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Monitoring ground water quality and heavy metals in soil during large-scale bioremediation of petroleum hydrocarbon contaminated waste in India: Case studies

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Abstract

Bioremediation using microbes has been well accepted as an environmentally friendly and economical treatment method for disposal of hazardous petroleum hydrocarbon contaminated waste (oily waste) and this type of bioremediation has been successfully conducted in laboratory and on a pilot scale in various countries, including India. Presently there are no federal regulatory guidelines available in India for carrying out field-scale bioremediation of oily waste using microbes. The results of the present study describe the analysis of ground water quality as well as selected heavy metals in oily waste in some of the large-scale field case studies on bioremediation of oily waste (solid waste) carried out at various oil installations in India. The results show that there was no contribution of oil and grease and selected heavy metals to the ground water in the nearby area due to adoption of this bioremediation process. The results further reveal that there were no changes in pH and EC of the groundwater due to bioremediation. In almost all cases the selected heavy metals in residual oily waste were within the permissible limits as per Schedule – II of Hazardous Waste Management, Handling and Transboundary Movement Act, Amendment 2008, (HWM Act 2008), by the Ministry of Environment and Forests (MoEF), Government of India (GoI).

Introduction

Disposal of petroleum hydrocarbon contaminated waste in an improper manner may cause serious environmental problems as its components are highly toxic to the environment [1]. Petroleum hydrocarbon contaminated solid waste generated by the oil and gas industries mainly in the form of tank bottom and effluent treatment plant (ETP) oily sludge, and oil contaminated soil, are commonly termed "oily waste". Oily wastes are identified as hazardous in India and in OECD (Organization for Economic Co-operation and Development) countries as well as by the US EPA (United States Environment Protection Agency) [2] and [3].

Conventional methods like land filling, incineration, air sparging, etc. have been applied for many years for oily waste remediation. The common drawback is that they are not a permanent solution for environmental pollution and they are sometimes not cost effective [4]-[7]. Bioremediation has emerged as one of the most promising treatment options for oil decontamination in terms of affordability, ecological approachability and its effectiveness in treating the contamination [8]-[10]. Microbes have been widely used in the bioremediation process where the toxic molecules are broken down to simpler nontoxic compounds like carbon dioxide, water and dead biomass through different metabolic pathways. All types of microbes, such as bacteria, archaeobacteria, yeast, algae and fungi, have been widely used and studied in association with bioremediation. Of these bacteria, *Bacillus*, *Pseudomonas*, *Achromobacter*, *Alcaligenes*, *Arthrobacter*, *Acinetobacter*, *Corynebacterium*, *Flavobacterium*, *Micrococcus*, *Mycobacterium*, *Norcardia*, *Vibrio*, *Rhodococcus*, *Sphingomonas*, *Burkholderia*, etc. are used for the treatment of contaminated sites containing a wide variety of pollutants. Yeast species such as *Candida*, *Clavispora*, *Debaryomyces*, *Leucosporidium*, *Pichia*, *Rhodosporidium*, *Rhodotorula*, *Sporidiobolus*, *Sporobolomyces*, *Stephanoascus*, *Trichosporon* and *Yarrowia* are used in bioremediation process and show biodegrading properties. Algal species such as *Aphanocapsa* sp., *Oscillatoria salina*, *Plectonema terebrans* and *Synechococcus* sp. have been successfully used in bioremediation of oil spills in different parts of the world. Fungi such as the white rot fungus *Phanaerochaete chrysosporium* and *Polyporus* sp. show the ability to degrade an extremely diverse range of persistent or toxic environmental pollutants such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), explosives, polychlorinated biphenyls (PCBs), and organochlorine pesticides [11]. Researchers at the author's institute alone have isolated more than 100 different species of bacteria for biodegradation of oily waste [5].

Although extensive research has been conducted on oil bioremediation, recent studies have concentrated on either evaluating the feasibility of the bioremediation process or testing specific products and methods [12]. Only limited numbers of pilot and field trials with small quantities of oily waste, possibly providing the most convincing demonstrations of this technology, have been carried out [13], [14], [7], [15].

In recent years large-scale bioremediation of >150,000 tonnes of

dissimilar types of oily waste has been successfully carried out in batches at assorted oil installations in India using an indigenously-developed microbial consortium which was able to biodegrade all the fractions of TPH of the oily waste to environmentally friendly end-products [16]. Bioremediation can be carried out *in situ* and *ex situ* in the field. Hence it is thought that there may be leaching of contaminated oil and some heavy metals present in the oil to local groundwater near the bioremediation site. In addition, for disposal of the bioremediated material to the environment, it is felt necessary to determine the concentration of selected heavy metals present in it, and match the same with the Schedule – II of HWM Act 2008, GoI. Presently there are no federal regulatory guidelines available in India for carrying out bioremediation of oily waste using microbes in the field. Hence, the MoEF, GoI, also insists that groundwater quality is monitored for the presence of oil and grease and selected heavy metals as well as the heavy metal concentration in the residual oily waste before and after bioremediation in the field.

The quality of water is of vital concern for mankind as it plays an important role in sustaining life on earth and is directly related to human welfare. A report by the Central Pollution Control Board (CPCB), GoI, states that ground water quality varies from place to place, with the depth of the watertable, and from season to season, and that it is primarily governed by the extent and composition of dissolved solids present in it [17]. A perturbation in the ecosystem comprising of water, air, oil and sediments as well as plant and animal life may be caused by the presence of metal ions and organic compounds beyond their natural levels [18]. One of the most visible tragedies caused by water pollution is Minamata disease caused due to Hg poisoning [19]. The contamination of ground water by heavy metals and pesticides has also assumed great significance during recent years due to their toxicity and accumulative behaviour [17]. The main threats to human health are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been studied and their effects on human health regularly reviewed by the World Health Organization (WHO) [20]. Arsenic concentrations in groundwater in Bengal, Southeast Asia, and elsewhere constitute a major hazard to the health of people using these waters for drinking, cooking, or irrigation purposes [21]. Another major concern is groundwater pollution due to leaching of pollutants from surface sources like agricultural fields and waste dumps, which leads to chronic health hazards [22]. In addition to drinking purposes, the major volume of groundwater is utilized for irrigation, cooling and general operation in industry, and domestic sanitation. Hence, analysis of groundwater quality not only ascertains its physiological or domestic acceptability but also its technological usage. Assessment of quality of soil and groundwater will, therefore, help in ensuring the effectiveness of the bioremediation process from an environmental impact point of view.

Keeping these in view, the present study was undertaken to monitor groundwater quality and selected heavy metals in soil during large-scale field case studies on bioremediation of oily waste carried out at selected oil installations in India.

Methodology

Outline of Bioremediation Process

Large scale bioremediation was carried out both *in situ* at the contaminated site itself and *ex situ*, where a HDPE (high density polyethylene) lined secured bioremediation site was prepared inside the installation's premises. The oily waste was excavated and transported to the secured site using an excavator, dumper and trailer. The required quantity of indigenous oil degrading microbial consortium was produced in bulk in a bioreactor and transported to the bioremediation site to be mixed with the oily waste at intervals. The tilling of the oily waste was carried out at regular intervals to ensure proper aeration of the microbes. In order to maintain moisture content, site was watered as required. The process was continued until completion, where the total petroleum hydrocarbon (TPH) content was ~ 10 g/kg waste [5], [16], [23], [24].

Selection of Bioremediation Sites

A large-scale bioremediation field study of a total of 88,438 tonnes of oily waste was carried out in 127 batches at oil installations located in a variety of climatic zones spread all over India: Indian Oil Corporation Limited (IOCL) refineries, Chennai Petroleum Corporation Limited (CPCL), Mangalore Refinery and Petrochemicals Limited (MRPL), Oil and Natural Gas Corporation Limited (ONGC), Oil India Limited (OIL), BG Exploration and Production India Limited (BGEPI) and Cairn Energy Pty India Limited (CEIL) (**Table 1**). The type of contamination included acidic oily sludge (at Digboi refinery, IOCL) and non-acidic waste oily sludge (at other IOCL refineries, CPCL, MRPL), ETP / Tank bottom oily sludge and oil contaminated soil (at ONGC), synthetic oil-based mud (SOBM) waste (at BGEPI) and oil contaminated drill cuttings (at CEIL).

Selection of Microbial Consortium

Over the past few years, indigenous microbial strains had been isolated by the authors' institute, from fifteen oil-contaminated sites located in different geo-climatic regions in India. The efficacy of the strains was evaluated for biodegradation of TPH component of oily waste and based on the functional diversity of the isolated strains, the best degraders for the major components of the TPH fractions were selected to form a consortium whose details have been reported in earlier studies by the institute [25-30], [14], [31]-[33], [6] and [34]-[37]. This consortium has been reported previously for application of biodegradation studies carried out either in the laboratory or in the field [5], [38]-[41], [16], [23], [24], and [42]. In all the field studies the application rate of the microbial consortium was in the range of 1.04 – 9.50 kg per tonne of waste depending upon various treatment conditions (**Table 2**).

Sampling

Residual oily waste samples from the bioremediation sites were collected at day zero, i.e. before application of the microbes to the waste, and at regular intervals until completion for monitoring

the performance of the process and the selected heavy metals. Groundwater samples from bore wells near the bioremediation sites were collected at day zero and after completion of the bioremediation process. The sampling was carried out as per the detailed method described in Mandal et al., [24].

Analysis of Residual Oily Waste and Groundwater Samples

1) Analysis of residual oily waste:

The residual oily waste samples were analysed for TPH, pH and selected heavy metals. TPH and pH was analysed as per the method described in Mandal et.al, [24].

Selected heavy metals, Zinc (Zn), Manganese (Mn), Copper (Cu), Nickel (Ni), Lead (Pb), Cobalt (Co), Arsenic (As), Cadmium (Cd), Chromium (Cr) (total) and Selenium (Se), were analysed in composite samples of the residual oily waste. The sample was digested in nitric acid as per the USEPA 3050 B method. The digested extract was diluted to the required concentration and used for determination of the selected heavy metals by the following methods depending upon the availability of resources:

- a) Using an Atomic Absorption Spectrophotometer (AAS) (AAS – TJA, SOLAAR M Series, Unicam, USA), where metals like Se, and As were analysed using an AAS equipped with a hydride generation system or cold vapour technique.
- b) By the Stripping Voltammetric method using a Voltammetry-Amperometry (VA) trace analyzer (757 VA Computrace) by Metrohm 663 VA Stand (Swiss made) combined with AUTOLAB 30 Potentiostat-Galvanostat by standard addition procedure using a hanging mercury drop (drop size 0.20 mm²) electrode (HMDE) as the working electrode, Ag/AgCl (3 mol/L KCl) as the reference electrode and a large area glassy carbon as the counter electrode in an inert atmosphere by purging XL grade N₂.

2) Analysis of Groundwater Samples

The groundwater samples were analysed for pH, Electrical conductivity (EC), Oil and grease and selected heavy metals (Zn, Mn, Cu, Ni, Pb, Co, As, Cd, Cr(total) and Se) and selected anions: Fluoride (F⁻), Chloride (Cl⁻), Bromide (Br⁻), Nitrate (NO₃⁻), Sulphate (SO₄⁻²) and Phosphate (PO₄⁻³).

The pH was measured directly, after filtration of the suspended solids if appropriate, using a standard pH meter (Orion Expandable Ion Analyzer, model: EA-940) which was calibrated using standard buffer solution before taking the reading. The EC was measured using a standard conductivity meter (Control Dynamics Conductivity Meter, model:APX 185) which was calibrated using standard potassium chloride (KCl) solution before determining EC. Oil and grease was determined as per the standard method IS 3025 (P 39): 1991. Selected heavy metals were analysed using the stripping Voltammetric method as well as using AAS as described above. The selected anions present in the groundwater samples were analysed by Ion Chromatography

using an Ion Chromatograph (IC) with a conductivity detector (Metrohm IC 734). The analysis was carried out as per the standard operating manual of IC 734 supplied by Metrohm. The IC instrument was calibrated each time before performing the experiments [43]-[45].

In both analyses, the monitoring parameters were selected considering the characteristics of crude oil used by the respective oil installations and also the quantum of environmental impact of the respective parameters as studied in the literature.

Table 1: Details of oily waste undertaken for large scale bioremediation at oil installations in India.

Particulars of oil installations	Geo-climatic conditions of the oil installation (Location/ climate/ temperature/ annual rainfall)	Type of oily waste undertaken for bioremediation	Quantity (tonnes) of oily waste	No. of batches
CPCL, Chennai	13°02'N & 80°10'E/ tropical coastal climate - hot & humid weather / ~16°C – 45°C / ~ 1,400 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	4,100	4
IOCL, Barauni	25°25'N & 86°08'E in Ganges plain/ continental monsoon climate/ ~ 7°C – 40°C/ ~ 1384 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	5,250	3
IOCL, Digboi	27°23'N & 95°38'E/temperate, tropical monsoon & high humidity/ 16°C to 28°C / ~2483 mm	~ Oily sludge generated from dewaxing process - Acidic oily sludge	9,258	12
IOCL, Gujarat	22°18'N & 73°11'E / semi-arid & tropical savanna climate / ~ 120°C - 400C / ~ 930 mm.	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	11,500	7
IOCL, Haldia	22°02'N & 88°04'E / typical moderate climate / ~ 7 °C - 39 °C / ~ 1703 mm (heavy rain in monsoon)	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	10,500	6
IOCL, Mathura	27°17'N & 77°25'E / essentially dry climate/ ~14°C - 45°C / ~593 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	2,850	3
IOCL, Panipat	29°23'N & 76°58'E / sub-tropical & semi-arid climate/ ~ 8°C - 40 °C / ~ 680 mm.	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	3,333	7
MRPL, Mangalore	12°05'N & 74°05'E/ coastal & fully terrain zone with tropical monsoon / 27 – 340C / 42418 mm.	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	2,150	2
ONGC Ankleshwar Asset	21°42'N & 72°58'E/ extreme & tropical savanna climate/ ~ 23 °C – 40 °C / ~800-1200 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP).	3,063	7
ONGC Cauvery Asset	10°56'N & 79°50'E/ coastal region with tropical maritime climate/ ~16°C – 35 °C / ~1,260 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP), emulsified oily sludge.	966	3
ONGC Mehsana Asset	23° 35' N & 72° 23' E/ semi-arid & extreme dry or semi dry / ~ 15°C - 50 °C max. / ~ 625 to 875 mm	Oil contaminated land, soil & water; effluent & sludge pits, heavy viscous asphaltic oily waste.	16,938	42
ONGC Assam Asset	26°55'N & 94°44'E/ humid subtropical monsoon / ~ 10 °C - 40 °C max./ ~ 2485 mm	Oily sludge from tank cleaning and Effluent treatment plant (ETP)/ oil contaminated site	9,739	13
OIL Assam	27°30'N & 94°22'E/temperate climatic zone with tropical monsoon/ ~ 9°C - 31°C/ ~2528 mm	Accidental oil spill on land due to fire accident and waste oily sludge pits.	5,805	10
BGEPIL, Bhavanagar	21°46'N & 72°09'E / semi-arid & fairly humid coastal climate/ ~12°C - 40°C / ~ 550 mm	Synthetic oil based mud waste generated during drilling operations.	2,185	3
CEIL, Barmer, Rajasthan	25°45' N & 71°23' E / desert climatic zone / ~ 0 °C – 51 °C / ~277 mm.	Heavy oil contaminated drill cutting waste generated during drilling operations.	641	3
Mumbai Oil Spill 2010, Mumbai	18 °54'N & 72°53'E / Tropical wet and dry climate / ~ 18 °C – 30 °C / ~ 2,422 mm	Furnace oil contaminated sand due to ship wreckage in sea.	160	2
Total / Range			88,438	127

Results and discussion

Analysis of residual oily waste:

The study of the bioremediation of 88,438 tonnes of oily waste was carried out in 127 batches at different oil installations in India. The initial TPH content range at all the installations was 57.50 - 662.70 g/kg waste, which was reduced to 0.50 - 57.10 g/kg after bioremediation. In most cases, the TPH content in the remediated soil was < 10 g/kg. The average time for bioremediation in each batch was 2 to 12 months. In a small number of cases, the bioremediation study took > 21 months depending on the initial oil content (ONGC Ankleshwar and Assam), type of waste (ONGC Cauvery and Mehsana, IOCL Digboi) and the geo-climatic condition of the site (MRPL, CPCL, ONGC Cauvery and Assam) (**Table 2**). The biodegradation rate varied from 0.07 to 1.93 Kg TPH/day/m² and in almost all the studies the initial TPH was biodegraded by more than 90%. **Figure 1** shows one oil contaminated site before and after bioremediation using the microbial consortium.



Figure 1: Oil contaminated site at IOCL Mathura refinery, India- Before (Left) and After (Right) bioremediation using indigenously-developed microbial consortium.

Table 2 describes the pH details of the residual oily waste samples of the respective oil installations before and after bioremediation. Throughout the bioremediation process, the pH of all the samples was within the safe range of 6.5 to 8.5, except for the acidic oily sludge at the Digboi refinery, where the initial pH of the oily sludge was < 2 which was increased to 5.5 after bioremediation.

The details of the concentrations of the selected heavy metals in the residual oily waste samples before and after bioremediation are depicted in **Table 3a** & **Table 3b**. **Figure 2** describes the Voltammetric diagram as a typical example for analysis of heavy metals using the Stripping Voltametry method. It can be observed that there was no considerable change in the concentration of selected heavy metals in the residual oily waste before and after bioremediation. However, the concentration of selected heavy metals varied among the oil installations, which was due to the type of crude oil processed by the respective installations. For example, the concentration range of Zn was 2 - 12 mg/kg in oily sludge from IOCL refineries, whereas the same was 130 - 150 mg/kg in acidic oily sludge from Digboi, 538 - 542 mg/kg in oily sludge from MRPL, 1 - 6 mg/kg in oily sludge from ONGC, 91 - 98 mg/kg in oily sludge from OIL, ~15 mg/kg in SOBMM waste from BGEPIIL, ~46 mg/kg in drill cuttings from CEIL and ~70 mg/kg in oily waste from the Mumbai oil spill. It was also observed

that the concentration of all the selected heavy metals in the oily sludge at IOCL refineries was <<10 mg/kg and in ONGC sludge it was << 6 mg/kg, whereas there was diversity in other installations, OIL, MRPL, CEIL, BGEPIIL and Mumbai. For example, in the case of the MRPL refinery, most of the selected heavy metals (except arsenic, cadmium and selenium) were at higher concentrations even more than 500 mg/kg. In almost all the studies the selected heavy metals in the residual oily waste was within the permissible limit as per Schedule - II of HWM Act 2008, GoI.

No change in the heavy metal concentration before and after the bioremediation process (**Table 3a** & **Table 3b**) indicated that the microbes used for biodegradation of the oily waste were not able to biodegrade the heavy metals present in the oily waste. From the analysis of the microbial population [5], [46], and [47], it can be observed that the respective concentration of the heavy metals present in the oily waste did not affect the survival of the microbes, i.e. the microbes could tolerate the heavy metals concentration levels (even the highest concentration of >500 mg/kg) present in the respective soils. While correlating the biodegradation rate (**Table 2**) with the heavy metal concentration present in the waste (**Table 3a** & **Table 3b**), it was observed that at 7 installations out of 16, the concentration of a few of the heavy metals was on the higher side i.e. >12 to <1388 mg/kg. However, the biodegradation rate in those installations varied from 0.07 to 1.93 Kg TPH /day/m², whereas, at the remaining 9 installations, the heavy metals concentration was <<12 mg/kg and the biodegradation rate varied from 0.19 to 0.43 Kg TPH /day/m². Hence, the impact of only heavy metal concentration on the biodegradation performance of the microbes could not be concluded, as the bioremediation performance also depends upon other factors such as climatic condition, frequency of tilling, composition of waste, quantity of microbes applied, initial TPH content, etc.. A separate manuscript, in this regard, entitled "Factors Affecting Large Scale Bioremediation of Petroleum Hydrocarbon Contaminated Waste in Indian climate" is under publication by the author.

Analysis of ground water samples:

The detailed groundwater characteristics near the bioremediation sites are described in **Table 4a** and **Table 4b**. **Figure 3** describes the ion chromatograph as a sample of analysis for groundwater using ion chromatography. It is observed that the pH in the groundwater samples before and after bioremediation was from 7.5 to 8.5, indicating no considerable change in pH after the bioremediation process. Similarly, there was no considerable change in EC after the bioremediation process. However, the EC range varied from 0.175 to 45.3 mS/cm depending on the geographical location of installations. In all groundwater samples the oil and grease was 'nil' indicating that no leaching of oil contamination to the underground water occurred during the bioremediation process. There was no considerable change in the concentrations of the selected heavy metals and anions before and after bioremediation. The results suggest that the bioremediation process of solid oily waste carried out in a secured HDPE lined bioremediation pit does not have any impact on groundwater quality. However, the selected heavy metals in the groundwater samples from the oil installations varied

considerably depending on geographical location. For example, the concentration range of zinc was 0.031 – 7.368 mg/l, manganese 0.02 – 0.950 mg/l, copper <0.001 – 0.414 mg/l, etc. It was also noted that in all the groundwater samples, the selenium content was < 0.001

mg/l. In groundwater samples for the cases studies, the heavy metals and anion concentrations were within the permissible limits as per WHO & the Bureau of Indian Standards (BSI) and the Environment Protection Agency - Liquid Industrial Effluent (EPA -LIE).

Table 2: TPH and pH of oily waste in the present case studies before and after bioremediation.

Oil refineries	TPH (g/kg oily waste)		% Biodegradation (w / w)	Time for bioremediation (months)	Biodegradation rate (Kg TPH / day/m ² area)	pH* of waste		Microbes applied (Kg/tonne waste)
	Before bioremediation	After bioremediation				Before bioremediation	After bioremediation	
CPCL, Chennai	129.50 - 437.10	8.80 - 14.30	93.20 - 97.80	3 - 13	0.21 ± 0.07	6.8	7.2	1.35 ± 0.31
IOCL, Barauni	162.00 - 212.20	3.70 - 50.70	70.18 - 98.14	5 - 5.5	0.43 ± 0.17	7.77	7.42	1.16 ± 0.11
IOCL, Digboi	170.40 - 560.00	8.70 - 49.00	86.93 - 97.27	2.5 - 15	0.86 ± 0.66	1.53	5.51	1.32 ± 0.15
IOCL, Gujarat	132.00 - 270.00	3.90 - 34.50	82.54 - 98.13	2 - 12	0.41 ± 0.36	7.12	7.52	1.46 ± 0.27
IOCL, Haldia	193.00 - 269.00	5.60 - 12.50	94.47 - 97.44	6 - 10	0.19 ± 0.05	7.68	7.81	1.54 ± 0.15
IOCL, Mathura	152.50 - 223.10	3.50 - 8.50	96.19 - 97.70	4 - 12	0.37 ± 0.20	7.65	7.35	1.14 ± 0.02
IOCL, Panipat	206.50 - 238.00	2.60 - 8.00	96.51 - 98.86	3 - 10	0.38 ± 0.09	7.93	7.42	1.04 ± 0.08
MRPL, Mangalore	83.50 - 198.60	8.40 - 9.10	89.94 - 95.12	21 - 24	0.07 ± 0.03	8.02	7.95	3.71 ± 1.03
ONGC, Ankleshwar Asset	424.80 - 662.70	6.70 - 12.80	97.75 - 98.60	5 - 15	0.50 ± 0.21	7.83	7.76	4.36 ± 2.18
ONGC, Cauvery Asset	161.00 - 515.00	5.30 - 6.80	96.71 - 98.91	14 - 21.5	0.34 ± 0.31	7.71	7.73	9.50 ± 3.87
ONGC, Mehsana Asset	69.20 - 475.40	5.80 - 15.00	90.98 - 97.78	4.5 - 33	0.22 ± 0.15	8.12	8.02	2.57 ± 1.44
ONGC, Assam Asset	109.60 - 641.90	2.10 - 57.10	91.09 - 98.49	2 - 19	1.10 ± 0.84	7.73	7.62	1.98 ± 0.82
OIL, Assam	351.00 - 601.70	7.70 - 9.80	97.57 - 98.53	6 - 13.5	0.64 ± 0.51	7.81	7.75	1.35 ± 0.33
BGEPIL, Bhavanagar	57.50 - 106.70	2.60 - 6.90	90.09 - 95.83	4 - 7.4	0.10 ± 0.03	7.77	8.01	3.42 ± 0.53
CEIL, Barmer	98.10 - 188.10	8.20 - 10.90	90.03 - 95.64	3 - 4	0.61 ± 0.30	8.04	7.84	2.99 ± 0.57
Mumbai Oil Spill	60.00 - 381.00	0.50 - 3.60	90.55 - 99.17	2 - 5	1.93 ± 0.64	8.4	8.28	6.33 ± 0.47

* pH of 20% (w/w) solution of oily waste sample in distilled water

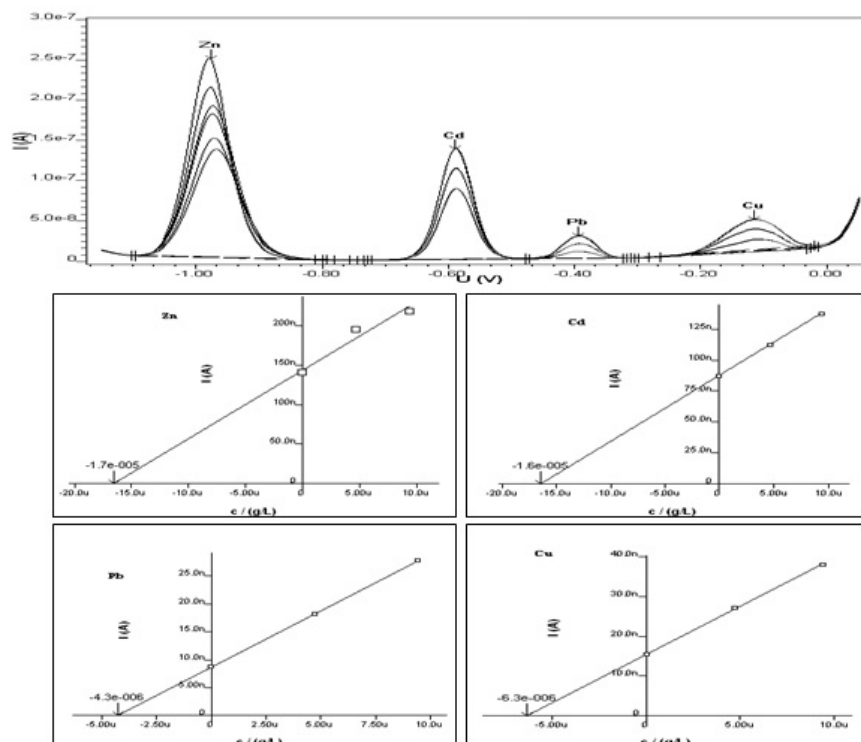


Figure 2: Typical Anodic Stripping Voltammogram and corresponding current-concentration plot for analysis of heavy metals.

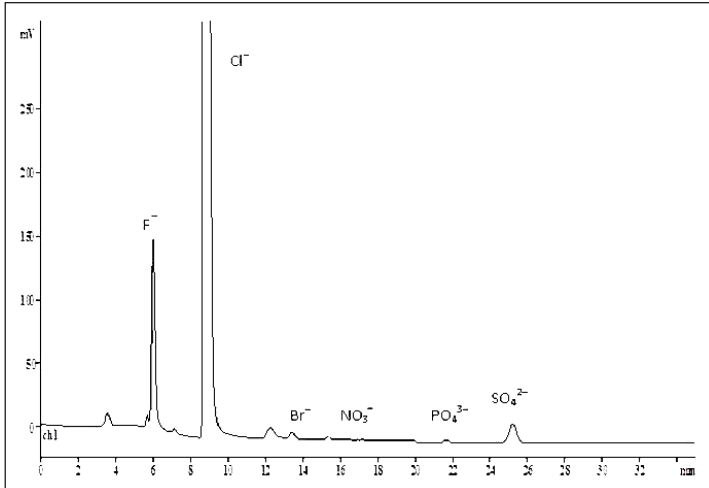


Figure 3: The chromatograms for the Anion analysis from bore well water using Ion Chromatography.

Conclusion

From the present study 88,438 tonnes of oily waste was successfully

bioremediated using an indigenously developed microbial consortium in 127 batches at different oil installations in India. The overall results show that the initial TPH content of 57.50 - 662.70 g/kg oily waste was biodegraded to 0.50 - 57.10 g/kg waste. The average time for bioremediation in each batch was 2 to 12 months depending upon the initial oil content and the climatic conditions at the contaminated site. The rate of biodegradation of the oily waste was 0.07 - 1.93 Kg TPH/day/m² area. There was no considerable change in the concentration of the selected heavy metals in the oily waste before and after bioremediation. This indicates that the existing heavy metal concentration of the oily waste does not have any negative impact on the bioremediation process and also the microbes used for bioremediation of the oily waste do not biodegrade the heavy metals. The bioremediation process restricts leaching of oil to the groundwater and hence it has no impact on groundwater quality with respect to contaminating heavy metals and anion concentrations. There was diversity in the concentration level of the selected heavy metals in the residual oily waste due to the types of crude processed by the respective oil installations. Diversity was also observed in groundwater quality depending on the geographical locations of the oil installations.

Table 3a: Heavy metal concentration in residual oily waste before and after bioremediation study.

Heavy metals	Permissible Limit (mg/kg waste) *	Concentration of heavy metal (mg/kg waste) in oily waste before and after bioremediation study (typical) at															
		CPCL, Chennai		IOCL, Barauni		IOCL, Digboi		IOCL, Gujarat		IOCL, Haldia		IOCL, Mathura		IOCL, Panipat		MRPL, Mangalore	
		Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Zinc (Zn)	20000	4.21	4.11	2.81	2.44	150.96	131.28	4.61	4.35	2.81	2.28	12.1	10.4	5.47	5.22	541.471	538.66
Manganese (Mn)	5000	5.1	5.01	0.35	0.24	233.79	277.63	1.28	1.21	2.5	2.36	0.12	0.11	0.61	0.58	316.897	312.69
Copper (Cu)	5000	4.68	4.48	0.21	0.33	49.51	36.34	0.32	0.29	1.21	1.01	0.43	0.32	<0.001	<0.001	66.575	64.57
Nickel (Ni)	5000	5.89	5.79	0.44	0.21	2.93	2.02	0.55	0.49	4.4	3.89	0.21	0.18	6.31	5.99	138.891	138.11
Lead (Pb)	5000	2.25	2.12	0.33	0.43	1.031	1.092	0.6	0.42	0.33	0.56	0.41	0.35	2.93	2.85	15.257	14.35
Cobalt (Co)	5000	0.88	0.86	<0.001	<0.001	0.365	0.361	<0.001	<0.001	0.22	0.32	0.33	0.31	0.54	0.51	29.729	28.11
Arsenic (As)	50	1.43	1.41	0.52	0.44	0.577	0.542	0.25	0.19	0.07	0.05	0.15	0.1	0.36	0.32	<0.001	<0.001
Cadmium (Cd)	50	0.05	0.04	<0.001	<0.001	0.005	0.004	<0.001	<0.001	<0.001	<0.001	0.17	0.11	<0.001	<0.001	<0.001	<0.001
Chromium (Cr) (Total)	5000	5.11	5.05	0.64	0.59	0.098	0.086	0.69	0.58	2.27	3.21	0.89	0.77	1.29	1.25	146.539	141.28
Selenium (Se)	50	2.26	2.11	0.22	0.21	0.097	0.077	0.31	0.22	0.21	0.16	0.54	0.49	0.41	0.38	<0.001	<0.001

* As per Schedule - II of Hazardous Waste Management, Handling and Transboundary Movement Act (Amendment 2008), by Government of India.

Table 4b: Ground water characteristics near bioremediation sites before and after bioremediation study.

Particulars	Permissible limits as per		Ground water quality near bioremediation site before and after bioremediation study (typical) at															
	BSI / WHO *	EPA (LIE) **	ONGC Ankles-hwar		ONGC, Cauvery		ONGC, Mehsana		ONGC, Assam		OIL, Assam		BGEPII, Bhavnagar		CEIL, Barmer		Mumbai Oil Spill	
			Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Selected Heavy Metals			(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Zn	5 ppm	1 ppm	0.081	0.076	2.312	2.131	7.368	7.286	2.044	1.79	1.27	1.23	0.058	0.05	0.049	0.044	0.088	0.079
Mn	0.1 ppm	1.5 ppm	0.033	0.03	0.076	0.069	0.336	0.302	0.651	0.579	0.83	0.95	0.046	0.037	0.036	0.031	0.059	0.052
Cu	1 ppm	1 ppm	0.03	0.026	0.008	0.006	<0.001	<0.001	0.047	<0.001	<0.001	<0.001	0.032	0.01	0.011	0.01	0.037	0.029
Ni	5 ppb	1 ppm	<0.001	<0.001	<0.001	<0.001	0.031	0.026	0.197	0.186	<0.001	<0.001	0.002	0.001	<0.001	<0.001	0.002	0.002
Pb	5 ppb	0.5 ppm	0.002	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.002	0.001	<0.001	0.003	0.002
Co	5 ppb	---	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.044	<0.001	<0.001	<0.001	0.001	0.001	<0.001	<0.001	0.002	0.001
As	5 ppb	0.5 ppm	0.002	0.001	<0.001	<0.001	0.025	0.021	0.071	0.068	<0.001	<0.001	0.003	0.002	0.003	0.002	0.001	0.001
Cd	1 ppb	0.01 ppm	0.008	0.006	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.007	0.004	<0.001	<0.001	<0.001	<0.001
Cr (Total)	5 ppb	1 ppm	0.007	0.005	<0.001	<0.001	<0.001	<0.001	0.05	<0.001	<0.001	<0.001	0.004	0.003	0.002	0.001	0.003	0.002
Se	0.5 ppb	0.5 ppm	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Physico-chemical properties:																		
pH	---	6 – 10	7.48	7.35	7.26	7.15	7.62	7.35	7.39	7.61	8.01	7.92	7.69	7.54	7.7	7.6	7.19	7.21
EC (mS/cm)	---	---	1.89	1.65	45.3	43.7	2.12	1.89	2.29	2.16	2.65	2.47	2.18	2.09	2.59	2.56	2.37	2.32
Oil / Grease	---	10 ppm	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

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