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EXECUTIVE SUMMARY

Oil and gas industry is considered to be one of the most important industries in a country. Apart from its contribution to the economic of the country, it has many side impacts. Oily sludge containing different contaminants pollutes the environment. Some oil industries are using various physical treatments to reduce oil contents. Bioremediation is an effective technique for the biodegradation of oil by using Microbial diversity. Disposal of refinery sludge is a difficult problem in the overall waste treatment management program of refineries. Even the most advanced methods give residues that are no longer amenable to cost effective treatment. In order to provide an effective solution that should be cost-effective, environment friendly and on site use, NCPC in collaboration with EM organization Japan, offered ARL a trail for bioremediation of refinery sludge through its consultants (EHSC) in Pakistan. Accordingly a trail project was designed to treat and convert 1.7 M tons of sludge into environment friendly residue (bio-fertilizer) under anaerobic condition. The trail was completed in a period of 6 week (29^{th} Oct. to 10^{th} Dec. 2002). The oily sludge was tested for various parameters like TPH value, pH, heavy metals concentration before and after the treatment with EM. During bioremediation the sludge was monitored on weekly basis and heap temperature was measured routinely. The data so obtained was tabulated and was compared with sludge before treatment. Results so obtained showed that Ba has been reduced by 85% in EM treated oily sludge as compared to original ARL oily sludge, and Pb, Fe,Zn and Ni have been reduced by about 50% in treated bio-sludge. The contents of As, Cr, Cu and Mn showed no change in their conc.

Following the above-mentioned phase I, the resultant treated sludge (biofertilizer) was then applied in phase II to agriculture land as bio fertilizer, after mixing with dry soil. Here the effectiveness of sludge treatment proved through physical growth and chemical analysis of the crop. N, P, K, and Organic Matter of the treated sludge mixed in 1:1 ratio with soil after treatment was compared to same analysis for field soil, where an agricultural experimentation was undertaken as part of phase II of this program.

The entire N, P, K, and Organic Matter of the treated sludge have the properties of bio-fertilizer, and indicate it is rich in macronutrients. Onions were grown using bio-fertilizer and FYM for yield comparison and also for comparison of their toxic metals levels. Sampling was undertaken on random basis after harvesting the crop and samples were sent for heavy metals analysis and also for analysis of micronutrients; both by University of Arid Agriculture Rawalpindi. The data so obtained showed that levels of heavy metals meet the FAO and NEQS standards and almost similar concentration found in FYM grown onions, which shows that the product is not harmful and the biofertilizer, is safe to use instead of FYM and hence is also saleable.

It may also be mentioned that the oily-sludge which was bioremediated and as mentioned above showed 50-85% reduction in heavy metals, was further tested after its application as a bio-fertilizer in the field and it showed further reduction in its toxic metal content to such an extent that its not harmful for agricultural applications. In fact the soil analysis showed that the heavy metals in the soil after application were all well below the internationally recognized permissible limits.
It is further concluded that the metal breakdown tested 9 months earlier after initial bioremediation/at time of application does not undergo any reversal back to elemental state.

Further, the data shows that the non-ionization process/breakdown of metals continues after the formal bioremediation of the oily sludge during the field application phase as well, which shows that microbial activity continues after the completion of the first phase (oily sludge bioremediation). It seems EM treatment of sludge reduces the content of heavy metals due to its ability to change the ionization of heavy metals. As a result the plants do not take up non-ionized heavy metals.

This work has demonstrated environment-friendly and safe disposal of petroleum sludge, and it indicates ISO 14000 compliance can be ensured.

Large-scale agricultural experimentation is recommended to further test the positive outcomes of this work. In addition to environment-friendly disposal of industrial sludges, it is recommended that special emphasis is laid on developing safe (meeting NEQS) and socially acceptable biofertilizer from bio-remediated sludges; to make the whole process sustainable and commercially viable.

1. INTRODUCTION

Natural gas and oil are natural resources, which contribute to almost all energy needs for domestic as well as industrial activities. Thus the exploration of this type of resources worldwide has been very extensive. Along with the production activities, environmental problems such as the accumulation of oil sludge and heavy metals as well as the generation of the any kind of wastewater containing petroleum hydrocarbons, phenol, ammonia, sulfur and other unwanted parameters became inevitably. These pollutants threat soil, ground water and also surface water. In addition, air pollution should also be considered as problem associated with the activities of oil and gas industry. Nowadays, where people awareness on environmental health is increasing, effort to minimize the impact caused by the release of wastes from natural oil and gas should also be maximized.

Some oil and gas industries are currently applying various physical treatments to reduce oil contents of their wastewater. Biological treatment, if any, is merely aimed to reduce phenol as well as ammonia but not for oil. In addition, oil sludge has become the major problem since no treatment can be introduced at the possibly tolerable cost. Bioremediation, though essentially is not to be applied for wastes continuously released such as oil sludge, nevertheless this term has been quite popular and is also applied in some industry to treat oil-sludge.

This sludge cannot be just open-dumped since it has great potential to leach and become persistent sources for soil and water environment. The sludge needs either treatment to reduce its potential or to be isolated. Isolation of sludge by storing in small storage tanks nevertheless can cause another difficulty since that tank may occupy spaces.

Bio-Treatment

Sludge and liquid waste from oil and gas industry contains mainly petroleum hydrocarbon. Petroleum hydrocarbon is mixture of aliphatic, aromatic, polycyclic hydrocarbon ranging from short C_3 to much longer carbon chains.

The most important role of microbes in the degradation of oily liquid waste or even sludge is to transform complex and may be toxic compounds to simple and harmless ones and more over to convert oil sludge to bio-sludge.

Industry needs a well-planned sludge management system as the Sludge poses various kinds of environmental hazards such as Fire Hazard (in case of oily sludge), Groundwater contamination, Soil Contamination, Threat to Marine life and Air pollution/Odor. EM with all its advancements made since its invention has the potential of biodegradation (anaerobic) of most type of sludges. In this regard NCPC in collaboration with EM organization offered a trail to ARL for the bioremediation of 1.7M tons of Oily sludge. This would provide the basis for further research and development. The trail was designed in to two phases:

3. OBJECTIVE

The 1st phase was the bioremediation of sludge that was completed successfully and bioremediated product was obtained. In 2nd phase; application of bioremediated product as fertilizer.was carried out the **main objective** of which is to provide ARL an effective environment-friendly waste disposal system for oily sludge treatment and the costeffectiveness through development of saleable by-product, after checking the toxicity.

4. METHODOLOGY

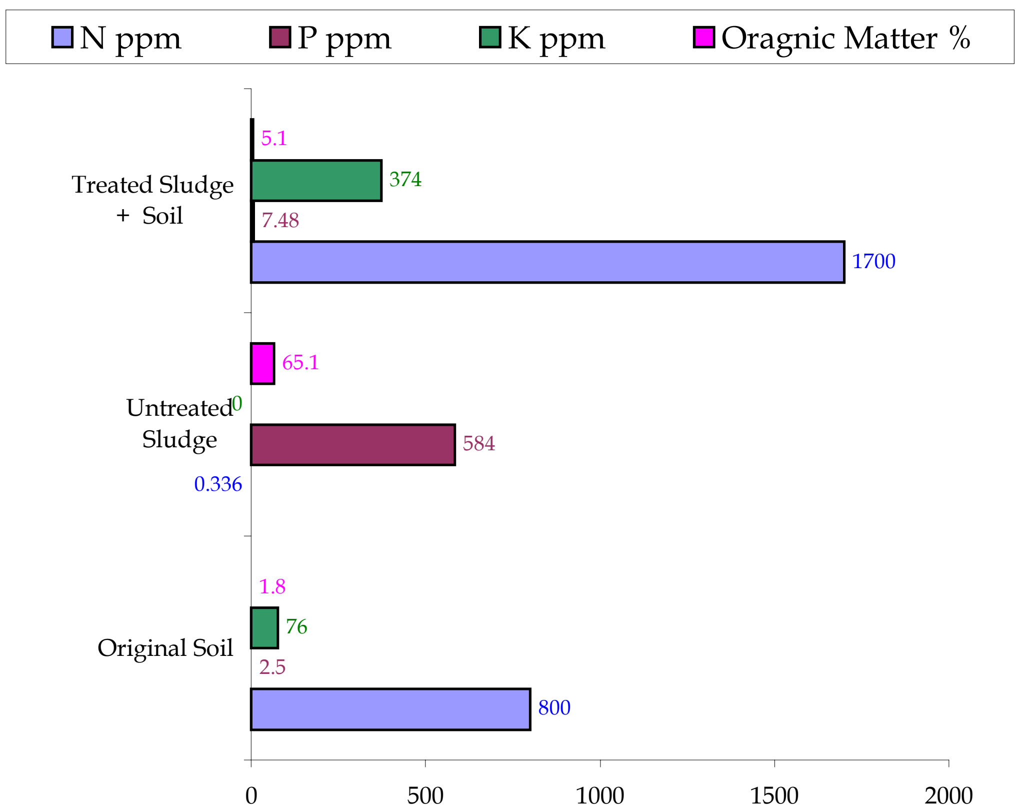
The effectiveness of the biofertilizer was checked through:

i. The physical growth of the crop.
ii. Chemical analysis of the crop.
iii. Nitrogen (N), Phosphorus (P), Potassium (K) Carbon Nitrogen ratio(C: N), Organic Matter.

4.1 NPK & OM Analysis.

The treated sludge (bio-fertilizer) was applied in phase II to agriculture land as bio- fertilizer, after mixing with dry soil in proper ratio (1:1) for easy handling, application, and transportation.. Here the effectiveness of sludge treatment was proved through physical growth and chemical analysis of the crop. N, P, K, and Organic Matter of the treated sludge mixed in 1:1 ratio with soil after treatment was compared to same analysis for field soil, where an agricultural experimentation is being undertaken as part of phase II of this program. *The entire N, P, K, and Organic Matter of the treated sludge have the properties of bio-fertilizer, and indicate it is rich in macronutrients.* Figure 1 below shows the NPK & OM Analysis.

NPK & OM Analysis



	Original Soil	Untreated Sludge	Treated Sludge + Soil
Oragnic Matter %	1.8	65.1	5.1
K ppm	76	0	374
P ppm	2.5	584	7.48
N ppm	800	0.336	1700

After the analysis of NPK and assuring that treated sludge contains enough nutrients and organic matters for vegetation, onions were grown in two fields having a plotted area of 64X20 feet using farm yard manure in one field and treated sludge, mixed with soil (1:1), in other field. The agronomical factors were kept in view such as number of plants (nursery plantation)

4.2 Field Parameters

Table 1

Field parameters		
Parameters	**EM treated area**	**FYM treated area**
Plotted Area	64X20 feet	64X20 feet
Yield enhancer added	EM 23mond(1:1) added	FYM 23mond added
Paneeri added	2,673 plants	2,673 plants

Once the onions were harvested, sampling was carried out on random basis and following samples were taken for evaluation of Toxicity.

4.3 Sampling Criteria

Table 2: Sampling Criteria

Yield enhancer	**Samples required to check the toxicity**
Biofertilizer	Onion, Soil, biofertilizer
Menure	Onion, Soil, manure

NOTE:
Naturally occuring Soil wasl also tested for its toxicity as control

In order to analyze the samples, 24 onions from different locations of the field were taken and their core was used as a samples. After taking the samples were crushed and grounded for uniform mixing of sample. The same procedure was carried out for the samples of onions from both bio-fertilizer from oily sludge, and FYM.

4.4 Dry Ashing For Micro Nutrients Cations Of Plants

Plant analysis by Dry ashing is simple, non-hazardous and less expensive compare with HNO3, HCLO4 wet digestion. Dry ashing is appropriate for analyzing all macro and micronutrients in plant tissues.

Procedure:

1. Place 0.5 to 1.0 gram portion of plant material (onion) in a glass beaker.
2. Place the beaker in cool muffle furnace and increase the temperature gradually to 550^0 C.
3. Continue ashing for 5 hours after attaining 550^0 C.
4. Shut off the muffle furnace and open the door cautiously for rapid cooling.
5. When cool, take out the beaker carefully.

6. Dissolve the cool ash in 5 ml portion of 2 N HCl and mix with the plastic rod
7. After 15 to 20 minutes, make up the volume (usually 50 ml) using 0.1 N HCl.
8. Mix thoroughly, allow standing for about 30 minutes, and filtering it.
9. Analyze the aliquots by using Atomic absorption spectroscopy.

Subsequently otesting was conducted using atomic absorption spectrophotometery.

4.5 Analysis For Micronutrients And Heavy Metals

For soil, the samples were prepared by the following method:

Apparatus required:

i. Reciprocal shaker
ii. Atomic absorption spectrophotometer.

Reagents:

i. Diethylenetriaminepenta acetic acid (DTPA).
ii. Standard Solutions.

Procedure:

i. Take 10 g soil sample.
ii. Add 20 ml of DTPA (Diethylenetriaminepenta Acetic Acid).
iii. Shake this solution for 15 min.
iv. Filter the solution and analyse using Atomic Absorption Spectrophotometry

5. RESULTS

5.1 Yield Comparison

The yield of he crop is summarized as in the following Table 3 below:

Table 3:

Treatments	*Yield (Kg)*	*Remarks*
FYM treated area	275 Kg	Plant growth was ok and their leaves were greenish at the time of cultivation as compared to those grown in EM treated plot.
EM treated area	230 Kg	Plant growth was good and the onions harvested were larger in size as compared to those grown in FYM treated plot.

The green colouration of leaves in FYM plot was due to the presence of more chlorophyll in these plants as compared to those plants that were grown in EM treated plot showing that using *biofertilizer the cultivation can be achieved earlier as compared to FYM.*

Similarly the large volume of onions grown in bio-fertilizer shows that *the bio fertilizer is richer in nutrients and organic matters as compared to FYM.*

5.2 Heavy Metal Contents in Soil Samples

Soil samples from both treatments were taken at the time of harvesting and were analyzed.

Table 4: Heavy metals content in Soil taken from EM treated area and FYM treated area:

Heavy metals	***FYM soil ppm***	***treated sludge (1:1) ppm***	***Permissible limit (ppm)****
Chromium (Cr)	0. 04	0. 07	1. 0ppm
Cadmium (Cd)	0. 17	0. 14	>1. 0 ppm
Copper (Cu)	0. 03	1. 05	3. 0 - 5. 0 ppm

Nickle (Ni) ppm	0. 45	0. 32	1. 0
Lead (Pb) 20 ppm	2. 0	1. 57	15 –

**Source for Permissible limits:* NEQS and Department of Plant & Soil Sciences Laboratory

It may be seen that the oily-sludge which was bio-remediated and showed 50-85% reduction in heavy metals initially through the bioremediation, was further tested after its application as a bio-fertilizer in the field (Table 4 above) and it showed that *the bioremediated sludge after mixing with soil resulted in dilution of its toxic metal content to such an extent that it is not harmful to the environment and agricultural applications.*

The soil analysis showed that the heavy metals in the soil after application were all well below the internationally recognized permissible limits which provides us the evidence that

the metal breakdown tested 9 months earlier after initial bioremediation/at time of application does not undergo any reversal back to elemental state.

From these findings it appears that the non-ionization process/breakdown of metals continues after the formal bioremediation of the oily sludge during the application phase as well.

5.3 Heavy Metal Contents In Onion Samples

Onion samples from both treatments were taken at the time of harvesting and were analyzed.

Table 5: Conc. of Heavy metals in onions grown using Biofertilizer and FYM.

Heavy metals	*FYM onions*	*treated sludge (1:1) oni\ons*	*Permissible limit (ppm)*
Chromium (Cr) ppm	0. 15	0. 21	1.0
Cadmium (Cd) ppm	0. 05	0. 04	0.24
Copper (Cu) ppm	4. 11	8. 14	05-20
Nickel (Ni) ppm	0. 14	0. 10	1.0
Lead (Pb) ppm	1. 87	3. 30	>1.0

Source: Pakistan Book Foundation, and FAO Standards

The results above show that the Chromium concentration in EM treated soil and in onions was far below than the NEQS (premissible level 1.0 ppm). This is the same for copper. Other standards were so far not available.

It seems EM treatment of sludge reduces the content of heavy metals due to its ability to change the ionization of heavy metals. The plants do not take up non-ionized heavy metals.

5.4 Micronutrients in Soil Samples

Table 6: Micronutrient conc. In originl soil, EM treted soil and in FYM treted soil

Micronutrients	original soil	EM treated soil	FYM treated soil	Premisive level (ppm)
Iron (Fe)	2. 8	4. 4	7. 13	2.0 – 8.0 ppm
Zinc (Zn)	ND	1. 43	2. 1	5.0 ppm
Maganese (Mn)	24. 7	10. 2	8. 1	>1.0 ppm

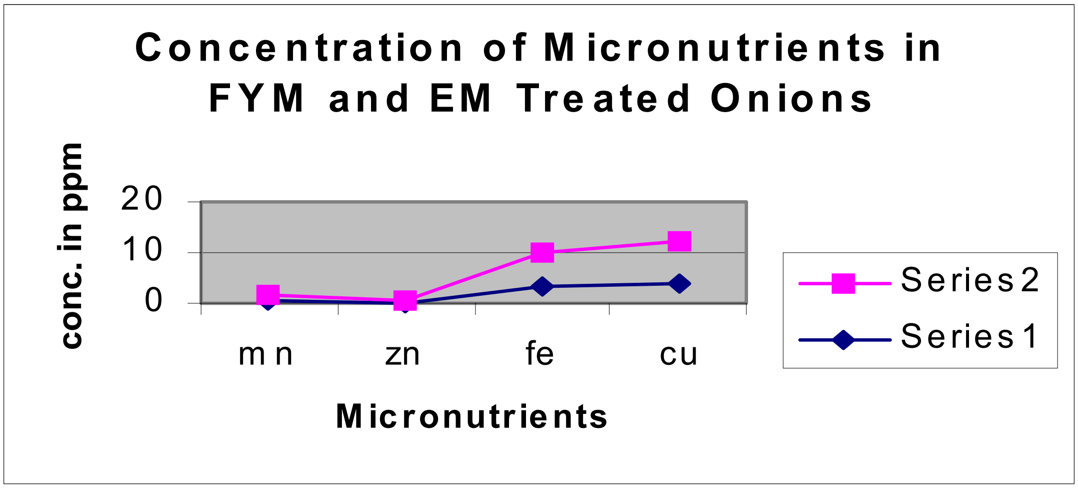
Source NEQS and Soil Science Book National Book Foundation 1996

It is clear from the above data that all the values for the micronutrients are with the NEQS and FAO standards and the soil is enriched with th e micronutrients essential for its growth.

Graphical Presentation of the results is also shown with respective headings below.

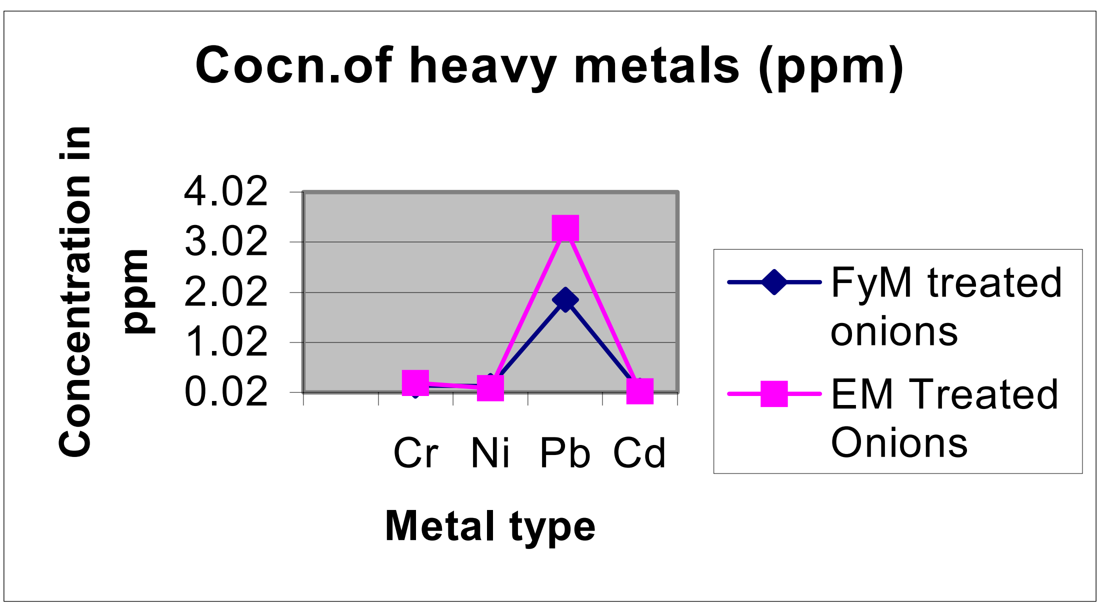
5.5 Concentration of Micronutrients in Onion Samples

The Comparison of Micronutrients is shown in graphical presentatin below:

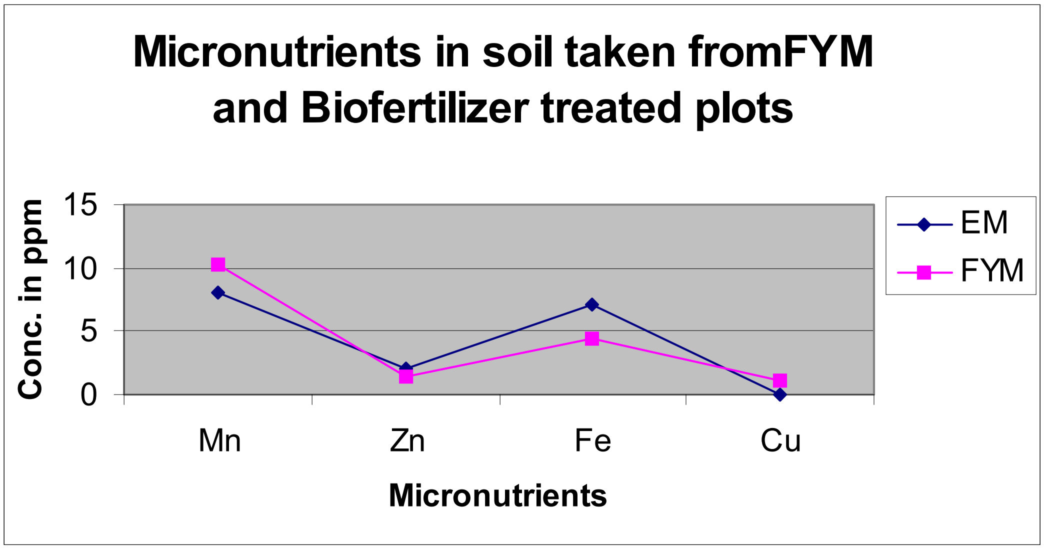


Series 2= micronutrients in EM treated onions
Series 1= micronutrients in FYM treated onions

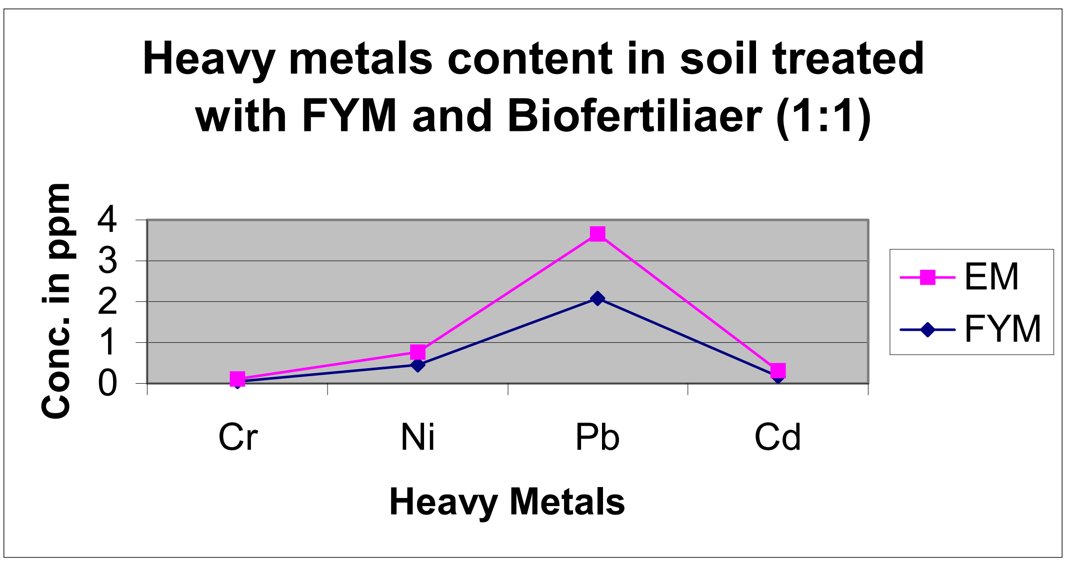
5.6 Concentration of heavy metals in onion samples



5.7 Micronutrients content in soil samples



5.8 Heavy Metals content in Soil Samples



6. CONCLUSIONS

From the above results it can be safely concluded that:

1. Through bio-fertilizer the same yield can be achieved as through FYM.

2. The bio-fertilizer is richer in all the essential nutrients and organic matters to support the plant growth, similar to FYM.

3. Bioremediation waste have increased the nutrient content as well as soil organic matter which resulted in enhanced plant growth. The bio-fertilizer may be used as a substitute to Farm-Yard Manure.

4. The bioremediated sludge after mixing with soil undergoes further reduction in its toxic metal content to such an extent that it is not harmful to the environment and agricultural applications.

5. In fact the soil analysis showed that the heavy metals in the soil after application were all well below the internationally recognized permissible limits.

6. It is further concluded that the metal breakdown tested 9 months earlier after initial bioremediation, does not undergo any reversal back to ionized state.

7. Further, the data shows that the non-ionization process/breakdown of metals continues after the formal bioremediation of the oily sludge during the field application phase as well, which shows that microbial activity continues aetr the completion of the first phase (oily sludge bioremediation).

8. The results show that the Cr concentration in onions from EM treated soil was far below than the NEQS (premissible level 1.0 ppm). The same is the situation for other metals.

9. It seems EM treatment of sludge reduces the content of heavy metals due to its ability to change the ionization of heavy metals. As a result the plants do not take up non-ionized heavy metals.

10. It is clear from the above data that all the values for the micronutrients conc. are also within the NEQS and FAO standards.

11. This work has demonstrated environment-friendly and safe disposal of petroleum sludge, and it indicates ISO 14000 compliance can be ensured.

7. RECOMMENDATIONS

1. Large-scale agricultural experimentation is recommended to further test the positive outcomes of this work.

2. In addition to environment-friendly disposal of industrial sludges, it is recommended that special emphasis is laid on developing safe (meeting NEQS) and socially acceptable biofertilizer from bio-remediated sludges; to make the whole process sustainable and commercially viable.

3. Motivate farmers to use biofertilizer through farmer's schools cooperation and also taking the help from agricultural institutes.

ANNEXURE 1: ANALYSIS RESULTS

Test	Original soil	FYM treated Soil	EM treated soil	Onions from FYM	Onions from EM
Cr	0.86	0.04	0.07	0.15	0.21
Ni		0.45	0.32	0.14	0.10
Pb	ND	2.08	1.57	1.87	3.30
Cd	1.56	0.17	0.14	0.05	0.04
Mn	24.7	8.1	10.2	0.80	0.89
Zn	ND	2.1	1.43	ND	0.45
Fe	2.8	7.13	4.44	3.33	6.85
cu	0.93	0.03	1.05	4.11	8.14