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SUMMARY

Soil contamination by petroleum hydrocarbons and heavy metals is one of the most serious problems due to their hazardous and toxic effects on soil, marine environment, plants and human health. These contaminants accumulate in plant tissues (fruits and vegetables) and causes many diseases in liver and kidney as well as may lead to cancer and death of human and animals.

In this work, four contaminated soils by hydrocarbons and heavy metals were studied as follows :

1- The first site was clay soils closed to petroleum companies group at Tanta city that contains several factories as pipe line company and company of oil refinery.

2- The second site was clay soils of Kafr El-Zayat city, Gharbiya governorate, beside group of factories that manufacture several types of fertilizers.

3- The third site was clay soils samples collected from mostorod city adjacent to petroleum compound group.

4- soils adjacent to Egypt-Alexandria agricultural road are selected as heavy metals polluted soils derived from automobiles and waste water collected from Benha and Sandyoun El-Kalioubiya governorate.

Soil samples were taken from three distances from the pollution sources i.e. 3 m (D1) , 50 m (D2) and 100 m (D3) and soil depth 0 – 30 cm. In soil samples of the first three sites, concentrations of hydrocarbons (aliphatic and aromatic) and heavy metals (Pb, Cd, Ni, Zn and Mn) were estimated. While in the samples taken from Benha and Sandyoun the available concentrations of the heavy metals were measured.

For remediation of hydrocarbons, five remedies were applied, namely, sodium dodecyl sulfate (SDS), humic acid (HA), Triton X-100, Tween 20 and Tween 80. However, for remediation of heavy metals, eight remedies were applied, namely, diethylenetriaminepentaacetic acid (DTPA), citric acid and oxalic acid in addition to the five remedies used in remediation of hydrocarbons. These remedies were added by rates 0 , 3 and 6 %, except DTPA , citric acid and oxalic acid that was added by rates 0 , 0.04 and 0.08 M. These remedies were added to the soil samples contaminated by 2 , 4 and 6 % of crude oil.

1. Chemical analysis of the crude oil :

The crude oil was taken from the pipe line company that transfers the crude oil to the petroleum compound of Tanta. This crude oil was subjected to analysis by Gas Chromatography (GC) to determine its components. For aliphatic hydrocarbons, eleven various n-paraffins were present, n-Hexacosane ($C_{26}H_{54}$) was the highest concentration which represents 12.36 % of the aliphatic hydrocarbons, followed by n-octacosane ($C_{28}H_{58}$) in 11.71 %, then n-docosane ($C_{22}H_{26}$) 11.04 %, while n-Hexadecane ($C_{16}H_{34}$) was the least percentage of aliphatic hydrocarbons (it was 5.82 %). For aromatic hydrocarbons, the highest percent was for acenaphthalene, it constituted 16.92 % of aromatic hydrocarbons of the crude oil, followed by phenanthrene 16.08 % then fluoranthene 15.89 %, while benzo(b)fluoranthene was the least component. It represented 10.21 % of the aromatic hydrocarbons in this crude oil.

2. Concentrations of contaminants in the soil samples :

2.1. Hydrocarbons :

For aliphatic hydrocarbons, the greatest concentration (698.51,346 and 396.81) µg/g was found in the soil samples closest to the petroleum compound (30 m distance) for the three sites (Mostorod, Kafr El-Zayat and Tanta) respectively. The aliphatic hydrocarbons concentration in soil samples at 50 m distance decreased to be 528.71,245.93 and 277.77 µg/g. The least concentration of aliphatic hydrocarbons 366.45,112.75 and100.84 µg/g respectively was recorded in soil samples far from the pollution source 100 m distance .

For aromatic hydrocarbons, the greatest concentrate pollution source (30 m) , it was 538.3,402.89 and 246.42 µg/g for samples of mostorod, Kafr El-Zayat and Tanta respectively. While these concentrations decreased to be 406.48,291.39 and 126.97 µg/g for D2 (50m) and 239.79,160.14 and 86.15 µg/g for D3 (100m).

2.2. Heavy metals :

The estimated available concentrations of the studied heavy metals (Pb, Cd, Ni, Zn and Mn) in soil samples under investigation indicated that their values were highly exceeded the normal levels in alluvial Nile Delta soil irrigated by Nile River water.

Soil samples of Tanta at D1(3 m) have the greatest concentrations of heavy metals Pd, Cd, Ni, Mn and Zn ,these concentrations were 12.36,00.56,8.96,59.21 and 28.17 µg/g respectively. While these concentrations decreased to be 5.62,0.13,2.29,25.31 and 12.61 µg/g for the same heavy metals respectively at D3(100 m).

Soil samples of Kafr El-Zayat and mostorod have the same manner and have the highest concentrations at D1(3 m). for Kafr El-Zayat concentrations of heavy metals Pd, Cd, Ni, Mn and Zn were 25.11, 0.82, 12.61, 85.14 and 38.14 µg/g while for mostorod samples these concentrations were 20.81, 0.70, 8.81, 58.16 and 29.18 µg/g. On the other hand these concentrations decreased at D3 to be 4.26, 0.51, 5.41, 40.16 and 6.18 µg/g for Kafr El-Zayat and 4.51, 0.00, 2.33, 21.32 and 9.61 µg/g for mostorod samples for the same heavy metals respectively.

Samples of Sandyoun have the highest concentrations 19.25, 0.064, 6.74, 65.17 and 116.24 µg/g for the same heavy metals at D1(3 m) and 9.66, 0.011, 2.11, 30.52 and 100.19 µg/gD3(100 m).

Samples of Benha at D1(3 m) have the concentrations 8 .24, 0.038, 5.26, 50.13 and 39.45 µg/g while for D3 these concentrations were 3. 53, .001, 3.15, 20.15 and 25.14 µg/g for the same heavy metals respectively.

3. Application of organic remedies

3.1. Remediation of hydrocarbons

Application of surfactants as organic remedies was very useful in remediation of hydrocarbons contaminated soils. Sodium dodecyl sulfate (SDS) was the best one in decreasing concentrations of hydrocarbons. samples contaminated with 2 % crude oil, that concentrations of aliphatic hydrocarbons were decreased with percent 54 and 57 % after applying 3 and 6 % of SDS (v/w), respectively. In 4 % oil contaminated samples treatment with the same rates of SDS decreased the concentrations of aliphatic hydrocarbons by 59 and 60 %. While these concentrations had been decreased by percent 89 and 89 % after remediation with SDS by rates 3 and 6 %, respectively for 6% crude oil . SDS also decreased concentrations of aromatic hydrocarbons in the polluted samples. In 2 %

crude oil contaminated samples treatment with SDS by rates 3 and 6 % has decreased concentrations of aromatic hydrocarbons by 66 and 76 %, respectively. In 4 % oil contaminated samples, these concentrations were decreased by 13 and 20 %. While in 6 % contaminated samples, application of 3 and 6 % of SDS reduced the aromatic hydrocarbons by percent 64 and 68 %, respectively

3.2. Remediation of heavy metals :

Treatment of the contaminated soil samples by the studied eight remedies led to decrease the available contents of the studied heavy metals by different rates. DTPA was the best remedy in decreasing the available contents of the studied heavy metals. When DTPA was added by rates 0.04 and 0.08M to 2 % oil contaminated soil samples, the available concentrations of the estimated heavy metals were decreased by percent ranged between 35 – 56 and 50 – 77 %, respectively. While in soil samples contaminated by 4 % crude oil, the concentrations of the studied heavy metals Pb, Cd, Ni, Zn and Mn were 11.21, 0.83, 6.81, 15.47 and 52.61 µg/g respectively,i.e. these concentrations are lower than those of un-treated samples by percent 19 - 43 %. In the highest contamination level (6 % crude oil) treatment with 0.04 and 0.08 M DTPA decreased the heavy metals contents by rates 33 – 50 and 49 – 68 %, respectively.