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Comparison of bio-augmentation and composting for remediation of oily sludge: A field-scale study in China

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Abstract

Two bioremediation technologies were performed in order to explore a better treatment process for an oily sludge restoration in China during 2004. The bioremediation by augmentation of biopreparation was compared with a conventional composting. The oily sludge and oil-polluted soil were received from an oil production plant. The total hydrocarbon content (THC) varied from 327.7 to 371.2 g kg^{-1} of dry sludge and the THC in contaminated soil was 151.0 g kg^{-1}. Before application of preparation, straw, sawdust, top sand and pure soil were added in different proportions to the sludge and soil and mixed thoroughly. Such sludge and soil composites were used for negative controls and for activation of indigenous oil degrading microorganisms with addition of fertilizer (positive controls). For composting, crude manure and straw were added to the oily sludge and the THC was 101.4 g kg^{-1}. The biopreparation was applied every 2 weeks and experiment lasted 56 days under the ambient temperature. The sludge was mixed and watered every 3 days. After three times of biopreparation application, the THC decreased by 46–53% in the oily sludge and soil, while in the positive controls (activation of indigenous microorganisms) the THC decreased by 13–23%, and there was no oil degradation in negative controls After composting, the THC decreased by 31% in the oily sludge. The planting of Tall Fescue (*Festuca arundinace*) revealed a decrease of sludge toxicity after application of both bioremediation technologies and additionally decreased the THC by 5–7%.

Keywords: Oily sludge; Preparation; Iindigenous oil degrading bacteria; Bio-augmentation; Composting

1. Introduction

A huge amount of oily sludge is produced during the oil production and processing activities. This sludge usually contains a considerable quantity of heavy oil, which should be removed before its land disposal. The physico-chemical treatments can be applied for the oily sludge, but these methods are extremely expensive [1–3]. In this respect, composting and bioremediation with an introduction of oil degrading microorganisms (bio-augmentation) or activation of indigenous ones are now considered as two major economic methods for the decontamination of oil pollutions [4–6]. Composting has some visible advantages including relatively low capital and maintenance costs, simple design and operation and some (but incomplete) removal of oil pollution. For example, Jiang applied composting for oil contaminated soil and achieved 45–57% of the THC decrease [7]. However, in general, the efficiency of composting is unsatisfactory to meet the current environmental regulations.

For more content of the oil, the oily sludge is much more difficult for the bioremediation. Numerous researches have demonstrated high bioremediation efficiency for oil polluted soils, but these methods have limitations for the oily sludge mainly dealt with extremely high pollution level and recalcitrance of contaminants for biodegradation [8–10]. Most of the experiments were carried out in the lab, while the field experiments were very few.

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Table 1
Chemical characteristics of the original oily sludges and oil contaminated soil

Samples	Initial THC (g kg^{-1} DW)	pH	Moisture content (%)	[N-NH_4^+] (mg kg^{-1} DW)	[P-PO_4^{3-}] (mg kg^{-1} DW)
Sludge 1	327.7	7.2	6.16	308.4	64.3
Sludge 2[a]	327.7	7.2	0.64	308.4	64.3
Sludge 3	371.2	7.6	5.23	136.7	77.8
Soil 4	151.0	7.7	0.17	102.1	5.5

[a] Without water sludge.

The bioremediation treatment of the oily sludge was just beginning. These experiments were meaningful for the advance of this technology. This article deals with the bioremediation of oily sludge using the bioaugmentation by preparation ''Rhoder'' and composting with manure in order to explore a better treatment process for this type of residues. The field experiments were performed at Shengli Oil Production Plant, (Dongying, China).

2. Materials and methods

The oily sludge and oil-polluted soil for this research were taken from Shengli Oil Production Plant and analysed before start the experiments (Table 1). Sawdust, straw, top sand and clean soils were used as additives to the sludge and soil. The moisture content of sawdust and straw was 23.7 and 7.4%, respectively. Carbamide and KH_2PO_4 were used as fertilizers.

The oil-degrading microbial preparation (''Rhoder'', Certificate number 77.99.04.515 D. 004855. 08. 01 issued by the Russian Ministry of Health) was developed in nineteen in Russia [11]. The preparation was successfully tested in the Western Siberia on different types of oil contaminated wetlands, marshy soils and water surfaces during 1995–1999 as well as in laboratory, pilot and field tests in Komi Republic during 2001–2003 [12,13]. The preparation consists of two *Rhodococcus* oil-degrading strains and represents dry powder of alive bacterial cells with concentration till 10^{10} CFU g^{-1}. The working suspension of preparation for bioremediation contained 10^6–10^7 oil degrading cells per ml.

The oily sludge samples were taken randomly every 3 days from the upper layer (5.0 cm of depth) and 0.5 month after the last treatment from five equidistant points. The THC was determined gravimetrically as follows. 7–8 g sludge samples were dried at 70 °C and after sieving through a 2 mm sieve were extracted with 50 ml petroleum ether by 7–10 times. The extract was evaporated to dryness in water-boring box, and then dried under 70 °C for 1 h and finally weighted.

Individual hydrocarbons were analysed by gas chromatographic (GC) (Trace 2000, TermoQuest, Milan, Italy) and mass spectrometric (Voyager Applied Biosystems, Foster City, CA, U.S.A.) methods. The initial and final oily sludge samples after applied three times of preparation were extracted by petroleum ether and re-dissolved in 10 ml. The samples were analysed for GC profiles. The hydrocarbon concentrations were calculated by comparing the peak areas of samples with internal standard (hexadec-1-en) [14]. The gas chromatograph was equipped with a flame ionisation detector and a 30 m stainless steel column. The operation conditions were as the following: initial temperature was 50 °C, and was increased at 10 °C min^{-1} to 200 °C and then increased at 5 °C min^{-1} to the final temperature of 290 °C. Helium as a carrier gas was delivered at a rate of 0.8 ml min^{-1}.

Numbers of microorganisms in the treated sludge were estimated by MPN method, using meat-peptone agar in Petry dishes. Ten grams of oil sludge was suspended in 90 ml of sterile water and submitted to vigorous shaking, and then the method of ten-fold dilutions and triplicate Petry dishes for each variant was applied.

To determine pH the samples were dried at 70 °C and sieved through a 1 mm sieve, then 5 g samples were extracted with distilled water by five times with electro-magnetic stirrer during 30 min. The water samples were measured after complete mixing.

The composting pile temperature was recorded every day randomly from the five-equidistant points of the upper layer (0.05 m depth) of the pile.

3. Experimental design

The field scale experiments were performed under roof on the surface of a concrete slab. There were four sections (2.5 m × 2.0 m × 0.2 m) for experiments with the biopreparation in oily sludges at the same time. Two sections (1.6 m × 1.0 m × 0.2 m) were used for positive controls (i.e., activation of indigenous microorganisms), 2 of the same size - for negative controls and 1 (0.75 m × 0.5 m × 0.2 m) – for composting.

Before composting (CM), 60 kg raw manure and 10 kg straw were added to 280 kg of oily sludge (the initial THC 126.8 g kg^{-1}), mixed thoroughly and made a pile. The THC in this modified sludge became 101.4 g kg^{-1}.

The initial concentrations of hydrocarbon (HC) in oily sludges varied from 327.7 to 371.2 g kg^{-1}, whereas in the old oil contaminated soil it was 151.0 g kg^{-1}. Straw, sawdust, top sand and clean soil were added to the sludges and soil, and mixed thoroughly before the first application of the biopreparation. The materials used for composting are presented in Table 2. The mentioned above supplements

Table 2
The composition of the materials subjected or treatment during field scale experiments

Variants	Oily sludge (kg)	Initial THC (g kg^{-1})	Manure (kg)	Straw (kg)	Sawdust (kg)	Top sand (kg)	Terminal THC (g kg^{-1})
CM	280	126.8	60	10	0	0	101.4
Sludge 1	750	327.7	0	12	15	0	251.3
Sludge 2	500	327.7	0	12	15	0	240.7
Sludge 3	600	371.2	0	8	15	100	121.2
Soil 4[a]	800	151.0	0	8	15	20	94.1

[a] 20 kg of pure soil were added.

were the source of additional nutrients and a structure-forming agents for the oily sludges and soil. The sludges and soil supplemented in the same way were also used for the activation of indigenous oil degrading microorganisms with addition of fertilizers. Experiments lasted 56 days under the ambient temperature. Mixing and watering were repeated every 3 days. Oily sludge in the negative controls was not subjected to any treatment.

Ten-liter solution containing 150 g microbe preparation (0.3 g dry preparation per 1 kg of modified sludge or soil) and 1000 g carbamide and 50 g KH_2PO_4 were spread onto the each section three times every 2 weeks. The same concentration of fertilizers was used for activation of indigenous microorganisms in the same time. The oily sludges were turned over to achieve fully mixing after application of microbe preparation and fertilizers in each section.

After the end of treatments, the Tall Fescue lawns (*Festuca arundinace*) were transplanted on the surface of all sections to identify the toxicity and perform a subsequent phytoremediation of these oily sludges and soil.

4. Results and discussions

4.1. Oil degradation

The effect of microbial preparation bio-augmentation (MPB) on degradation of HC in oily sludges 1–3 and soil is shown in Fig. 1. The THC decreased by 45–47% and 53%, in

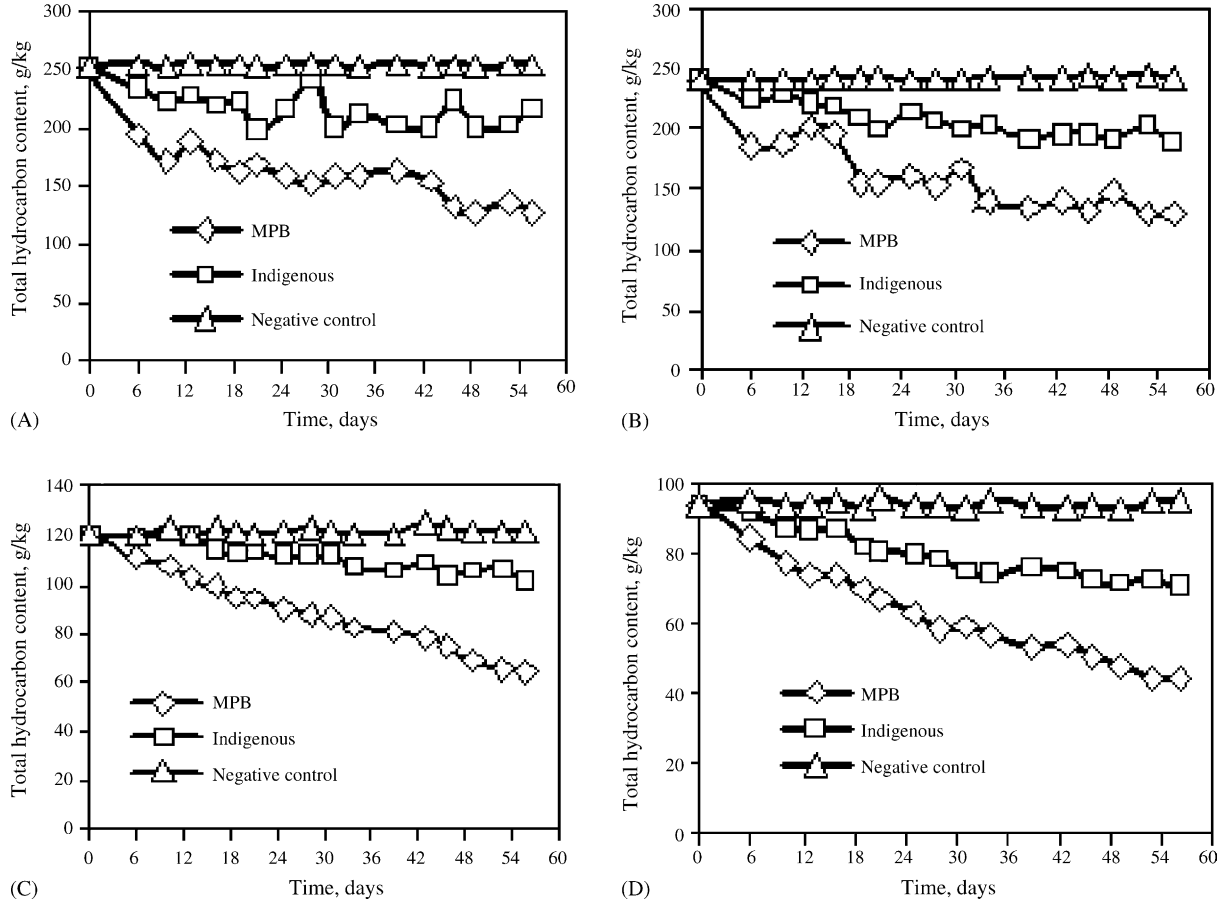

Fig. 1. Hydrocarbon degradation in oily sludge 1 (A), 2 (B), 3 (C) and soil (D) during experiments.

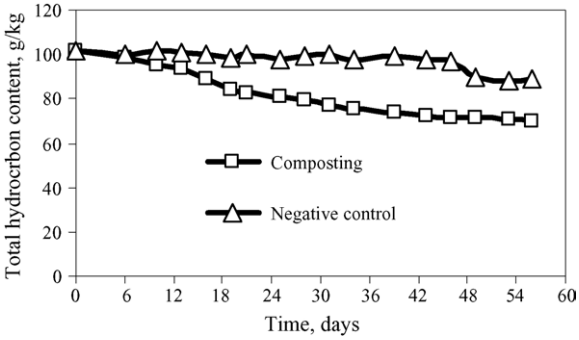

Fig. 2. Hydrocarbon degradation in oily sludge by composting.

sludges and soil, respectively, (Fig. 1). At the same time, activation of indigenous microorganisms with fertilizers (positive controls) decreased the THC by 13–20% and 23% in sludges and soil, respectively. By improving the living conditions, the indigenous microorganisms can degrade the oily sludge efficiently. It is an effective way to treat the oily sludge. By contrasted the removal rate, we can knew that the microbial preparation has the advantages of the remediation on the indigenous microorganisms. There was no THC decrease in negative controls. After composting, the THC decreased by 31% (Fig. 2). The obtained results showed that the MPB increased the rate of HC degradation in oily sludges. The degradation of HC by preparation was the most rapid during the first month and then the rate declined with time.

On the sites, where heavy oil pollution is taken place, vegetation is usually scarce or absent. Various annual plants are able to survive and grow in oil-contaminated areas if the contamination level is moderate or weak (usually the content of hydrocarbon was less than 10%) [15]. Plants support the growth and metabolic activities of soil microorganisms through the photosynthate secretion in their rhizosphere. In contaminated soils, the bacterial numbers are significantly

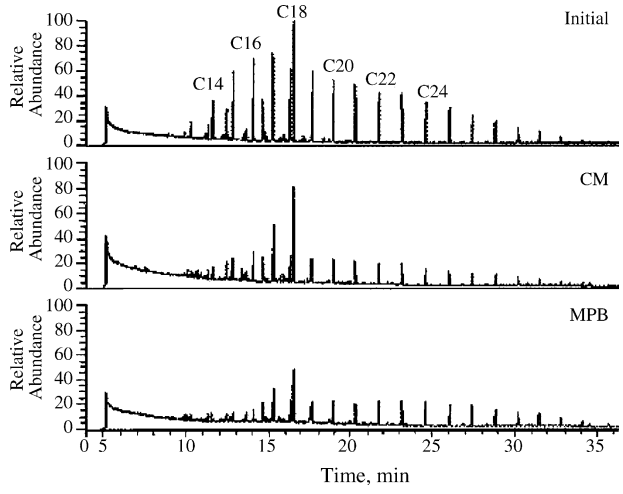

Fig. 3. Gas chromatographic profiles of the HC extracted from the treated sludge by MPB (number 3), CM and initial untreated sludge.

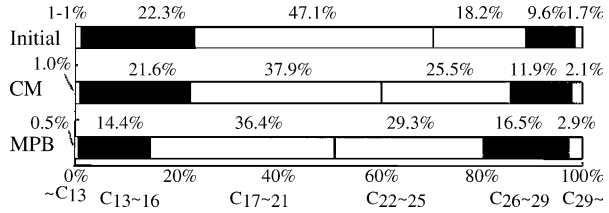

Fig. 4. The ratio of six groups of the hydrocarbons in the untreated and treated by MPB and CM.

higher and oil degradation is more efficient in the rhizosphere than in the bulk soil [16,17]. Our own experience also indicates the usefulness of phytoremediation after application of bioremediation with augmentation of oil degrading preparations and/or activation of indigenous microorganisms [18,19]. Based on these facts, fescue (*Festuca arundinace*) lawns were transplanted on oily sludges treated by microbe preparation and CM on the 56th day. The combination of the oil degrading microorganisms and vegetation led to further decrease of oil content in the sludge. On 90th day, the THC in the sludges 1–3, soils and CM decreased additionally by 5–6% (on the average).

4.2. Analysis of hydrocarbon content by GC-MS

The alkanes in the range of C13–C29 were found to be major compounds in the initial oil pollution (Fig. 3). They were mainly linear ones and the C18 was the most with a 5.3% content. The smaller peaks between the linear alkanes (Fig. 3) indicate a presence of the branched-chain alkanes and most of them contained less that four methyl groups according to the MS data. The most branched compound in the oil was phytane (2,4,10,14-tetramethylhexadecane, $C_{20}H_{42}$) with a 10.9% content. The GC data for treated samples also showed an enhanced oil degradation of the MPB compared to the CM – the peaks of *n*-alkanes ($n < 18$) in the CM were taller than those for the sludge number 3 (Fig. 3).

In order to have better insight on degradation pattern, all alkanes were arbitrarily divided into six groups by carbon atoms (<C13; C13–C16; C17–C21; C22–C25; C26–C29; >C29). The percentage of every group from the sludge by MPB (number 3), CM and the untreated sludge was calculated (Fig. 4). The highest ratio in the initial untreated oily sludge was for the group C17–C21 (47.1%). On day 56, the percentage of this group dropped to 37.9 and 36.4% for the CM and the MPB, respectively. At the same time, the oil content in the sludge number 3 decreased from 121.2 to 58.2 g kg^{-1}, so, the removal of C17–C21 HC by the microbial preparation from sludge number 3 was 62.9%. In the CM, the removal rate of the C17–C21 HC was 44.6%.

The initial ratio of the group >C29 HC was 1.7%. After 56 days, the percentage of this group increased to 2.1 and 2.9% in the CM and the MPB, respectively. Based on the HC content decreased in the whole sludge, the removal of >C29 HC by MPB was 18.1%. The removal rate of it in the CM

Table 3
Bacterial (CFU) monitoring in the MPB and the positive control sections

Variants	Monitoring, days (CFU g^{-1} sludge)					
	1	10	23	33	45	58
MPB, sludge number 3	2×10^9	4×10^{12}	3×10^{11}	3×10^{11}	2×10^{11}	4×10^9
Positive control number 3	1×10^7	5×10^9	1×10^{10}	4×10^9	4×10^8	6×10^8

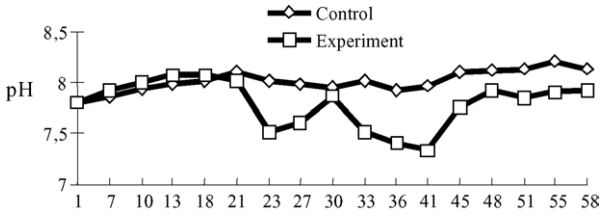

Fig. 5. pH monitoring in sludge number 3 and its positive control during bio-augmentation.

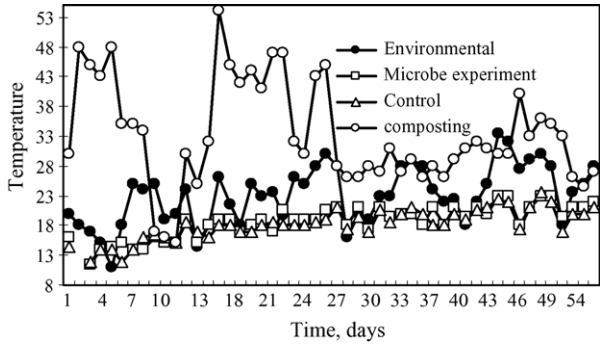

Fig. 6. Temperature monitoring in oily sludges during bioremediation process.

was 14.8%. Contrasted to the removal rate of C17–C21 HC, it can be concluded that the hydrocarbons with more than 29 carbons were much more resistant to the bioremediation. The branched alkanes are more resistant to microbial degradation than *n*-alkanes due to their molecular structure. Furthermore, larger molecular are considered to be less degradable than smaller ones [20,21]. Our data confirm these observations.

4.3. Change of pH during the bio-augmentation treatments

Since the pH is one of the key factors for microbial metabolism, its value in the sludge samples from the CM and MPB sections, positive and negative controls was monitored every 3 days because in the conditions of excess of nutrients and oxygen, the pH values of oily sludge under microbial degradation would drop evidently [22]. At the beginning, the pH values were 7.6–8.1 in all sections. The pH values in the controls sections fluctuated in a very small range (7.80–8.21) (Fig. 5) while during bioremediation process, these fluctuations were more pronounced but they did not go out of the range 7–8 (Fig. 5). This range is optimal for oil-degrading microflora [23]. The period of pH value fluctuation was synchronized with the time of the microbe preparation addition, proving that the preparation had an effect on decontamination of oily sludges.

4.4. Composting temperature

The MPB and control sludges temperatures were lower by 5–8 °C compared to the ambient ones (Fig. 6), probably, because of all experimental sections were situated under roof on the surface of the concrete slab. In case of composting, a distinct increase of pile temperature during the first month was observed (Fig. 6). The temperature rise was related with the addition of the manure. As the first addition, the temperature rose quickly to 48 °C and kept at this level during 4 days. The pile temperature reached the maximum 54 °C after the second addition of manure. The duration of the high temperature was about 10 days and then dropped to 16 °C at the 29th day. However, the third addition of manure did not increase the temperature. From the 34th day, the pile temperature did not fluctuate. It was supposed that the period of intensive microbial activity during composting was 30 days based on the pile temperature fluctuations and oil content of the sludge. However, comparing the THC decrease and temperature changes during composting, everybody can conclude that the high temperature was not the major factor of the oil degradation.

4.5. Microbial activity

The data on CFU counts of microorganisms in the sludges and soil during bioremediation process are shown in Table 3. It is seen that the microbial counts in the MPB section number 3 varied from 2×10^9 to 4×10^{12} CFU g^{-1} sludge during 23 days and decreased to 4×10^9 CFU g^{-1} sludge at day 58. The microorganisms in positive control number 3 fluctuated from 1×10^7 to 1×10^{10} CFU g^{-1} sludge at the same time and decreased to 6×10^8 CFU g^{-1} at day 58. Thus, the addition of selected oil-degrading bacteria with microbe preparation allowed to have a higher counts of microorganisms in the MPB sections of oily sludges and more efficient degradation of oil (Fig. 1)

5. Conclusions

(1) Bio-augmentation with the microbe preparation decreased the oil contamination of oil sludge by 45–53% after three-fold application of the preparation (the

initial hydrocarbon content varied from 121 g kg^{-1} till 251 g kg^{-1}) while composting of the same sludge decreased the oil contamination by only 31% (the initial hydrocarbon content was 101 g kg^{-1}). In the positive controls (activation of indigenous oil-degrading microorganisms by fertilisers), the THC decreased by 13–23% and there was no oil degradation in negative controls.

(2) The planting of Tall Fescue (*Festuca arundinace*) revealed a decrease of sludge toxicity after application of both bioremediation technologies (microbial bioaugmentation and composting) and additionally decreased the THC content by 5–7%.

(3) The field experiments proved that the microbial preparation bio-augmentation (MPB) sludges was an effective treatment for the oily. By better the living conditions, the indigenous microorganisms played an important role in the degradation. The composting was demonstrated an economic and efficient way for the oily sludge.

(4) The successful field experiments were an example for the bioremediation of oily sludges in China.

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