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## **Physico-Chemical Properties of Petroleum Polluted Soil Collected From Transport Nagar (Jaipur)**

**\*Hardik Pathak, Kamna Bhatnagar and DP Jaroli**

*Department of Biotechnology Mahatma Gandhi Institute of Applied Sciences, JECRC Campus, Sitapura, Tonk Road, Jaipur 302023*

*\*Author for Correspondence*

### **ABSTRACT**

Since a decade or so due to human intervention significant changes in various ecosystems have taken place. Increased use or accidental spilling of fossil fuel such as petroleum has affected soil and marine ecosystem to some extent. This fact evoked the interest of scientists to investigate the effect of petroleum oil on distribution system and its fate in the environment, especially the soil environment. Physico-chemical analysis of contaminated soil was carried out using different methods. Physical analyses like soil texture, soil pH, bulk density, C/N ratio, Soil moisture content, organic matter, presence of heavy metal etc. were performed. All of these parameters play an important role in bioremediation of petroleum compounds. Chemical analysis of soil was also performed using GC-MS. Presence of heavy metal ions was estimated by using atomic absorption spectroscopy (AAS). Excess hydrocarbons adversely altered the properties of the contaminated soils. Low water holding capacity, porosity, very high C: N ratio and bulk density were observed in every contaminated sample of soil.

**Key Words:** Bioremediation, contaminated soil, Hydrocarbons, Petroleum, Soil parameters.

### **INTRODUCTION**

Soil and water represent the first lines of recipients of oil pollution. Ground water contamination by crude oil therefore is becoming an increasing sensitive issue in India because most of the water supply is derived from shallow and unconfined aquifers. Furthermore, contamination of land is of paramount importance to man in that it is on this portion of the earth that the anvil of man's existence and activities lie. The damaging effects are due to suffocation and toxicity of the crude oil. Apart from this, it has been reported that Nitrate formation was reduced. Even 0.1% (v/w) of oil when mixed with soil practically checked nitrate formation and this is inimical to soil fertility.

Aromatic Hydrocarbons in the environment mostly originate from anthropogenic source like mineral oil spill or gas works plants and to a minor extent, from biological production in anoxic sediments. Numerous aerobic bacteria have been isolated that can breakdown aromatic hydrocarbons as carbon and energy sources. The degradation pathways have already been elucidated (Cerniglia, 1992; Lal et al., 2004; Pathak et al. 2008). PAHs present as natural constituents in fossils fuels, are formed during the incomplete combustion of organic material and are therefore present in relatively high concentration in products of fossil fuels refining (Nestler, 1974; Lee et al., 1981; Bos et al., 1984; Nishioka et al., 1986; Wang et al., 1990; Desche Anes et

al., 1996; Wang et al., 1999). Petroleum refining and transport activities are major contributors to localized loadings to PAHs into the environment. Such loadings may occur through discharge of industrial effluents and through accidental release of raw and refined products. However, PAH released into the environment may originate from many sources including gasoline and diesel fuel combustion (Lim et al., 1999; Marr et al., 1999) and tobacco smoke (Gundel et al., 1996). PAHs are detected in air (Koeber et al., 1999; Lim et al., 1999), soil and sediment (Heitkamp and Cerniglia, 1989; Van et al., 1996; Zeng and Vista, 1997; Lamoureux and Brownawell, 1999; Ohkouchi et al., 1999), surface water groundwater, and road runoff (Boxall and Maltby, 1997; Holman et al., 1999; Martens et al., 1997; Pitt et al., 1995) are dispersed from the atmosphere to vegetation (Wagrowski and Hites, 1997) and contaminate foods (Lee and Grant, 1981; Edwards, 1983; Sims and Overcash, 1983). In the present investigation, main aim was to investigate as many as physical parameters which could be beneficial for biodegradation in soil environment.

### **MATERIAL AND METHODS**

#### **Collection of sample**

Two contaminated (Site polluted with petroleum hydrocarbon and engine oil)

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Two contaminated (Site polluted with petroleum hydrocarbon and engine oil) and two uncontaminated sites (Site **is** not polluted with petroleum hydrocarbon and engine oil) situated in Jaipur were chosen for the study. Soil samples were collected from these sites in the month of July 2010. Samples were collected from up to a depth of 6 cm from the vicinity of Indian Motor Garage at Transport nagar, as such samples were highly polluted with engine oil. The contaminated samples were named as PCS-1 and PCS-2, respectively.

#### **Physical analysis of soil**

Physical properties of soil like soil texture, bulk density, moisture and water holding capacity of all the four soil samples were determined. Soil texture was determined by using sieves of different sizes. Bulk density was determined gravimetrically, while water holding capacity was evaluated by flooding the soils with water. The weight of flooded soil was determined. After 24 hours of drying at 80°C temperature amount of soil remained was determined and the percentage of water evaporated was calculated. Moisture content was determined similarly. Soil chemical properties like pH, electrical conductivity, available phosphorus, nitrogen, organic matter, available carbonate and bicarbonate, chloride, nitrogen and phosphorus content were determined by using standard titrimetric procedures (Pandey and Sharma, 2003). Concentration of Sodium, Potassium, Iron, Manganese Lead, Zinc, Nickel were analyzed by atomic absorption spectroscopy.

#### **Total Petroleum hydrocarbons analysis**

Total Petroleum hydrocarbons present in the sample were estimated with the help of column chromatography and gas chromatography (Hewlett Packard Model 6890, with a column ULBON HR-1 which is equivalent to Ov-1 fused silica capillary (0.25 mm\*50 mm) with thickness of 0.25 micron; 1ml/min; pressure 18.5 psi and split ratio 20 %.) Aliphatic and Aromatic fractions present in soil samples were separated by column chromatography, Silica gel of 60-120 mesh size activated at 90°C was used for column packing. The flow rate was maintained at 1 ml/min. The aliphatic fractions were separated with hexane (petroleum fraction) as an eluent. The aromatic fractions were separated with toluene. Both of these fractions were analyzed using gas chromatograph- Mass spectroscopy. The GC/MS analyses were performed using a MS 5973 spectrometer coupled with 9 Hewlett Packard Model 6890, with a column ULBON HR-1 which is equivalent to Ov-1 fused silica capillary (0.25 mm\*50 mm) with thickness of 0.25 micron; 1ml/min; pressure 18.5 psi and split ratio 20%. The solvent used in analysis was chloroform.

### **RESULTS AND DISCUSSION**

Utilization of chemical contaminant present in the soil as source of carbon and energy by different bacterial communities leads to ameliorate a wide range of contaminants like petroleum and polyaromatic hydrocarbons. Prevailing environmental conditions are among the most important limiting factors for optimum bioremediation. The factors affecting the success and rate of microbial bioremediation are nutrient availability, moisture content, soil reaction (pH), temperature, C/N ratio, soil texture etc. The present study was carried out to assess the quality of contaminated soils. These qualities determine the capability of bacterial isolates to biodegrade petroleum compounds and their wastes like oily sludge, a hazardous hydrocarbon waste generated by the petroleum industry. The bacterial communities are believed to adapt the local soil environment. These environmental factors play a vital role in the bioremediation of soil.

All soil microorganisms require moisture for growth and functioning. Moisture affects diffusion of water and soluble nutrients into and out of the microbial cells. In the present investigation the moisture content recorded during the experiments ranged from 13.18 % to 16.01%. A better degradation of PAH was recorded in soil sample PCS-1 having moisture content 16.01 % as compared to PCS-2 with 13.18% moisture content. Excess moisture, in saturated soil is undesirable because it reduces the amount of available oxygen for aerobic respiration. The soil water holding capacity between 45 and 85 percent is optimal for petroleum hydrocarbon degradation (US-EPA, 2006). The water holding capacity of the contaminated soil samples under investigation was 58.56% in PCS-1 and 59.18% in PCS-2 (Table 1), i.e. in the range suggested to be optimal for bioremediation (US-EPA, 2006). It is also difficult to control moisture content in fine soil because their small pores and high surface area allow better water retention. In water saturated condition the movement of water is relatively slow in fine soils than the soils with higher texture. In such soils the movement of air and oxygen through soil profile is not adequate for microbial activities (US-EPA, 2006).

Soil reaction (pH) is a critical factor for microbial growth and survival. Different microbial strains exhibit their maximum growth potential in a limited pH range. A pH value of near neutral is suitable for growth of diverse bacterial populations. The most appropriate range for bioremediation has been suggested to be pH 6-8 (US-EPA, 2006). In current investigation, the soil reaction (pH) of all the soil samples falls

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**Table 1: Physico-chemical properties of petroleum contaminated soil and Normal soil**

Parameters	Unit	Petroleum contaminated soil 1	Petroleum contaminated soil 2	Normal soil 1	Normal soil 2
pH	-	7.2	7.20	7.05	7.25
Electric conductivity (EC)	µs/cm	317	328	167	159
Total dissolved salt(TDS)	ppm	177.3	188	70	73
Soil organic carbon(SOC)	%	4.96	4.33	0.56	0.65
Available phosphorus	mg/kg	3.6	1.5	5.5	5.8
Total nitrogen	%	0.04	0.07	0.68	0.55
C/N Ratio	-	12.15	9.71	1.03	1.33
Sodium	ppm	863	498	456	235
Potassium	ppm	185	172	192	156
Sulphur	ppm	760	824	373	296
Organic matter	%	6.33	6.11	1.30	1.25
Salinity	ppm	174	190	80	92
Carbonate (CO <sub>3</sub> <sup>-2</sup> )	mg/100 gm	0.22	0.35	0.63	0.69
Biocarbonate (HCO <sub>3</sub> <sup>-</sup> )	mg/100 gm	1.68 (ns)	1.22	2.47	2.14
Chloride	mg/100 gm	805.1	717	270	211
Iron	mg/kg	715	660.1	215.18	ND
Manganese	mg/kg	75.08	82.19	52.08	57.38
Lead	mg/kg	0.60	0.73	0.3	0.19
Zinc	mg/kg	0.72	0.61	0.3	0.26
Nickle	mg/kg	0.65	0.33	0.13	0.08
Moisture content	%	16.01	13.18	11.38	12.69
Water holding capacity	%	58.56	59.18	54.12	53.18
Bulk density	gm/ml	0.90	0.95	0.74	0.68
Porosity	%	66.30	67.10	69.39	69.95
Total Petroleum Hydrocarbon (TPH)	mg/kg	11149	14244	700	614

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**Table 2: Soil Texture of Petroleum Contaminated Soil (PCS) and Normal Soil (NS)**

Samples	Sand %	Slit %	Clay %
PCS-1	35.2	40.6	23.9
PCS-2	37.09	36.05	27.06
NS-1	47.20	35.8	17.6
NS-2	42.28	39.90	17.22

well within the range suggested by US-EPA(2006) (Table 1).

The rate and extent of degradation of hydrocarbons greatly depends on nutrient composition of soil. The amount of various nutrients and ratio of particular nutrients like C, N and P is quite conceivable regarding success of a bioremediation process. The organic carbon content in all the contaminated soils was very high. This is attributed to the continuous input of petroleum hydrocarbons. The optimum C:N ratio closer to 12.5:1 by Hupe *et al.*, (1996). Relatively more PAH degradation has been noticed in soil samples with a C:N ratio closer to 12.5:1 (Luepromchai *et al.*, 2007). In the present investigation, analysis of the soil samples revealed C: N ratio of 12.1:1 and 9.7:1 in PCS-1 and PCS-2, respectively (Table 1).

Chemical composition, quantity and toxicity of contaminants are also among the critical factors for microbial diversity of contaminated soils. Comparatively, higher amount of TPH (Total petroleum hydrocarbon) was recorded in PCS-2 soil sample. This suggests the probability of reduced microbial (bacterial) population in this soil sample. The PCS-1 soil sample had considerably less TPH content (11149 mg/kg) than PCS-2 (14244 mg/kg) (Table 1). The high amount of contaminants may be toxic to soil microorganisms (Luepromchai *et al.*, 2007). Heavy metal concentration was found higher in both the contaminated soil samples as compared to their normal counterparts. Iron content was exceptionally higher in PCS-1. Presence of high concentration of metal ions attributes to greater electrical conductivity in both the contaminated samples. Higher electrical conductivity also indicates high salinity in the contaminated samples. In the present study, salinity of both the contaminated samples was much higher than their uncontaminated counterparts (Table 1). Physical properties of soil like soil texture and bulk density have also been considered to be very important for bioremediation because several factors affecting the degradation process like soil aeration, movement of nutrients through soil pores, water holding capacity and

several others are also under the direct or indirect influence of soil physical properties (Atlas, 1981; Luepromchai *et al.*, 2007) (Table 1). In the present investigation PCS-1 had low clay percentage (23.9%) as compared to PCS-2 (27.9%), indicating possibility of a higher degree of hydrocarbon degradation in PCS-1. Increased ventilation has a direct impact on microbial growth which can enhance the biodegradation of petroleum compounds (Pathak *et al.*, 2010) (Table 2).

From the above results, it could be concluded that hydrocarbon contamination adversely alters the soil properties. The water holding capacity and porosity which determines the extent of water retention and aeration in the soil become reduced. Both of these properties have profound importance to the biological status of the soil. The high C: N ratio even makes the problem more critical for the proper sustenance of life. Presence of heavy metals and high concentration of petroleum hydrocarbons cause further decline in the soil quality. The altered properties makes the soil potent toxic and carcinogenic and hence very harmful for human beings. It is necessary to restore the contaminated sites and much is needed to be done in this direction.

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