McGrath, S. P. and Giller, K. E., Mycorrhizal infection of white clover is delayed in soils contaminated with heavy metals from past sewage sludge applications. *Soil Biol Biochem*; **22**, 871– 873 (1990).

Koutny, M. ; Ruzicka, J. and Chlachula, J., Screening for phenol-degrading bacteria in the pristine soils of south Siberia. *Appl. Soil Ecol*; **23**, 79-83 (2003).

Krause, E. and Ettl, V. A., Solubilities and stabilities of ferric arsenate compounds. *Hydrometallurgy*; **22**, 311-337 (1989).

Kumar, C. S. ; Sastry, K. S. and Mohan, P. M., Use of wide type and nickel resistant *Neurospora crassa* for the removal of Ni²⁺ from aqueous medium. *Biotechnology letters*; **14**, 1099-1102 (1992).

LaGrega, M. D. ; Buckingham, P. L. and Evans, J. C., Hazardous waste management, McGraw Hill, N.Y.(1994).

Le Dréau, Y. ; Jacquot, F. ; Doumenq, P. ; Guiliano, M. ; Bertrand, J. C and Mille, G., Hydrocarbon balance of a site which had been highly and chronically contaminated by petroleum wastes of a refinery (from 1956 to 1992). *Marine Pollution Bulletin*; **34 (6)**, 456-468 (1997).

Leahy, J. G. and Colwell, R. R., Microbial degradation of hydrocarbons in the environment. *Microbiol. Rev*; **54**, 305-315 (1990).

Lee, H. K., Wright, G. J. and Swallow, W. H., A qualitative UV spectroscopic method as an initial guide to source origins of polycyclic aromatic hydrocarbons. *Environ. Pollution*; **49**,167-175 (1988).

Leo, C. O. and Samuel, O. A., Extractable hydrocarbons, nickel and vanadium contents of Ogbodo-Isiokpo oil spill polluted soils in Niger Delta, Nigeria. *Environ. Monitoring and Assessment*; **110**, 129-139 (2005).

Lister, S. K. and Line, M. A., Potential utilization of sewage sludge and paper mill waste for biosorption of metals from polluted water ways. *Bioresour. Technol.*; **79**, 35-39 (2001).

Lofts, S. ; Spurgeon, D. J. ; Svedesn, C. and Tipping, E., Deriving soil critical limits for Cu, Zn, Cd, and pH: a method based

on free ion concentrations. *Environ. Sci. Technol.*; **38**, 3623-3631 (2004).

Lorenz, S. E. ; Hamon, R. E. ; Domingues, H. C. ; Sequeira, E. M. ; Christensen, T. H. and McGrath, S. P., Cadmium and zinc in plants and soil solutions from contaminated soils. *Plant and Soil*; **189**, 21-31 (1997).

Lors, C. and Mossnann, R. J., Characteristics of PAHs intrinsic degradation in two coke factory soils. *Polycyclic Aromatic Compounds*; **25**, 67-85 (2005).

Maier, R. M., Biosurfactant: Evolution and diversity in bacteria. *Adv. Appl. Microbiol*; **52**, 101-121 (2003).

Maliszewska-Kordybach, B., Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Appl. Geochem*; **11**, 121-127 (1996).

Margesin, R. ; Zimmerbauer, A. and Schinner, F., Monitoring of bioremediation by soil biological activities. *Chemosphere*; **40**, 339-346 (2000).

Margesin, R. and Schinner, F., Bacterial heavy metal-tolerance: extreme resistance to nickel in *Arthrobacter* strains. *J. Basic Microbiol*; **36(4)**, 269-282 (2001).

Margesin, R. and Schinner, F., Low-temperature bioremediation of a waste water contaminated with anionic surfactants and fuel oil. *Appl. Microbiol. Biotechnol*; **94(4)**, 482-486 (1998).

Marin, J. A. ; Moreno, L. J. ; Hernandez, T. and Garcia, C., Bioremediation by composting of heavy oil refinery sludge in semiarid conditions. *Biodeg.*; **17**, 251- 261 (2006).

Marwood, M. T. ; Knoke, K. ; Yau, K. ; Lee, H. ; Trevors, J. T. ; Suchorski, T. ; Flemming, C. A. ; Hodge, V. ; Liu, D. L. and Seech, A. G., Comparison of toxicity detected by five bioassays during bioremediation of diesel fuel-spiked soils. *Environ. Toxicol Water Qual*; **13**, 117-129(1998).

Masters, C. D. and Root, D. H., World Resources of Crude Oil, Natural Gas, Natural Bitumen and Shale Oil. Twelfth World Petroleum Congress, Chichester, England John Wiley & Sons, Topic 5, (1987).

McCarthy, K. ; Walker, L. ; Vigoren, L. and Bartel, J., Remediation of spilled petroleum hydrocarbons by in situ landfarming at an arctic site. *Cold Regions Sci. and Technol.*; **40**, 31–39 (2004).

Means, J. L. and Hinchee, R. E., Emerging technology for bioremediation of metals, Lewis Publishers, Boca Raton, FL, (1994).

Medeiros, P. M. and Bicego, M. C., Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. II. São Sebastião, SP—Brazil. *Marine Pollution Bulletin*; **49(11-12)**, 892-899 (2004).

Meintanis, C. ; Chalkou, K. I. ; Kormas, K. A. and Karagouni, A. D., Biodegradation of crude oil by thermophilic bacteria isolated from a volcano island. *Biodeg.*; **17(2)**, 3-9 (2006).

Méndez, E. M ; España, M. S. A. and García, F. J., Chemical fingerprinting applied to the evaluation of marine oil pollution in the coasts of Canary Islands (Spain). *Environ. Pollution*; **111 (2)**, 177-187 (2001).

Miller, J. S. and Olejnik, D., Ozonation of polycyclic aromatic hydrocarbons in water solution, in: Proceedings of the 15th Ozone World Congress, International Ozone Association, London, United Kingdom, September 11–15, 478–492 (2001).

Milles, M. A. ; Bonner, J. S. ; Page, C. A. and Autenrieth, R. L., Evaluation of bioremediation strategies of a controlled oil release in a wetland. *Marine Pollution Bulletin*; **49**, 425-435 (2004).

Mishra, S. ; Jyot, J. ; Kuhad, R. C. and Lab, B., Evaluation of inoculum addition to stimulate in situ bioremediation of oily-sludge-contaminated soil. *Appl. Environ. Microbiol.*; **67**, 1675-1681 (2001).

Mishra, S. ; Sarma, P. M. and Lal, B., Crude oil degradation efficiency of a recombinant *Acintebacter baumannii* strain and its survival in crude oil-contaminated soil microcosm. *FEMS Microbiol. Lett*; **235**, 323-331 (2004).

Molinerio, A. L. and Castillo, J. R., Analytical Letter, Determination of nickel and vanadium in oil by inductively coupled plasma-atomic emission spectrometry with microemulsion sample introduction. *Analytical Letter*; **31 (5)**, 903-911 (1998).

Moran, A. C. ; Olivera, N. ; Commendatore, M. ; Esteves, J. L. and Sineriz, F., Enhancement of hydrocarbon waste biodegradation by addition of a biosurfactant from *Bacillus subtilis* O9. *Biodeg.*; **11**, 65-71(2000).

Morera, T. M. ; Echeverria, C. J. and Garridce, J. J., Mobility of heavy metals in soil amended with sludge. *Canadian J. of Soil Sci.*; **52**, 405-41(2001).

Morgan, P. and Watkinson, R. J., Hydrocarbon degradation in soils and methods for soil biotreatment. *Crit. Rev. Biotechnol*; **8(4)**, 305-333(1989).

Moustafa, Y., Monitoring of oil pollution in Red Sea. MSc. Thesis, Cairo University, Egypt (1990).

Mrayyan, B. and Battikhi, M. N., Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. *J. Hazardous Materials*; **120**, 127-134 (2005).

Mukherjee, A. K. and Das, K., Correlation between diverse cyclic lipopeptides production and regulation of growth and substrate utilization by *Bacillus subtilis* strains in a particular habitat. *FEMS Microbiol. Ecol*; **54**, 479-489 (2005).

Naidu, R. and Herter, R. D., Effect of different organic ligands on cadmium sorption by extractability from soils. *Soil Sci. Soc. of Am. J.*; **62**, 644-650 (1998).

Nannipieri, P. ; Ascher, J. ; Ceccherini, M. T. ; Landi, L. and Pietramellara, G., Microbial diversity and soil function. *European J. Soil Sci*; **54**, 655-670 (2003).

Nocentini, M. ; Pinelli, D. and Fava, F., Bioremediation of soil contaminated by hydrocarbon mixture: the residual concentration problem. *Chemosphere*; **41**, 1115-1123 (2000).

NRC, Alternatives for ground water cleanup, national research council, national academy press, Washington, D.C. (1994).

Oades, J. M., The role of biology in the formation, stabilization and degradation of soil structure. *Geoderma*; **56**, 377– 400 (1993).

Odokuma, L. O. and Dickson, A. A., Bioremediation of a crude oil polluted tropical rain forest soil. *Global J. Environ. Sci*; **2** (1), 29- 40 (2003).

Ogoke, N. J., Rehabilitating crude oil polluted land. In: Aina EOA, Adedipe NO, editors. The petroleum industry and the environmental impact in Nigeria. FEPA Monograph, vol. 5. Abuja (Nigeria): Federal Environmental Protection Agency (FEPA), 180–190 (1996).

Olaniran, A. O. ; Pillay, D. and Pillay, B., Biostimulation and bioaugmentation enhances aerobic biodegradation of dichloroethenes. *Chemosphere*; **63**, 600-608 (2006).

Oliveira, A. and Pampulha, M. E., Effect of long term heavy metals contamination on soil microbial characteristics. *J. Biosci. Bioeng.*; **102**(3), 157-161(2006).

Pannu, J. K ; Singh, A. and Ward, O. P., Vegetable oil as a contaminated soil remediation amendment: application of peanut oil for extraction of polycyclic aromatic hydrocarbons from soil. *Process Biochem*; **39**, 1211–1216 (2004).

Peters, K. E. and Moldowan, J. W., The Biomarker Guide: Interpreting molecular fossils in petroleum and ancient sediments. Prentice-Hall, New Jersey (1993).

Piddington, C. S. ; Kovacevich, B. R. and Rambosek, T., Sequence and molecular characterization of a DNA region encoding the dibenzothiophene desulfurization operon of *Rhodococcus* sp. strain IGTS8. *J. Appl. Environ. Microbiol*; **61(2)**, 468-475 (1995).

Pierce, M. L. and Moore, C. B., Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.*; **16**, 1247-1253 (1982).

Ping, L. F. ; Luo, Y. M. ; Zhang, H. B. ; Li, Q. B. and Wu, L. H., Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environ. Pollution*; **147**, 358-365 (2007).

Poli, A. ; Romano, I. ; Caliendo, G. ; Nicolaus, G. ; Orlando, P. ; De-Falco, A. ; Lama, L. ; Gambacorta, A. and Nicolaus, B., *Geobacillus toebii* subsp.nov., a hydrocarbon-degrading, heavy metals resistant bacterium from hot compost. *J. General Appl. Microbiol*; **52(4)**, 223-234 (2006).

Radwan, S. S. ; Al-Maillem, D. ; El-nemr, I. and Salamah, S., Enhanced remediation of hydrocarbone contaminated desert soil fertilized with organic carbons. *Int. Biodeter. Biodeg.*; **46**, 129-132 (2000).

Rahman, k. S. M. ; Rahman, T. J. ; Kourkoutas, Y. ; Petsas, I. ; Marchant, R. and Banat, I. M., Enhancement bioremediation of n-alkane in petroleum sludge using bacterial consortium amended with rhamnolipid and micronutrients. *Bioresour. Technol*; **90**, 159-168 (2003).

Raja, C. E. ; Anbazhagan, K. A. and Selvam, G., Isolation and characterization of metal-resistant *Pseudomonas aeruginosa* strain. *World J. of Microbiol & Biotechnol.*; **22**, 577-585 (2006).

Raymond, C. L. ; Rogers, L. A. and Erickson, D. C., Mobility of residues at petroleum industry hazardous wastes land treatment sites. *Water Sci. Tech.*; **25**, 191-196 (1992).

Reed, J. F. and Rigney, J. A., Soil sampling from fields of uniform and non-uniform appearance and soil types. *J. Am. Soc. Agronomy*; **39**, 26-40 (1947).

Riis, V. ; Babel, W. and Pucci, O. H., Influence of heavy metals on the microbial degradation of diesel fuel. *Chemosphere*; **49**, 559-568 (2002).

Rossini, O. S. and Fernández, E. A. J., Monitoring of heavy metals in topsoils, atmospheric particles and plant leaves to identify possible contamination sources. *Microchemical J.*; **86**, 131-139 (2007).

Rumer, R. R. and Ryan, M. E., Barrier containment technologies for environmental remediation applications. John Wiley & Sons, N.Y. (1995).

Sabate, J. ; Vinas, M. and Solanas, A. M., Bioavailability assessment and environmental fate of polycyclic aromatic hydrocarbons in biostimulated creosote-contaminated soil. *Chemosphere*; **63**, 1648-1659 (2006).

Sabate, J. ; Vinas, M. and Solanas, A. M., Laboratory-scale bioremediation experiments on hydrocarbon-contaminated soils. *Int. Biodet. Biodeg.*; **52**, 19-25 (2004).

Salvo, V. S. ; Gallizia, I. ; Moreno, M. and Fabiano, M., Fungal communities in PAH-impacted sediments of Genoa-Voltri Harbour (NW Mediterranean, Italy). *Marine Pollution Bulletin*; **50(5)**, 553-559 (2005).

Samanta, S. ; Singh, O. V. and Jain, R. K., Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. *Trends in Biotechnol.*; **20**, 243-248 (2002).

Sandrin, T. R. ; Chech, A. M. and Maier, R. M., A rhamnolipid biosurfactant reduces cadmium toxicity during naphthalene biodegradation. *Appl. Environ. Microbiol.*; **66(10)**, 4585-4588 (2000).

Sandrin, T. R. and Marier, R. M., Impact of metals on biodegradation of organic pollutants. *Environ. Health Perspect.*; **111(8)**, 1093-1101 (2003).

Sartori, G. ; Ferrari, G. A. and Pagliai, M., Changes in soil porosity and surface shrinkage in a remolded, saline clay soil treated with compost. *Soil Sci.*; **139**, 523– 530 (1985).

Schnoor, J. L., Phytoremediation, TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA. (1997).

Schock, M. R., Causes of temporal variability of lead in domestic plumbing system. *Environ. Monitoring and Assessment*; **15**, 59-66 (1990).

Shen, G. ; Lu, Y. and Hong, J., Combined effect of heavy metals and polycyclic aromatic hydrocarbons on urease activity in soil. *Ecotoxicology and Environ. Safety*; **63**, 474-480 (2006).

Shi, Z. ; Tao, S. ; Pan, B. ; Fan, W. ; He, X. ; Zuo, Q. ; Wu, S. ; Li, B. ; Cao, J. ; Liu, W. ; Xu, F. ; Wang, X. ; Shen, W. and Wong, P., Mercury contamination in human hair and fish from Cambodia: levels, specific accumulation and risk assessment. *Environ. Pollution*; **134**, 79-110 (2005).

Shively, W. ; Bishop, P. ; Gress, D. and Brown, T., Leaching tests of heavy metals stabilized with portland cement. *J. WPCF*; **38**, 234-241 (1986).

Sikkema, J. ; De-Bont, J. A. M. and Poolman, B., Mechanism of membrane toxicity of hydrocarbons. *Microbiol. Rev*; **59**, 201-222 (1995).

Siunova, T. V. ; Anokhina, T. O. ; Mashukova, A. V. ; Kochetkov, V. and Boronin, A. M., Rhizosphere strain of *pseudomonas chloroaphis* capable of degrading naphthalene in the presence of cobalt/nickel. *Microbiol*; **76**, 212-218 (2007).

Smith, I. C. ; Ferguson, T. L. and Carson, B. L., Metals in new and used petroleum products and by-products. *Quantities and Consequences, Elsevier*; 124–144(1999).

Smith, L. A. ; Means, J. L. ; Chen, A. ; Alleman, B. ; Chapman, C. C. ; Tixier, J. S. ; Brauning, S. E. ; Gavaskar, A. R. and Royer, M. D., Remedial options for metals-contaminated sites, Lewis Publishers, Boca Raton, FL. (1995).

Sokhn, J. ; De Leij, F. A. M. ; Hart, T. D. and Lynch, J. M., Effect of copper on the degradation of phenanthrene by soil microorganisms. *Letter Appl. Microbiol*; **33**, 164-168 (2001).

Sposito, G. The chemistry of soils, Oxford University Press, N.Y. (1989).

Straube, W. L. ; Jones-Meehan, J. ; Prichard, P. H. and Jones W. R., Bench-Scale optimization of bioaugmentation strategies for treatment of soils contaminated with high molecular weight polyaromatic hydrocarbons. *Resources, Conservation and Recycling*; **27**, 27-37(1999).

Struthers, I. ; Hinz, C. and Sivapalan, M., Conceptual examination of climate–soil controls upon rainfall partitioning in an open-fractured soil II: Response to a population of storms. *Advances in Water Resources*; **30(3)**, 518-527(2007).

Tan, K. H., Environmental soil science. Marcel Dekker, Inc., N.Y. (1994).

Tan, K. H., Humic matter in soil and the environment. Principles and Controversies. Marcel Dekker. Inc., N.Y. (2003).

Tan, K. H., Principles of soils chemistry. Marcel Dekker, Inc., N.Y. (1982).

Tao, S. ; Cui, Y. H. ; Xu, F. L. ; Li, B. G. ; Cao, J. ; Liu, W. X. ; Schmitt, G. ; Wang, X. J. ; Shen, W. R. ; Qing, B. P. and Sun, R., Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin. *Sci. Total Environ.*; **320** 11–24 (2004).

Tipping, E. ; Griffith, J. R. and Hilton, J., The effect of adsorbed humic substances on the uptake of copper (II) by goethite. *Croatica Chemica Acta*; **56 (4)**, 613-621(1983).

Tolosa, I. ; De-Mora, S. ; Reza, S. M. ; Villeneuve, J. P. ; Bartocci, J. and Cattini, C., Aliphatic and aromatic hydrocarbons in coastal caspian sea sediments. *Marine Pollution Bulletin*; **48**, (1-2), 44-60 (2004).

Trabelsi, S. and Driss, M., Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. *Marine Pollution Bulletin*, **50**, 344-359 (2005).

Trindade, P. V. O. ; Sobral, L. G. ; Rizzo, A. C. L. ; Leite, S. G. F. and Soriano, A. U., Bioremediation of a weathered and recently oil-contaminated soils from Brazil: a comparison. *Chemosphere*; **58**, 515- 522 (2005).

U.S. Salinity Laboratory Staff, Diagnosis and improvement of saline and alkali soils, USDA Handbook 60. U.S. Government Printing Office, Washington, DC, U.S.A. p.1-160 (1954).

U.S.EPA, Environmental Protection Agency. Design and Construction of RCRA/CERCLA Final Covers, Report EPA/625/4-91/025, U.S. Environmental Protection Agency, Cincinnati, OH (1991).

U.S.EPA, Environmental Protection Agency. Guides to Pollution Prevention: The Metal Finishing Industry." Rep. No. EPA/625/R-92/011, Office of Research and Development Washington, D.C. 20460 (1992).

U.S.EPA, Environmental Protection Agency. Report: Recent Developments for In Situ Treatment of Metals contaminated Soils, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, draft. (1996).

Ueno, A. ; Hasanuzzaman, M. ; Yumoto, I. and Okuyama, H., Verification of degradation of n-alkanes in diesel oil by *Pseudomonas aeruginosa* strain WatG in soil microcosms. *Microbiol.*; **52(3)**, 182-185 (2006).

Uraizee, F. A. ; Suidan, M. T. and Venosa, A. D., Effects of temperature and chemical composition on crude oil biodegradation. *In Site On-Site Bioremediation*; **5**, 66- 68 (1997).

Urum, K. ; Pekdemir, T. and Copur, M., Surfactants treatment of crude oil contaminated soils. *J. of Colloid and Interface Sci.*; **276**, 456–464 (2004).

Vega, F. A. ; Covelo, E. F. ; Andrade, M. L. and Marcet, P., Relationships between heavy metals content and soil properties in minesoils. *Analytica Chimica Acta*; **524**, 141–150 (2004).

Viguri, J. ; Verde, J. and Irabien, A., Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay, Northern Spain. *Chemosphere*; **48**,157-165 (2002).

Wang, Z. D. ; Fingas, M. ; Blenkinsopp, S. ; Sergy, G. ; Landriault, M. ; Sigouin, L. ; Foght, J. ; Semple, K. and Westlake, D. W. S., Comparison of oil composition changes due to biodegradation and physical weathering in different oils. *J. Chromatography A*; **809**, 89-107 (1998).

Wang, Z. D. ; Fingas, M. ; Owens, E. H. ; Sigouin, L. and Brown, C. E., Long-term fate and persistence of the spilled Metula oil in a marine salt marsh environment degradation of petroleum biomarkers. *J. of Chromatography A*, **926**, 275-290 (2001).

Wang, Z. D. ; Fingas, M. and Sergy, G., Chemical characterization of crude oil residues from an arctic beach by GC/MS and GC/FID. *Environ. Sci. and Technol.*; **29**, 2622-2631 (1995).

Wang, Z. D. and Fingas, M., Fate and identification of spilled oils and petroleum products in the environment by GC-MS and GC-FID. *Energy Sources*; **25(6)**, 491-510 (2003).

Wang, Z. D. and Fingas, M., Use of methylthiophenes as Mmarkers for differentiation and source identification of oils. *Environ. Sci. and Technol.*; **29(11)**, 2841-2849 (1995).

Watanabe, K., Microorganisms relevant to bioremediation. *Curr. Opin. Biotechnol.*; **12**, 237-241 (2001).

Welch, J. and Chaney, R. L., Soil properties, irrigation water quality and soil moisture level influenced on movement of nickel in sewage-treated soils. *J. Environ. Qual.*; **16**, 403-410 (1987).

White, M. C. and Chaney, R. L., Zinc, cadmium and manganese uptake by soybean from two zinc and cadmium amended coastal plain soil. *Soil Sci. Soc. of Am. J.*; **44**, 308-313 (1980).

Wild, A., Russell's soil conditions and plant growth. 11th Edition, Longman, London. (1988).

Willard, H. H. and Diehl, H., Advanced qualitative analysis. Van Nostrand, N.Y.(1943).

Willett, I. R. and Bond, W. J., Sorption of manganese, uranium, and radium by highly weathered soils. *J. Environ. Qual.*; **24**, 834-845 (1995).

Wong, K. W. ; Toh, B. A. ; Ting, Y. P. and Obbard, J. P., Biodegradation of phenanthrene by indigenous microbial biomass in zinc amended soil. *Lett. Appl. Microbiol.*; **40**, 50-55 (2005).

Wu, Y. ; Zhang, J and Zhijian, Z., Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. *Marine Pollution Bulletin*; **46(5)**, 619-625 (2003).

Yaron, B. ; Sutherland, P. ; Galine, T. and Acher, A. J., Soil pollution by petroleum products II. Adsorption of kerosene vapors on soils. *J. of contam. Hydrology*; **4**, 347-358 (1989).

Ye, B. ; Zhang, Z. and Mao, T., Pollution sources identification of polycyclic aromatic hydrocarbons of soils in Tianjin area, China. *Chemosphere*; **64**, 525-534 (2006).

Yu, S. H. ; Ke, L. ; Wong, Y. S. and Tam, N. F. Y., Biodegradation of polycyclic aromatic hydrocarbons (PAHs) by a bacterial consortium enriched from mangrove sediments. *Environ. Int.*; **31**, 149-154 (2005).

Yu, X. Z. ; Gao, Y. ; Wu, S. C. ; Zhang, H. B. ; Cheung, K. C. and Wong, M. H., Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. *Chemosphere*; **65**, 1500–1509 (2006).

Zhang, J. ; Cai, L. ; Yuan, D. and Chen, M., Distribution and sources of polynuclear aromatic hydrocarbons in Mangrove surficial sediments of Deep Bay, China. *Marine Pollution Bulletin*; **49(5-6)**, 479-486 (2004).

Zhang, S. Z. and Shan, X. Q., The determination of rare earth elements in soil by inductively coupled plasma mass spectrometry. *At. Spectr.*; **18**, 140-144 (1997).

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ARABIC SUMMARY

تقييم الملوثات البترولية في التربة وطريقة المعالجة

رسالة مقدمة

من

رائد محمد محمد حجازي

بكالوريوس علوم - ١٩٩٩

كجزء متمم لنيل درجة الماجستير في العلوم
كيمياء

إلى

قسم الكيمياء - كلية العلوم - جامعة حماه

٢٠٠٨

تقييم الملوثات البترولية في التربة وطريقة المعالجة

رسالة ماجستير

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الملخص العربي

تعتبر التربة أحد مكونات البيئة، ونظراً لأهمية التربة بالنسبة للإنسان، فإن تلوثها سوف يؤثر عليه بطريقة مباشرة أو غير مباشرة، ومن هذه الملوثات التي تتعرض لها التربة الملوثات البترولية. لذلك هدفت الدراسة إلى تقييم هذه الملوثات في التربة، ومعرفة مدى تأثيرها عليها وقد تم إختيار طريق القاهرة- الإسكندرية الزراعي من ضمن مناطق الدراسة نظراً لإتساع الرقعة الزراعية على جانبي هذا الطريق ولتعدد مصادر الملوثات عليه، حيث تم أخذ ١٠ عينات من هذه المنطقة من مسافات تبعد ١٠، ٢٠ و ٣٠ كم من بداية الطريق، وتراوحت أماكن جمع العينات بين عينات جمعت من على جانب الطريق مباشرة، إلى عينات تبعد عن جانب الطريق مسافة ١ كم، وقد أخذت من كل عينات سطحية وعينات من عمق ٣٠ سم، كما تم أخذ عينه من محمية زراعية تابعه لوزارة الزراعة المصريه تبعد مسافة ٣٢ كم من بداية الطريق. وأما المنطقه الثانيه فقد تم أخذ عينه واحده من منطقة توشكى، حيث أنها تعتبر منطقة جديدة تم استصلاحها منذ عدة سنوات، وبالتالي فإنها كانت أقل عرضة للتلوث. فى حين شملت المنطقه الثالثه جمع ٥ عينات من سطح التربة، من المنصورة بداية من منطقة دكرنس حيث أخذت العينة الأولى من حقل بترول وسط الأراضى الزراعية ومعدلات التلوث بها عالية جداً ثم تم اخذ ٤ عينات من التربة على أبعاد ١، ١٠، ٢٠، ٥٠ كم من هذا الحقل.

وفى البداية تمت دراسة بعض الخواص الفيزيقيه والكيميائية لعينات التربة. ومن الخواص الفيزيقيه التى تم دراستها، دراسة قوام التربة للعينات الذى يوضح نسبة توزيع الأحجام المختلفه فى كل عينه، وكذلك تعيين نسبة الرطوبة بها والتي اتضح أنها أقل فى عينات السطح عنها فى عينات العمق وذلك نتيجة لارتفاع معدل البخر فى عينات السطح عنها فى عينات العمق والكثافة الظاهرية، وهى التى وجد أنها تزداد مع العمق نتيجة لزيادة الضغط مع انخفاض نسبة المادة

العضوية. وتضمنت دراسة الخواص الكيميائية دراسة المادة العضوية وهي التي تقل مع العمق حيث تقل مصادرها، التوصيل الكهربى والذى وجد أنه يزداد أويقل تبعاً لتركيز الأيونات والكاتيونات الذائبة، الأس الهيدروجينى وهو الذى يعتبر أهم خاصية كيميائية للتربة لأنه يؤثر بشكل مباشر أو غير مباشر على ذوبان أو ترسيب العناصر الثقيلة وتراوحت العينات من متعادلة إلى قلوية، وتم أيضاً دراسة السعة التبادلية الكاتيونية حيث وجد أنها تتأثر بنسبة الحبيبات الطينية فى العينة، فنجد أن العينة رقم ٣ أقل العينات فى نسبة الحبيبات الطينية وهى أيضاً أقلهم فى قيمة السعة التبادلية الكاتيونية والعكس وجد فى عينة رقم ١٢. وتم دراسة العناصر الثقيلة وذلك نظراً لإعتبارها ملوثات خطيرة على التربة، وبالتالي على صحة الإنسان، حيث تم التركيز على عدة عناصر منها الرصاص، النيكل، الكروم، الكاديوم، النحاس، المنجنيز، الكوبلت، والزنك، وهذه العناصر وجد أن تركيزاتها تختلف من عينة لأخرى. وجد أن الاختلافات فى نسبة الحديد فى العينات ضئيلة ماعدا العينة رقم ١٣، وأن نسبة المنجنيز تزداد بالابتعاد عن الطريق، فى حين وجد الكاديوم بكميات قليلة جداً وكان أقل العناصر من حيث نسبة التواجد ثم جاء الرصاص فى المرتبة الثانية، حيث وجد فى العينات التى تم أخذها من على بعد ٣٠ كم، وربما كان هذا نتيجة تراكمه فى التربة لاستخدامه فى وقود السيارات خلال سنوات ماضية أو نظراً لوجود مصادر رصاص قريبة من هذا الموقع. وبالنسبة للنيكل وجد أن نسبته تقل كلما ابتعدنا عن الطريق، فى حين وجد أن نسبة النحاس متقاربة إلى حد ما فى جميع العينات ويعتقد أن تكون المخصبات الزراعية أحد مصادره الرئيسية.

ثم تطرقت الدراسة بعد ذلك للتعين الكمي للملوثات البترولية وهى التى وجد أن نسبتها تراوحت بين ٦٤٧ و ١٥٦٠ جزء فى المليون ماعدا العينتين رقمى ١٢ و ١٣، وكان ذلك متوقفاً، حيث أن العينة رقم ١٢ تم أخذها من منطقة توشكى وهى منطقة نظيفة ومصادر الملوثات البترولية بها تكاد تكون منعدمة، بينما العينة

رقم ١٣ تم أخذها من جانب بترولي وبالتالي معدل التلوث بها مرتفع جداً وهي أعلى من المعدلات المسموح بها. وتم أيضاً تعيين المركبات البرافينية ذات السلسلة المستقيمة والمتفرعة بواسطة استخدام كروماتوجرافيا الغاز حيث وجد أن الملوثات في مجملها ناتجة من أصل بترولي كما في العينات أرقام ١، ٧، و١٣ أوبترولي مضاف إليه بعض المركبات البرافينية الناتجة من أصل حيوي كما في العينات أرقام ٣، ١١، ١٤، و١٥.

وفي الجزء الأخير من الرسالة تمت دراسة أنسب الظروف لمعالجة هذا التلوث البترولي بيولوجياً باستخدام كائنات دقيقة متواجدة أصلاً في مكان التلوث لمحاولة إزالة أو الإقلال من هذه المركبات الهيدروكربونية، حيث تم عزل ٧ من الكائنات الدقيقة والتعرف عليها وتم إختيار أكثرها نمواً وتحملاً لتركيزات عالية من العناصر الثقيلة وكانت هي (*Cellulomonas hominis*) ثم تم إختيار أربعة عناصر وهي النيكل والمنجنيز والنحاس والزنك حيث أنها مثلت أعلى التركيزات في التربة التي تم عزل الكائنات الدقيقة منها، وتمت دراسة تأثير كل عنصر بصفة منفردة وفي تركيبات مختلفة على عملية المعالجة، ثم دراسة تأثير خليط من العناصر الأربعة بتركيزات مختلفة أيضاً. وتوصلت الدراسة إلى أنه بعد ٣٥ يوم من المعالجة، تمكنت (*Cellulomonas hominis*) من الإقلال من الملوثات البترولية بنسبة ٨٠% وهذا ما وضحة العينات عند تحليلها باستخدام كروماتوجرافيا الغاز وتم أيضاً استخدام أحد المركبات العطرية عديدة الحلقات (*phenantherene*) لدراسة تأثير كل عنصر بصفة منفردة بتركيزات مختلفة على عملية معالجته، ثم دراسة تأثير خليط من العناصر الأربعة بتركيزات مختلفة وقد إنخفضت نسبة الإزالة مع زيادة تركيز العناصر الثقيلة، حيث وصلت إلى نسبة ٧,٦% في حالة الخليط، بينما وصلت نسبة الإزالة إلى ٤٠,٨% ، ٤٠,٤% ، ٦٠,٠% ، ٨٠,٠% في حالة استخدام كل من المنجنيز، الزنك، النحاس، والنيكل بالترتيب.

وخلصت الدراسة إلى ضرورة الرصد المتكرر من أن لأخر لتواجد
الملوثات البيئية في المناطق محل الدراسة والعمل على حماية التربة ووضع
الضوابط اللازمة لحمايتها والحفاظ عليها.