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Treatment of Oil Polluted Soil by Chemical, Biological and Thermal Methods

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This paper aims to investigate the different treatment options like chemical, biological and thermal treatments at lab scale on oil contaminated soil. The data revealed that maximum oil reduction was observed in chemical treatment. Hydrogen peroxide, sulphuric acid, ferrous sulphate, calcium hypo-chlorite and kerosene/surfactant were used either in single or in combination to get maximum reduction of oil at different dose rate. Best result was obtained (92.60 %) in treatment having 15 mL of hydrogen peroxide in 100 g soil sample in combination of sulphuric acid (3 mL) at pH 2 and in biological treatments maximum oil reduction (89.22 %) occurred in 20 g of cow dung in 100 g soil sample in combination with 1 g of KH_2PO_4. In thermal treatment exposure at 450 °C for 15 min gave maximum reduction (78.22 %) in oil polluted soil sample as compared to 400 and 300 °C.

Keywords: Chemical treatment, Biological treatments, Oil reduction, Thermal treatment.

INTRODUCTION

Soil pollution caused by different oil products is a serious geo-environmental problem that badly affects the quality of soil as well as pollute the groundwater resources. Now-a-days the area of oil polluted soil has been increasing continuously. Oil spillage is a widespread phenomenon and has raised considerable concern on the subject of petroleum oil pollution especially on arable agricultural. Petroleum oil is spilled on soils due to several factors such as pipeline destruction leakage of oil tankers, *etc.*[1].

The common sources of oil contaminants are explorations, extractions and transportation, production, processing and storage places. Toxicity of petroleum hydrocarbon has been a motivating force in finding sustainable biological methods of remediation of these compounds[2].

Bioremediation when compared with physical and chemical treatments are found to be cost effective treatment method for hydrocarbon polluted soil[3]. Some bioremediation approach could only be conducted at lightly polluted site like phytoremediation, as the high concentration of hydrocarbon inhibited seed germination and plant growth[4]. Thus, suitable biological method to deal with the severely contaminated soil should be explored. During normal operation of oil fields, leakage and spillage of crude oil result in soil contamination at many sites and thus affect environment by the alteration of essential elements of the habitat and direct toxic effects[5-7].

To date, the technologies of soil remediation have been developed including biological treatment, soil washing with surfactants, air stripping thermal treatment, *etc*. Among these technologies, thermal treatment is found to be more effective method to remediate heavily contaminated soil[7-13].

The addition of organic matter (compost, cow dung and sludge) to the hydrocarbon contaminated soil can be beneficial, as it is a source of co-substrates, nutrients and microorganisms and amends the structure and water-retaining capacity of the soil[14]. The literature showed that composting of petroleum contaminated soil and petroleum-based oil wastes is increasing[15,16]. Elevated temperatures stimulate hydrocarbon degradation and enhance the contaminant availability by increased solubility and mass transfer[17]. In present study the treatment of oil polluted soil was done by using biological, chemical and thermal treatment methods.

EXPERIMENTAL

The soil sample was collected from a leakage area in Attack Refinery Limited, Morgah-Rawalpindi Pakistan. The sample was mixed and dried under ambient conditions, then ground and screened through a 60-mesh sieve to remove the rubbles. In present study biological, chemical and thermal treatment methods were used in different experiments at laboratory scale.

Chemical treatment of oil contaminated soil: Chemical oxidation is a promising innovative process for degrading an

extensive variety of hazardous compounds in remediation of soil at waste disposal and spill sites. Hydrogen peroxide is one of the most successfully used remedial chemical for contaminated soil remediation. Three chemicals (hydrogen peroxide, calcium hypochlorite, kerosene oil and surfactant) were applied on oil contaminated soil. First chemical treatment was done by using H_2O_2 (30 %) by changing its amount (5, 10 and 15 mL) and analyze the oil reduction after 6 h. H_2O_2 was also used in combination with H_2SO_4 and $FeSO_4$. In second experiment 5, 10 and 20 % solution of calcium hypochlorite were applied on oil contaminated soil and place for 6 h. Kerosene oil and surfactant used for treatment oil contaminated soil in combination and after 6 h the oil concentration were measured for comparison.

Biological treatment of oil contaminated soil: In sewage sludge treatment 100 g of oil polluted soil were taken for each experiment. In first experiment 5 g of sewage sludge, in second and third experiment added 10 and 20 g of sewage sludge respectively and kept wet for 15 days. The same procedure was adopted in case of compost. Added 5, 10 and 20 g of compost in three experiments on 100 g of soil and kept wet for 15 days.

The cow dung was used for biological treatment of oil polluted soil. In treatment added 5, 10 and 20 g of fresh cow dung in three different experiments. The residing time was 15 days as given in above experiment.

The biological material *i.e.*, compost, sludge and cow dung were used in combination with KH_2PO_4. In treatment 100 g of oil contaminated soil were taken. Approximately 5, 10 and 20 g of compost with 1g of KH_2PO_4 were added in three separate experiments and kept under observation for 15 days at in moist conditions. The cow dung and municipal sludge were added in second and third treatment by using the same methodology.

Thermal treatment of oil contaminated soil: The thermal treatment was done at different temperature (300, 400 and 450 °C) on 100 g of oil contaminated soil at time period of 5, 10, 15 min and reduction of oil contents were measured.

Analysis of oil contaminated soil: Concentration of the oil in soil sample was determined according to an ASTM Method (D 7066-04). The percentage reduction of oil (P_r) before and after treatment was calculated as follows:

$$P_r = \frac{C_o - C_r}{C_o} \times 100\ \% \quad (1)$$

where, C_o is the original concentration of the oil, C_r is the residual concentration of the oil in soil sample after treatment. Values in the tables indicate the mean values ± SD based on independent three determinations (n = 3).

RESULTS AND DISCUSSION

Chemical treatment: Initial residual hydrocarbons concentration in the soil was around 72.36 g/kg of soil sample collected from refinery area. Chemical treatments were applied by using hydrogen peroxide, sulphuric acid, ferrous sulphate, calcium hypochlorite and kerosene/surfactant to oil polluted samples. Out of them combination of H_2O_2 and H_2SO_4 (with pH=2) was found to give maximum oil reduction in sample. Minimum reduction was found in kerosene/surfactant (0.05 % surfactant and 10 mL of kerosene oil). Hydrogen peroxide is one of the most successfully used remedial chemical for oil contaminated soil remediation. At high concentrations hydrogen peroxide could compete with organics for hydroxyl radicals reducing the efficacy of organic compounds oxidation with hydroxyl radicals[18].

Oxidation with hydrogen peroxide can be direct and/or through the generation of free radicals (hydroxyl radicals OH). However, hydrogen peroxide show good result when used in combination with sulphuric acid and ferrous sulphate which enhance the production of OH^- radicals. The maximum reduction of oil was found H_2O_2 in combination with H_2SO_4 (92.6 %) and with Fe_2SO_4 (68.77 %) whereas without any combination H_2O_2 gave percentage reduction (65.83 %) as shown in Fig. 1.

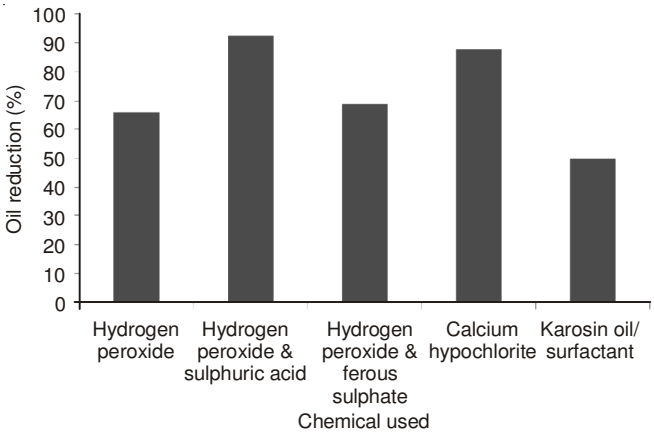

Fig. 1. Chemical treatments with hydrogen peroxide, sulphuric acid, calcium hypochlorite, kerosene/surfactant

The treatment result of hydrogen peroxide, calcium hypochlorite and kerosene oil/surfactnat were shown in Fig. 2. Different concentration of these chemicals were applied that is 5, 10 and 15 mL of these chemicals were applied on 100 g of oil polluted soil samples. Treatment with 15 % calcium hypo-chlorite reduced oil contents (88.03 %) while kerosene/ surfactant (49.8 %) to oil remediation from soil samples as shown in Table-1. Calcium hypo-chlorite showed best result as compared with Kerosene/surfactant and hydrogen peroxide when used without combination shown in Fig. 2.

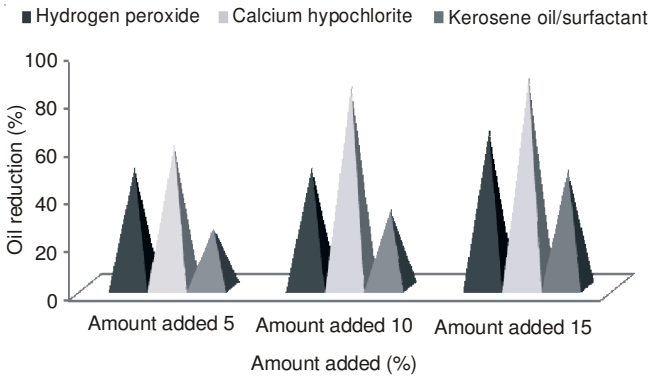

Fig. 2. Chemical treatments with changing concentrations (5, 10, 15 %)

TABLE-1
REMOVAL EFFICIENCY OF CONTAMINATED SOIL BY THE CHEMICAL TREATMENT

Chemical treatment	Amount used on 100 g soil	Initial oil content (g/kg)	Final oil content (g/kg)	Percentage reduction (%)
H_2O_2	5 mL	72.36±0.04	35.74±1.20	50.6
	10 mL	72.36±0.04	35.60±1.40	50.8
	15 mL	72.36±0.04	24.72±1.01	65.83
H_2O_2+3 mL H_2SO_4	5 mL	72.36±0.04	13.19±0.50	81.76
	10 mL	72.36±0.04	9.36±0.50	87.06
	15 mL	72.36±0.04	5.35±0.50	92.6
H_2O_2+3 g $FeSO_4$	5 mL	72.36±0.04	26.52±1.09	63.34
	10 mL	72.36±0.04	23.9±1.08	66.97
	15 mL	72.36±0.04	22.59±0.07	68.77
Calcium hypo chlorite	20 mL of 5 %	72.36±0.04	28.76±0.09	60.25
	20 mL of 10 %	72.36±0.04	10.70±0.05	85.21
	20 mL of 15 %	72.36±0.04	8.66± 0.04	88.03
Kerosene oil/surfactant	10 mL of 0.5 % surfactant and 10 mL of kerosene oil	72.36±0.04	54.05±0.50	25.3
	10 mL of 0.1 % surfactant and 10 mL of kerosene oil	72.36±0.04	48.63±3.50	32.8
	10 mL of 0.2 % surfactant and 10 mL of kerosene oil	72.36±0.04	36.04±1.07	49.8

TABLE-2
COMPARISON OF OIL REDUCTION IN THE CONTAMINATED SOIL BY THE BIOLOGICAL TREATMENTS

Name of treatments	Amount used on 100 g soil	Initial oil contents (g/kg)	Final oil content (g/kg)	Percentage Reduction (%)
Compost (fruit/vegetable waste)	5 g	72.36	42.82±1.06	42.21
	10 g	72.36	30.34±1.08	58.06
	20 g	72.36	20.51±0.67	71.65
Municipal sludge	5 g	72.36	31.27±1.08	56.78
	10 g	72.36	20.51±1.03	71.65
	20 g	72.36	10.79±1.34	85.09
Cow dung	5 g	72.36	28.78±1.45	60.23
	10 g	72.36	20.19±1.45	72.09
	20 g	72.36	10.22±1.20	85.88
Compost (fruit/ vegetable waste) + 1 g KH_2PO_4	5 g	72.36	41.24±1.09	43.01
	10 g	72.36	29.59 ± 1.40	59.11
	20 g	72.36	19.86 ± 1.20	72.55
Municipal sludge + 1 g KH_2PO_4	5 g	72.36	30.19 ± 1.02	58.28
	10 g	72.36	19.79 ± 0.67	72.65
	20 g	72.36	9.34 ± 0.45	87.09
Cow dung + 1 g KH_2PO_4	5 g	72.36	18.42 ± 1.05	74.55
	10 g	72.36	8.62 ± 1.01	88.09
	20 g	72.36	7.8 ± 1.10	89.22

Biological treatment: Microbial degradation is the major and ultimate natural mechanism by which one can clean up the oil pollutants from the soil and water[19]. Biological methods utilized for the contaminated land remediation depend on one or more of the four basic processes that is biodegradation, biological transformation, biological accumulation and biological mobilization.

Biological treatments of compost, municipal sludge and cow dung were applied in single and in combination with KH_2PO_4 to reduce oil contents. The amount of 5, 10, 15 g of these biologicals materials were added in 100 g of soil samples. The maximum reduction 85.88 % was found in case of 20 % cow dung whereas minimum reduction 42.21 % was noticed in case of compost shown in Fig. 3. Environmental factors like oxygen level, temperature, nutrients, pH and moisture content may influence the biodegradation of hydrocarbons in soil. Biological materials were used in combination to produce good results. The maximum reduction (89.22 %) in soil samples as shown in Table-2. In case of municipal sludge 87.09 % reduction with 20 % sludge with 1 g KH_2PO_4 and for 5 % reduction was 58.28 %. The result showed that the addition of KH_2PO_4 enhanced the oil removal from soil which concluded that it increases cell division so amount of bacterial growth increases. For soil bioremediation, suitable microorganisms are necessary for an optimal treatment of soils contaminated with oil. Fig. 4 shows that best result was obtained in case of cow dung when compared with other biological treatment of municipal sludge and compost respectively.

Thermal treatment: Oil polluted soil samples were subjected to three temperatures (300, 400 and 450 °C) at different time periods (5, 10 and 15 min) and observed the percentage reduction of oil in samples. Table-3 showed that best result of oil reduction was observed in thermal treatment at 450 °C and increase by increasing time period and reaches its maximum value at time period of 15 min that is 78.22 %.

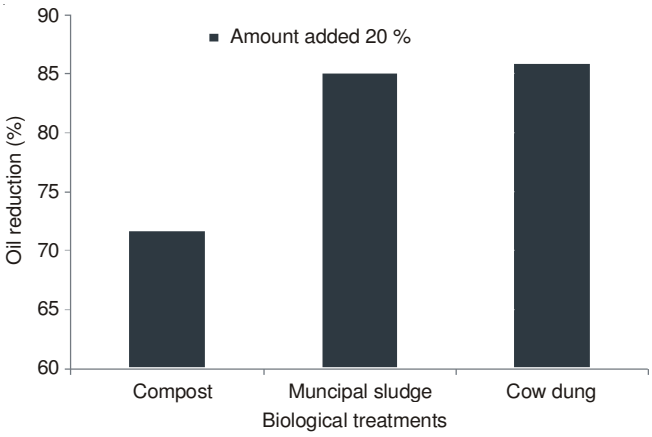

Fig. 3. Comparison of biological treatment methods

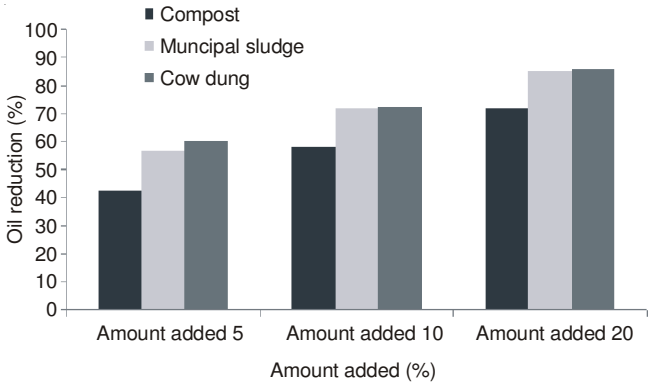

Fig. 4. Comparison of biological materials compost, municipal sludge, cow dung

The result obtained at 450 °C was good as compared to 300 and 400 °C shown in Fig. 5.

Conclusion

From the results of the present laboratory scale investigations, the following conclusions can be drawn:

TABLE-3
PERCENTAGE REDUCTION OF OIL BY USING THERMAL TREATMENT

Thermal treatments	Time durations (min)	Final oil content g/kg	Percentage reduction (%)
At 450 ºC	5	34.66 ± 1.39	52.10
	10	21.65 ± 1.20	70.08
	15	15.76 ± 0.45	78.22
At 400 ºC	5	03.46 ± 0.25	42.10
	10	44.92 ± 0.75	62.08
	15	49.36 ± 0.85	68.22
At 300 ºC	5	29.10 ± 1.05	40.10
	10	39.13 ± 1.35	54.08
	15	42.13 ± 1.15	58.22

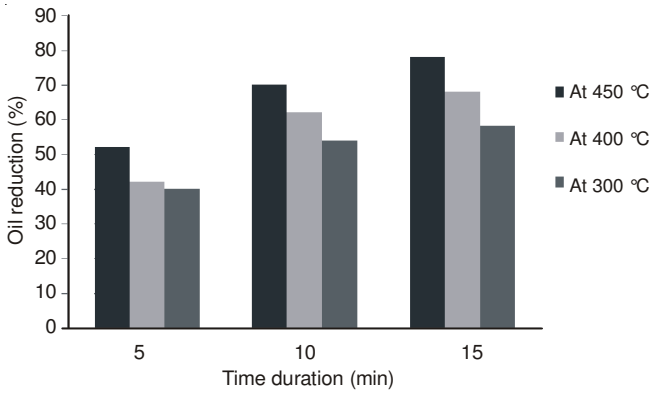

Fig. 5. Treatment by using thermal treatment methods at different time durations

• Maximum oil reduction was observed in chemical treatment as compared to thermal and biological treatment.

• The combination of hydrogen per oxide and sulphuric acid has maximum oil reduction (92.60 %) as compared to other chemical like ferrous sulphate, calcium hypo-chlorite and kerosene/surfactant.

• In biological treatment the most effective one is cow dung with 1 g of KH_2PO_4 compared to other biological materials.

• In thermal treatment the best result was obtained at 450 °C (78.22 %) for 15 min of heat exposure.

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