SUMMERY 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-C_{25}. 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 has 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 operations. 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 contaminates 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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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 حلوان

٢٠٠٨

تقييم الملوثات البترولية في التربة وطريقة المعالجة

رسالة ماجستير

أسماء السادة المشرفين	التوقيع
أ.د / جلال الدين حمزه الجميعي	
أ.د/ سامية رضوان العزباوي	
أ.د/ ياسر محمد محمود مصطفي	
أ .م. د/ الزهراء عبد الرحمن الفقي	

الملخص العربي

تعتبر التربة أحد مكونات البيئة، ونظراً لأهمية التربة بالنسبة للإنسان، فإن تلوثها سوف يؤثر عليه بطريقة مباشرة أوغير 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 جانبى هذا الطريق ولتعدد مصادر الملوثات عليه، حيث تم أخذ ١٠ عينات من هذه المنطقة من مسافات تبعد ١٠، ٢٠ و٣٠ كم من بداية الطريق، وتراوحت أماكن جمع العينات بين عينات جمعت من على جانب الطريق مباشرة، إلى عينات تبعد عن جانب الطريق مسافة ١كم، وقد أخذت من كل عينات سطحية وعينات من عمق ٣٠ سم، كما تم أخذ عينه من محميه زراعيه تابعه لوزارة الزراعة المصريه تبعد مسافة ٣٢ كم من بداية الطريق. وأما المنطقه الثانيه فقد تم أخذ عينه واحدة من منطقة توشكى، حيث أنها تعتبر منطقة جديدة تم استصلاحها منذ عدة سنوات، وبالتالى فانها كانت أقل عرضة للتلوث. فى حين شملت المنطقه الثالثة 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 الفيزيقية والكيميائية لعينات التربة. ومن الخواص الفيزيقية التى تم دراستها، دراسة قوام التربة للعينات الذى يوضح نسبة توزيع الأحجام المختلفة فى كل عينه، وكذلك تعيين نسبة الرطوبة بها والتى 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 وهى التى تقل مع العمق حيث تقل مصادرها، التوصيل الكهربى والذى وجد أنه يزداد أويقل تبعاً لتركيز الأيونات والكاتيونات الذائبه، الأس الهيدروجينى وهو الذى يعتبر أهم خاصية كيميائية للتربة لأنه يؤثر بشكل مباشر أوغير مباشر على ذوبان أوترسيب 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 الطينيه 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، وبالتالى على صحة الإنسان، حيث تم التركيز على عدة عناصرمنها الرصاص، النيكل، الكروم، الكادميوم، النحاس، المنجنيز، الكوبلت، والزنك، وهذه العناصر وجد أن تركيزاتها تختلف من عينة لأخرى. وجد أن الإختلافات فى نسبة الحديد فى العينات ضئيلة ماعدا العينة رقم ١٣، وأن نسبة المنجنيز تزداد بالابتعاد عن الطريق، فى حين وجد الكادميوم 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 ٣٠كم، وربما كان هذا نتيجة تراكمه فى التربة لاستخدامه فى وقود السيارات خلال سنوات ماضية أونظراً لوجود مصادر رصاص قريبة من هذا الموقع. وبالنسبة للنيكل وجد أن نسبتة تقل كلما ابتعدنا عن الطريق، فى حين وجد أن نسبة النحاس متقاربة إلى حد ما فى جميع العينات ويعتقد أن تكون المخصبات الزراعية أحد مصادرة الرئيسية.

ثم تطرقت الدراسة بعد ذلك للتعيين الكمي للملوثات البترولية وهى التى وجد أن نسبتها تراوحت بين ٦٤٧ و١٥٦٠ جزء فى المليون ماعدا العينتين رقمى ١٢ و١٣، وكان ذلك متوقعاً، 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 بئربترولى وبالتالى معدل التلوث بها مرتفع جداً وهى أعلى من المعدلات المسموح بها. وتم أيضاً تعيين المركبات البرافينية ذات السلسلة المستقيمة والمتفرعة بواسطة استخدام كروماتوجرافيا الغاز حيث وجد أن الملوثات فـي مجملهـا ناتجـة مـن أصـل بترولـي كمـا فـى العينـات أرقـام ١، ٧، و١٣ أوبترولي مضاف إليه بعض المركبات البرافينيه الناتجة من أصل حيوي كما فى العينات أرقام ٣، ١١، ١٤، و١٥.

وفى الجزء الأخير من الرسالة تمت دراسة أنسب الظروف لمعالجة هذا التلوث البترولي بيولوجياً بإستخدام كائنات دقيقة متواجدة أصلاً في مكان التلوث لمحاولة إزالة أوالإقلال من هذه المركبات الهيدروكربونية، حيث تم عزل ٧ من الكائنات الدقيقة والتعرف عليها وتم إختيار أكثرها نمواً وتحملاً لتركيزات عالية من العناصر الثقيلة وكانت هى *(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 تاثير كل عنصر بصفة منفردة وفى تركيزات مختلفة على عملية المعالجة، ثم دراسة تأثير خليط من العناصر الأربعة بتركيزات مختلفة ايضاً. وتوصلت الدراسة إلى أنه بعد ٣٥ يوم من المعالجة، تمكنت *(Cellulomonas hominis)* من الإقلال من الملوثات البترولية بنسبة ٨٠% وهذا ما وضحتة العينات عند تحليلها بإستخدام كروماتوجرافيا الغاز وتم أيضاً إستخدام أحد المركبات العطرية عديدة الحلقات (phenantherene) لدرسة 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% فى حالة الخليط، بينما وصلت نسبة الإزالة إلى ٤٠,٨ % ، ٣٠,٤% ، ٦٠,٠ % ، ٨٠,٠ % فى حالة إستخدام كل من المنجنيز، الزنك، النحاس، والنيكل بالترتيب.

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