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Biodegradation of oil tank bottom sludge using a new two-phase composting process: kinetics and effect of different bulking agents

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Abstract

In this study, the effect of adding various bulking agents on the performance of a two-phase composting method in bioremediation of petroleum compounds from oily sludge was surveyed. The utilized system included the primary stage composting (PSC) using 6 windrow piles and the secondary stage composting (SSC) using 6 in-vessel bioreactors. Various amounts and combinations of immature compost, mature compost, and green waste were blended with oil tank bottom sludge (OTBS). Then, the mixture was added to the PSC and SSC experiments and composted for a period of 12 and 6 weeks, respectively. The results showed that the degradation percentages of total petroleum hydrocarbons in the PSC and SSC experiments were 63.56–84.50% and 57.59–88.95%, respectively. The removal efficiency reached through the two-phase system was higher than that of the single-stage process. Biodegradation was fitted to the first- and second-order kinetic with the rate constants of 0.076–0.389 day^{-1} and 0.006–0.176 g kg^{-1} day^{-1}, respectively. The bacteria identified from the composting mixtures were *Bacillus* sp., *Pseudomonas* sp., *Staphylococcus* sp., and *Klebsiella* sp. It was concluded that the two-stage composting system, as an inexpensive and efficient method, is practically applicable for remediation of OTBS.

Keywords Two-phase composting · Highly contaminated sludge · Immature compost · Mature compost · Green waste · Bacterial isolation

Abbreviations

FID	Flame ionization detector
GC	Gas chromatograph
GW	Green waste
IC	Immature compost
MC	Mature compost
OC	Organic carbon
OTBS	Oil tank bottom sludge
PSC	Primary stage composting
SSC	Secondary stage composting
TPH	Total petroleum hydrocarbons

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Introduction

Due to the important role of petroleum in societies' development, the need for its generation and utilization is continuously increasing. Consequently, considerable volumes of petroleum wastes are released into the environment without enough treatment [1, 2]. Petroleum pollutants are a worldwide challenge which can threaten the environment and human health [3]. One of the sources of environmental pollution with petroleum hydrocarbons is oily sludge produced from the accumulation of crude oil materials at the bottom of storage tanks. The oil tank bottom sludge (OTBS) contains high concentrations of petroleum

hydrocarbons and other components such as sand, clay, soil, and heavy metals. The OTBS should be treated and disposed of as a hazardous waste in an environmentally safe manner [3, 4].

To achieve acceptable contamination levels of petroleum hydrocarbons residues, environmental organizations all over the world have been employing various technologies for treating different kinds of oily sludge [5, 6]. However, the effective treatment of OTBS has still remained a worldwide problem due to its hazardous nature and complicated structure of the component blend [7, 8]. The hydrocarbon contents of oily sludge can be reduced by applying physicochemical technologies such as incineration, solidification/stabilization, solvent extraction, and ultrasonic treatment. However, owing to the recalcitrant nature of OTBS, few technologies can reach an acceptable efficiency to meet strict environmental regulations. While most physicochemical techniques are ecohazardous, bioremediation has been adopted as an influential, practical, and environmentally benign measure for treating these pollutants [9, 10].

In this sense, two common techniques of composting, windrow and in-vessel, have been widely employed to purify soil, sludge or sediment polluted with oily compounds [3, 11]. Major advantages of windrow composting include relatively low costs and simple design and operation. In contrast, microbial activity and removal efficiency enhance using in-vessel composting since operating factors of the system can be adjusted well [12, 13]. Composting efficiency depends on a few factors like the types and levels of bulking agents and amendments used. In the composting process, organic amendments such as immature compost (IC), mature compost (MC), food waste, and sludge can be added to supplement microorganisms, nutrients, and readily biodegradable organic matter [14, 15]. Furthermore, addition of some materials such as green waste (GW) as bulking agents could promote aeration and water penetration through the composting mixture, and thereby increase the removal rates of petroleum hydrocarbons. Moreover, it shortens the composting duration and reduces offensive odors generated [3, 16]. However, the amount of amendments and bulking agents must be supplied in a suitable proportion to balance target contaminant concentrations and promote microbial activity. Moreover, the economy of a composting process depends largely on the amount of these added materials [3, 7].

It has been reported that bioremediation of petroleum products is performed in two stages. The first phase starts with a fast decomposition and then the process falls in a slow degradation because most easily biodegradable are removed over the first stage [3, 17]. Thus, so as to keep contaminant degradation at a maximum rate, the utilization of the two-phase method can be a reasonable alternative. Accordingly, removal rate of petroleum hydrocarbons in the two-stage system is higher due mainly to the fact that maximum temperature occurs twice and in a longer period compared to single-stage method [16, 18].

To our best knowledge, the use and impact of IC, MC, and GW as amendment and bulking materials during the two-stage composting of OTBS has not been previously studied. Hence, the objective of this research was to determine how adding various amounts of IC, MC, and GW affect the removal rates of total petroleum hydrocarbons (TPH) during the two-stage composting of OTBS. The current two-stage composting method included a windrow mode as the primary stage composting (PSC) and in-vessel mode as the secondary stage composting (SSC).

Materials and methods

Preparation of MC, IC, GW, and OTBS

MC was purchased from a local market, passed through a 10-mm sieve, and stored under dried conditions until use. IC was prepared from a compost facility during the second week of the process because of its sufficient diversity and activity of microorganisms. All IC samples were passed a 1–2 cm pore size sieve to both remove impurities like plastic and glass and enhance homogeneity. GW was prepared from a mixture of wood chips, tree trimmings, leaves, and other similar constituents. Plastic containers were employed to sample OTBS from the oil refinery plant situated in Shazand, Iran. Next, the OTBS samples were milled to pass through a 2-mm sieve. All the samples of MC, IC, GW, and OTBS were kept at 4 °C for less than 48 h before starting the experiments.

PSC composting experiments

The PSC tests were performed in six non-covered windrow piles of approximately 2 m length, 1 m width and 1 m height (Fig. 1). The time period at this stage continued for 12 weeks. The piles were conducted with the 1:5 and 1:7 mixing ratios (dry weight) of OTBS to IC, MC, and GW (as amendments and bulking agents), as follows:

W_1: 1:5 mixing ratio of OTBS to IC
W_2: 1:5 mixing ratio of OTBS to MC
W_3: 1:5 mixing ratio of OTBS to GW
W_4: 1:7 mixing ratio of OTBS to IC
W_5: 1:7 mixing ratio of OTBS to MC
W_6: 1:7 mixing ratio of OTBS to GW

All these levels were examined to select the optimum ratio required for TPH degradation. Our previous works verified that the optimum C/N/P ratio for oily sludge composting was 100/5/1 [19–21]. For this reason, the initial C/N/P ratio
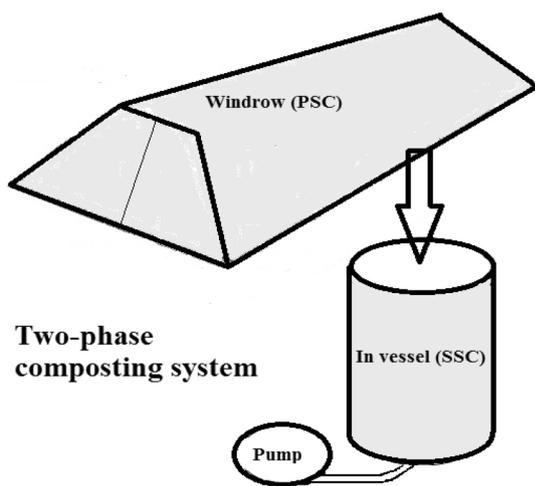
Fig. 1 The two-stage composting system used in the present study

of the current experiments was adjusted to 100/5/1 by adding NH_4Cl and KH_2PO_4. To reach maximum homogeneity and contact between existing microorganisms and petroleum hydrocarbons, the composting mixtures were thoroughly mixed. So as to provide sufficient aeration, all the piles were manually mixed every 5 days for 30 min.

SSC composting experiments

Six 3-L cylindrical bioreactors were operated for 6 weeks (Fig. 1). Two kilogram of composting materials obtained from PSC (at the end of week 6) was used to fill each bioreactor. The treatments W_4, W_5, and W_6 with the highest TPH removal were moved to the SSC experiments under in-vessel condition. The contents of these experiments were remixed with IC, MC, and GW, as follows:

I_1: 1:7 mixing ratio of OTBS to IC
I_2: 1:7 mixing ratio of OTBS to MC
I_3: 1:7 mixing ratio of OTBS to GW
I_4: 1:7 mixing ratio of OTBS to IC + MC
I_5: 1:7 mixing ratio of OTBS to IC + GW
I_6: 1:7 mixing ratio of OTBS to MC + GW

The C/N/P ratios of all the experiments were again readjusted to 100/5/1. Oil-free diaphragm pumps (HAILEA Model ACO 5505) were used to maintain aerobic conditions in the composting mixtures at the rate of $1 \, min^{-1} \, kg^{-1}$ [22]. The volatilized compounds generated during the process were also vented outdoors. The initial moisture contents of the composting mixtures (both the PSC and SSC) were adjusted in the range of 50–60% (w/w) by adding water. The moisture content was also measured and maintained continually to verify that it was inside the desired amount over the whole duration of the process.

Chemical analyses

The contents of TPH, nitrogen (N), phosphors (P), and organic carbon (OC) were detected biweekly. The samples were gathered from the top, middle, and bottom of PSC and SSC; next, the three samples were completely mixed to prepare a mixture [23]. The loss-on-ignition method was applied for detection of the samples' OC concentration [23]. TPH, N, P, and OC were calculated on a dry matter basis. The samples' moisture content was detected after oven drying at 105 °C [24]. All pH values were determined using a digital pH meter (HACH CO) after preparing the sample slurry according to TMECC [23]. P and N were measured based on APHA [24]. A portable thermometer with a probe 8×1000 mm was utilized to record daily temperature of all experiments and ambient throughout the composting time. All tests were done in duplicate.

Isolation and characterization of bacteria

All bacterial strains in this study were determined through the selective media and methods explained in the references [25, 26]. Confirmation of the extracted isolates detected phenotypically was carried out via the PCR assay. In addition, the reaction was performed using Bio-Rad Thermal Cycler. So as to amplify the 16S rRNA gene, the universal bacterial primer 27F was utilized. PCR mix contained 1 μL (10 pmol) of each primer, 2 μL template DNA, 25 μL PCR Master Mix in a final 50 μL reaction volume. A thermal cycler was utilized to amplify DNA, under the following conditions: initial denaturation at 94 °C for 5 min, followed by 30 cycles of denaturation at 94 °C for 45 s, an annealing temperature at 48 °C for 50 s, an extension at 68 °C for 1 min, followed by a final extension at 68 °C for 7 min. Electrophoresis of the amplified DNA fragments, with a 100 bp DNA ladder, was performed using 2% agarose gel in Tris–Borate–EDTA (TBE) buffer. One sample of each PCR product (amplicons) was sequenced by Bioneer Co., Korea mediated by Pishgam Co., Iran and the data were analyzed using the Chromas software and aligned with the ClustalW program. The sequences were compared to those present in the databank via blast and aligned with the ClustalW program (homology > 99%).

Gas chromatograph (GC) procedure

n-Pentane was used to extract TPH and GC (VARIAN Model CP-3800) was utilized for detection of its concentration, based on TNRCC [27]. This method can measure the concentration of petroleum hydrocarbons between nC_6 and nC_{35}. The extract was injected into a GC equipped with a flame ionization detector (FID) equipped with a 30 m capillary column (CP-Sil 8CB), 0.32 mm diameter, and 0.25-μm film thickness. The n-alkane markers nC_6

(n-Hexane) and nC_{35} (n-pentatriacontane) were used to establish the boiling point range boundaries. The initial temperature was kept at 35 °C (held for 2 min) and then was raised in the speed of 10 °C min^{-1} to achieve 300 °C and kept sustained for 5 min. The final temperature was adjusted at 325 °C (held for 5 min) to make sure that the column is clean. Forty-five minutes were spent for each test. The temperatures of injection port and detector were, respectively, 280 and 325 °C. Helium was used as a carrier gas (in the speed of 2.9 ml min^{-1}) for 30 min and then (at 6 ml min^{-1}) for the final 10 min of the run. The actual pressure and split ratio were 11 psi and 25%, respectively. The flow rates of hydrogen gas, air, and makeup for FID were 40, 450, and 30 ml min^{-1}, respectively.

Statistical analysis

Regression analysis of Microsoft Excel software was used to assess the relationship between the variables. SPSS 19.0 statistical software for Windows was also used for performing statistical analysis. To identify differences among treatments, a one-way analysis of variance (ANOVA) was used. The significance level was considered at 0.05.

Results and discussion

Characterization of IC, MC, GW, and OTBS

Table 1 shows the physicochemical characteristics of IC, MC, GW, and OTBS. Since OTBS was kept in an uncovered place, its moisture level was not high. The pH of IC, MC, GW, and OTBS were inside of the appropriate range essential for supporting microorganisms' growth. In addition, the N and P contents in the IC, MC, GW, and OTBS were low in comparison to the optimal levels required for composting. It was found that TPH concentrations in MC and IC were low which may be because of the presence of a few petroleum products in the compost feedstock.

Table 1 Physicochemical properties of IC, MC, GW, and OTBS used in the present study

Parameter	Unit	IC	MC	GW	OTBS
TPH	g kg^{-1}	1.09	0.17	0.00	131.72
OC	g kg^{-1}	289.92	205.21	533.38	412.58
N	g kg^{-1}	2.94	3.14	0.63	1.59
P	g kg^{-1}	2.58	2.74	0.42	1.11
Moisture content	%	49.10	35.2	22.40	12.38
pH	–	7.46	7.51	7.08	6.40

TPH removal in PSC and SSC

The trend of petroleum hydrocarbons degradation in the PSC experiments has been presented in Fig. 2a. The removal rates of TPH in the experiments W_1, W_2, W_3, W_4, W_5, and W_6 were 78.79, 67.82, 58.82, 84.50, 75.32, and 63.53%, respectively. The short-term lag period observed is due the fact that the microorganisms need time to adapt with the new carbon sources. Following this period, petroleum hydrocarbons were effectively consumed by the microbial populations. Accordingly, the content of TPH declined sharply over the first 6 weeks of composting. But, after week 6, a gradual degradation was seen in TPH concentration. The reason behind this is that the easily biodegradable components of TPH are decomposed first, resulting in a fast biodegradation and then less biodegradable materials, with an extremely lower bioremediation rate, remain in the system. Another reason is
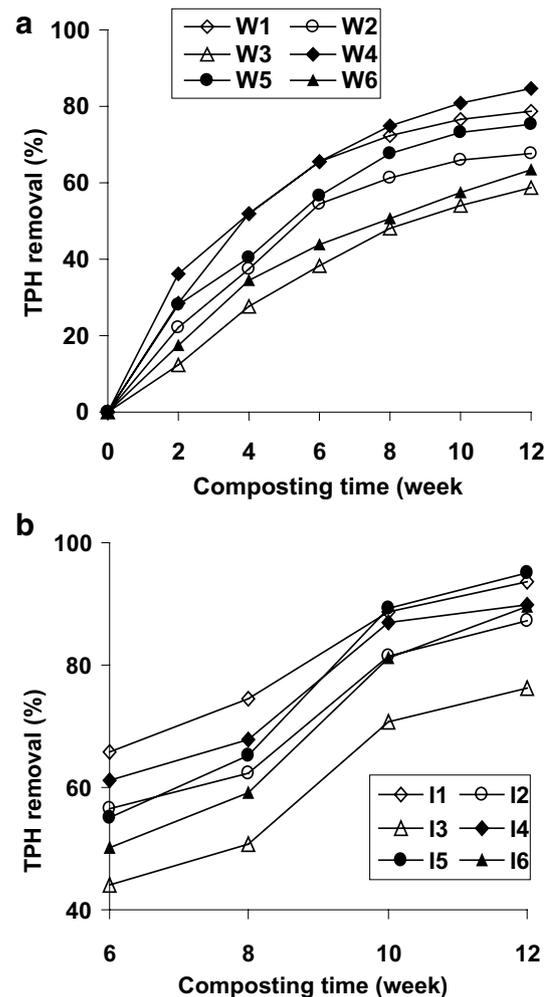

Fig. 2 Trend of TPH degradation over the PSC and SSC duration of the process

the low content of degradable OC and nutrients needed for the effective activity of microorganisms [28]. As an acceptable level of microorganisms' activities should be maintained over the whole composting time, a two-phase composting reactor was designed in the current work to enhance microbial activities for consuming residual petroleum hydrocarbons.

Figure 2b clearly shows that a similar pattern of TPH removal did not happen in SSC and PSC. Apparently, it was expected to see a longer lag phase in SSC because easily biodegradable substances were decomposed in PSC. The removal rates of TPH in the piles W_4, W_5, and W_6 were 65.67, 56.48, and 44.50%, respectively, over the first 6 weeks of the PSC, while only 18.83, 18.84, and 19.06% were, respectively, observed during the second 6 weeks. In contrast, over the SSC process (6 weeks), corresponding values for the experiment I_1, I_2, and I_3 were 81.77, 70.95, and 57.59%, respectively. Hence, TPH removal rates over the 6-week SSC were more than the rates in the second 6 weeks of PSC. Despite the fact that most biodegradable fractions of petroleum hydrocarbons were treated in PSC, TPH removal was improved via the readdition of MC, IC, and GW in the SSC. In the composting processes, if amendments are added, they can act as a source of biodegradable OC. As a result, microorganisms are biostimulated and hence they can actively degrade recalcitrant petroleum hydrocarbons [7]. As can be observed, the advanced system used in this study (6-week windrow plus 6-week in-vessel composting) had higher removal efficiency compared to single system (windrow process) in the same time. In accordance with our results, similar findings were reported in the studies in which a two-stage composting system was utilized [16, 29]. It is also important to note that only the residual TPH of the reactor I_5 (Table 2) was under 1 g kg^{-1}, which is appropriate for landfilling. This observation justifies the application of the advanced two-phase composting process for remediation of various environments contaminated with high levels of TPH.

Effect of IC, MC, and GW addition

In composting process, determination of the minimum amount of the mixing ratio of petroleum sludge to amendment and bulking materials is of primary importance because it affects the economy of the process. Furthermore, when the mixing ratio is adjusted to the optimum level, microbial growth and activities and in turn, TPH removal efficacy increases. Figure 2 illustrates that the removal rates of TPH in the experiments containing the mixing ratio of 1:7 were higher than those with the ratio of 1:5. Thus, the mixing ratio of OTBS to the amendments and bulking agents is an effective factor in bioremediation of TPH via composting. These findings accord with our previous works illustrating that the performance of composting processes relies greatly on the amount of introduced organic amendments [30, 31].

Due to the application of various types of organic amendments and bulking agents in oily sludge composting, different removal rates of target contaminants have been obtained. The organic matters used as amendment can adjust C/N ratio and carbon availability during the process so as to increase the rate of degradation. The presence of an easily decomposable carbon source is necessary to initiate and maintain the activity of microorganisms. Furthermore, the addition of organic amendments accelerates the succession of microbial communities and supports microbial diversity. This will increase the microbial decomposition of petroleum hydrocarbons and also result in the increased generation of heat and in turn, more extensive and more rapid degradation. These organic matters can also provide nutrients and prevent their volatilization and leaching during the process [16, 28]. In the present study, IC, MC, and GW were applied to enhance the biodegradation efficiency of TPH. The results showed that there were significant differences ($P < 0.05$) in TPH biodegradation for the various experiments. The IC- and MC-amended treatments had the higher removal rates of TPH compared to the GW ones. As IC and MC appear to have more microbial population and diversity than GW, higher contaminant biodegradations are obtained through their application. Hence, the mere application of GW as an additive was found to be inefficient

Table 2 Residual TPH in the PSC and SSC experiments over the composting period

Composting duration (week)	Residual TPH (g kg^{-1})											
	W_1	W_2	W_3	W_4	W_5	W_6	I_1	I_2	I_3	I_4	I_5	I_6
0	22.86	22.10	21.95	17.42	16.61	16.47	–	–	–	–	–	–
2	16.34	17.24	19.20	11.12	11.95	13.59	–	–	–	–	–	–
4	11.00	13.84	15.87	8.40	9.87	10.77	–	–	–	–	–	–
6	7.85	10.10	13.54	5.98	7.23	9.22	5.98	7.23	9.22	6.61	7.6	8.23
8	6.30	8.54	11.44	4.41	5.36	8.14	4.45	6.25	8.11	5.47	5.9	6.77
10	5.35	7.54	10.11	3.30	4.45	7.02	1.95	3.08	4.84	2.20	1.84	3.12
12	4.85	7.11	9.04	2.70	4.10	6.00	1.09	2.10	3.91	1.74	0.84	1.71

in removal of petroleum hydrocarbons. Other studies have also reported that the amendment materials exhibited various removal rates of contaminants, due to the fact that they contain different amounts of OC, nutrients, and microorganisms [32, 33].

In contrast, the composting reactors I_5 (IC + GW) and I_6 (MC + GW) were found to be more efficient than another combination (IC + MC). This indicates that the combination of IC and MC with GW had a positive effect on the degradation rates of TPH. GW and other similar materials can increase the water-retaining capacity of the composting mixtures, which would promote the microorganism's growth. Furthermore, addition of bulking agents facilitates oxygen diffusion through the composting mixture and hence increases the aerobic biodegradation of petroleum hydrocarbons [14]. Due to the benefits of IC + GW and MC + GW addition, these combinations can be a feasible and practical way to improve the efficiency of a two-stage composting system in TPH removal.

Microbial populations and kinetics

It is imperative that microbial community be identified because of its underlying impact on bioremediation of petroleum products. *Bacillus* sp., *Pseudomonas* sp., *Staphylococcus* sp., and *Klebsiella* sp. were the main petroleum-degrading bacteria identified in the present study. Analysis of microbial kinetics should also be established to investigate the biodegradation rate of TPH in the composting process [28, 32]. The first- and second-order kinetic models (Eqs. 1–4) were applied using linear data plots of ln C_0/C_t and $1/C_t$ versus time (t), respectively.

For the first-order reactions:

$$\ln \left(C_t/C_0 \right) = -k_1 t, \tag{1}$$

$$t_{1/2} = \ln 2/k_1 = 0.693/k_1. \tag{2}$$

For the second-order reactions:

$$1/C_t = k_2 t + \left(1/C_0 \right), \tag{3}$$

$$t_{1/2} = 1/k_2 C_0, \tag{4}$$

where C_0 and C_t are the TPH concentrations (g kg^{-1}) at times zero and t, k_1 (day^{-1}) and k_2 (g kg^{-1}day^{-1}) are the kinetic constants of petroleum compounds degradation for the first-and second-order kinetics, respectively. $t_{1/2}$ or half-life time represents the time (day) needed for consuming half of the initial contents of petroleum compounds.

Table 3 summarizes the R values for both the first- and second-order reactions. Based on the values, the kinetics of TPH degradation in the experiments W_4, I_1, I_2, I_3, and I_6 were fitted to the first-order model. Therefore, the rate of TPH degradation in these treatments is proportional to its concentration. On the other hand, petroleum biodegradation in the experiments W_1, W_2, and I_5 were fitted to the second-order reaction. Other studies also expressed that the kinetic of petroleum hydrocarbons biodegradation fitted to the first- and second-order models [28, 32]. The half-lives for the first- and second-order kinetics were in the range of 1.78–9.12 and 0.75–7.59 day, respectively. The corresponding values of the rate constants were also calculated to be 0.076–0.389 day^{-1} and 0.006–0.176 g kg^{-1} day^{-1}, respectively. The first-order rate constants reported by Gomez and Sartaj [10] (in the range of 0.004–0.043 day^{-1}) are lower than the values obtained in the present study. The reason of difference between the values of rate constant is the fact that it is dependent upon some variables like the method of bioremediation, the nature of target contaminants, and the type of amendments and bulking agents applied [34, 35]. The rate constants of TPH degradation in the SSC reactors were more than PSC. Thus, TPH biodegradation in the SSC experiments is more efficient compared to those in the PSC.

Table 3 Kinetic analyses of TPH biodegradation in the PC and SC experiments

Experiments	First-order model			Second-order model		
	Rate constant, k_1 (day^{-1})	Half-life, $t_{1/2}$ (day)	R^2	Rate constant, k_2 (g kg^{-1}day^{-1})	Half-life, $t_{1/2}$ (day)	R^2
W_1	0.133	5.21	0.959	0.015	2.92	0.993
W_2	0.099	7.00	0.962	0.009	5.03	0.985
W_3	0.076	9.12	0.994	0.006	7.59	0.994
W_4	0.155	4.47	0.992	0.026	2.21	0.971
W_5	0.121	5.73	0.981	0.016	3.76	0.982
W_6	0.083	8.35	0.991	0.009	6.75	0.993
I_1	0.297	2.33	0.972	0.127	1.32	0.913
I_2	0.221	3.14	0.948	0.059	2.34	0.928
I_3	0.155	4.47	0.949	0.026	4.17	0.944
I_4	0.246	2.82	0.925	0.077	1.97	0.925
I_5	0.389	1.78	0.952	0.176	0.75	0.872
I_6	0.274	2.53	0.956	0.078	1.56	0.899

Relationship of TPH degradation with temperature elevation and OC consumption

The regression analysis (Fig. 3a) showed that TPH removal and temperature enhancement correlated linearly. Elevation of temperature is due to the biological degradation of available substances releasing heat. As a result, the rate of TPH degradation increases because of an improvement in enzyme kinetics stemming from this increase in temperature [14, 35]. Moreover, the bioremediation of TPH and consumption of OC in both PSC and SSC treatments correlated linearly (Fig. 3b, c). This relationship is also verified by the similar patterns of OC and TPH decrease during the process time (Fig. 4a, b). When the organic materials added as amendments or bulking materials are preferred over the target contaminant, the biodegradation process could be retarded or even inhibited. Therefore, the additives should not be applied at a level in which they are preferred as the sole source of carbon and energy [7, 16]. As can be seen from Fig. 4c, d, the rise of the OC/TPH ratio is accompanied with the higher degradation rate of TPH compared to OC consumption. Therefore, the IC, MC and GW utilized in the current work not only did not act as a competing carbon source, but also it improved the degradation efficiency of TPH. In the case of large-scale composting facilities, these correlation models can be employed to project TPH degradation.

Changes in temperature

We recorded temperature daily over the whole composting time because it highly influences the performance of composting process. As presented in Fig. 5a, temperature changes in all the PSC experiments followed a similar pattern. The temperature of the treatments W_1, W_4, and W_5 increased rapidly and peaked on days 25, 20, and 24, respectively. On the other hand, in the experiments W_2, W_3, and W_6, the temperature moderately reached the zenith on days 27, 33, and 28, respectively. The mean temperatures in the bioreactors W_1, W_2, W_3, W_4, W_5, and W_6 were 37.54, 36.03, 32.60, 39.88, 38.54, and 34.86 °C, respectively. The corresponding values of maximum temperature were 40.5, 39.5, 35.5, 42.5, 41.5, and 37.5 °C, respectively. Owing to the enhancement of microbial activity, temperature goes up over the composting time [36]. The positive effect of temperature elevation is the higher bioavailability of petroleum hydrocarbons which are less soluble at lower temperatures. Furthermore, toxic and biorefractory molecules are degraded by thermophilic microorganisms to generate easier products and provide additional substrates for other microorganisms [37, 38]. Accordingly, the temperatures in the mixing ratio of 1:5 containing higher amounts of petroleum hydrocarbons were lower than those in the mixing ratio of 1:7 because heat generation is closely linked to the consumption of
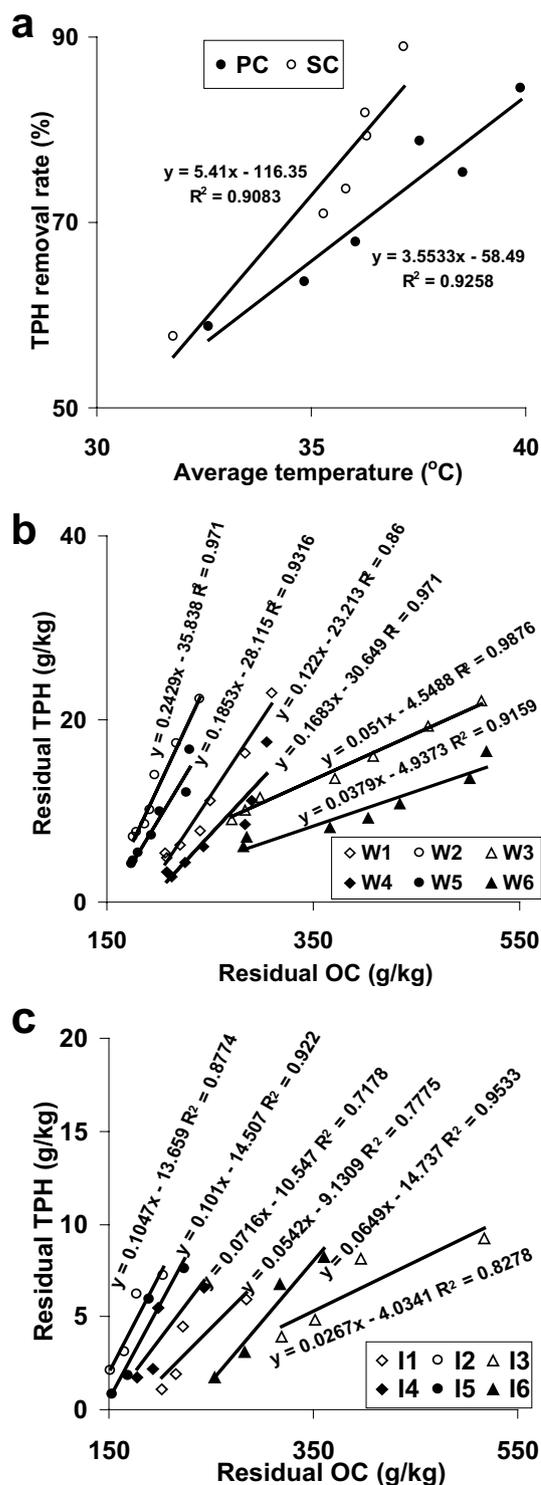
Fig. 3 Relationship of TPH degradation with OC consumption and temperature elevation in the composting experiments

easily biodegradable carbon sources. The mean raise rate of temperature for the runs W_1, W_2, W_3, W_4, W_5, and W_6 were, respectively, 0.48, 0.40, 0.20, 0.71, 0.52, and 0.31 °C day^{-1}. Since transformation rate of petroleum combinations

Fig. 4 Trend of OC and OC/TPH changes over the PSC and SSC duration of the process
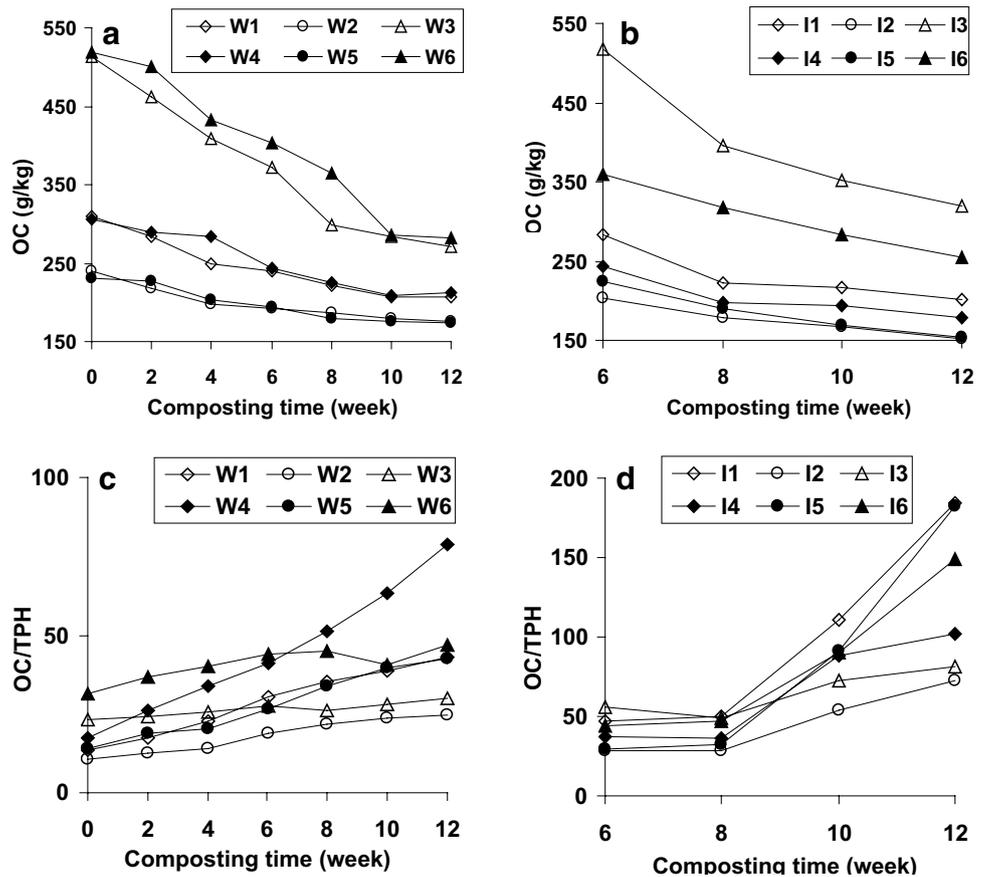
highly influences the rate of temperature rise, the increase rates were higher in the experiments W_1, W_4, and W_5 with the higher efficiency of TPH removal. Other studies also reported that the amount of readily biodegradable carbons is a factor affecting maximum temperature over the composting process [14, 35]. From the maximum point onwards, due to the reduction of microbial activities, the temperatures slowly diminished (at the rate of 0.12–0.17 °C day^{-1}) to get to the ambient air temperature.

Figure 5b indicates temperature fluctuations in the SSC experiments over the whole composting time. As shown, the temperature of the reactors I_1, I_2, I_3, I_4, I_5, and I_6 peaked at 42.5, 41.5, 36.5, 42, 43.5, and 42.5 °C, respectively, on days 54, 57, 60, 55, 54, and 57. Moreover, the average temperatures of these reactors were 36.28, 35.29, 31.78, 35.81, 37.16, and 36.29 °C, respectively. Due to the increase of microbial metabolic activities in the SSC reactors, higher temperatures were obtained compared to the PSC experiments. The increase rate of temperature in the experiments I_1, I_2, I_3, I_4, I_5, and I_6 were calculated to be 0.29, 0.23, 0.25, 0.27, 0.38, and 0.23 °C day^{-1}, respectively. These values were lower than those in the PSC experiments due mainly to the fact that the main parts of the remaining petroleum products in the SSC reactors were recalcitrant. After the peak point, temperature rapidly fell (at the rate of 0.61–0.80 °C

day^{-1}) stemming from declined TPH degradation. Since the volume of the SSC reactors was small, their temperature was highly influenced by the average temperature of ambient air (30.06 °C), in particular, over the final days of composting period. In addition, when small volume of a moist mixture is aerated, temperature begins to decline rapidly. Hence, the decrease rates of temperature in the SSC reactors were higher than those in the PSC piles.

Changes in pH

pH is found to be one of the crucial factors affecting microbial populations involved in petroleum hydrocarbons biodegradation. Figure 6 shows changes in pH values during the composting time. After starting the process, the pH of all the experiments declined and then gradually increased to stay at a relatively stable level. The decline of pH values is because of organic acids generated during the petroleum hydrocarbon decomposition. On the other hand, the increase of pH generally results from the microbial decomposition of organic acids and subsequently the release of ammonium [28]. The lowest pH values in the experiments W_1, W_2, W_3, W_4, W_5, W_6, I_1, I_2, I_3, I_4, I_5, and I_6 were 6.98, 7.04, 6.75, 6.84, 6.95, 6.65, 7.01, 7.07, 6.50, 6.99, 6.52, and 6.87, respectively. The higher pH decrease observed in the experiments W_1, W_4,

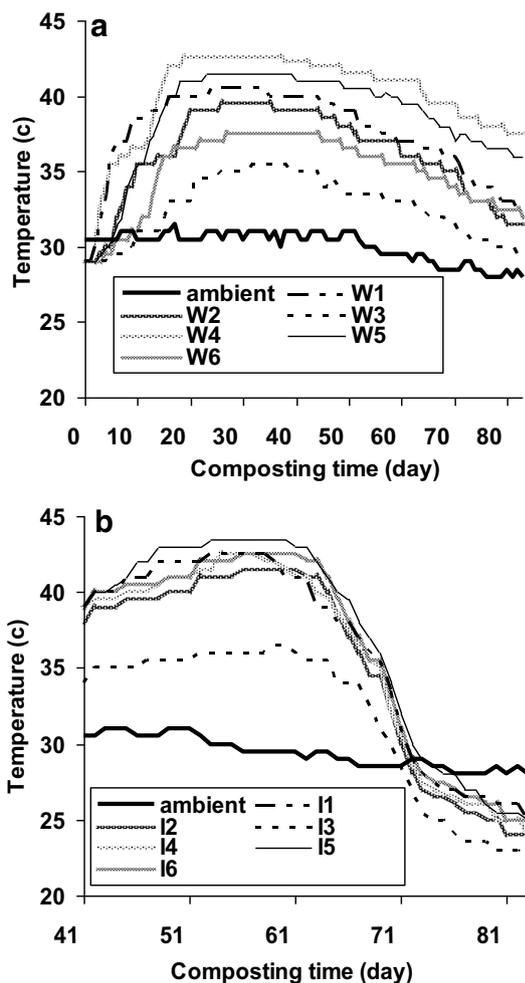**Fig. 5** Trend of temperature changes over the PSC and SSC duration of the process

Fig. 6 Trend of pH change over the PSC and SSC duration of the process

W_5, I_1, I_5, and I_6 were because of their higher rates of TPH biodegradation. During the composting process, a pH range of 6.5–8.5 would support biological removal of petroleum compounds by microorganisms. Zhang and Sun [16] stated that petroleum-degrading microorganisms have the highest activity and performance at neutral pH values. It should be noted that all the pH values measured over the process was within the optimum range.

Changes of nutrients

Changes of N and P in the PSC and SSC experiments have been shown in Fig. 7. Like other microorganisms, petroleum-degrading bacteria existing in composting process need enough amounts of N and P to grow and be influential in bioremediation. Hence, it is entirely natural to observe a change in the levels of these nutrients over composting. Howe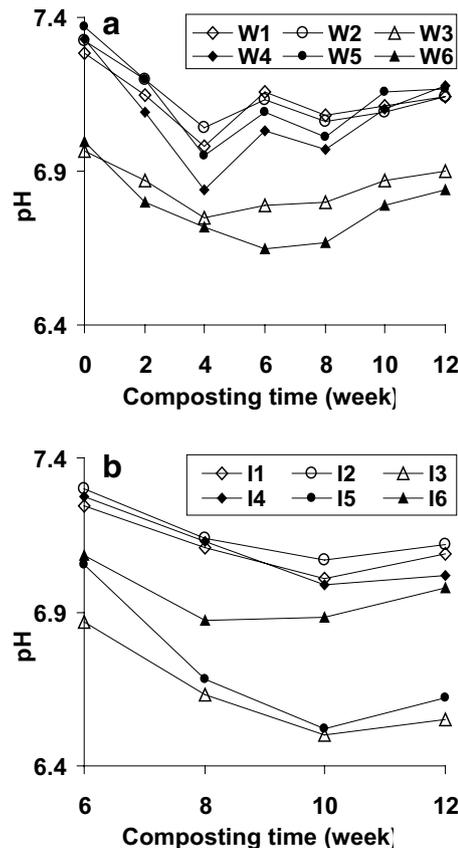ver, the major cause of this decline is attributed to the fact that they leached out from the composting mixtures. Moreover, at high levels of temperature and pH, nitrogen is lost from the system through NH_3 volatilization [16, 39].

Conclusions

In this research, the oily sludge comprised of a great deal of petroleum substances was bioremediated through an advanced two-phase composting method. Pollutants were well treated by means of indigenous degrading-hydrocarbon microorganisms present in the system. To attain the effective performance of the process, it is necessary to add adequate amounts of amendments and bulking agents. The addition of combined amendments and bulking materials gave better results than they were used alone. It was found that the two-stage composting system is practically applicable for bioremediation of different kinds of oily sludge such as OTBS.

Fig. 7 Trend of N and P changes over the PSC and SSC duration of the process
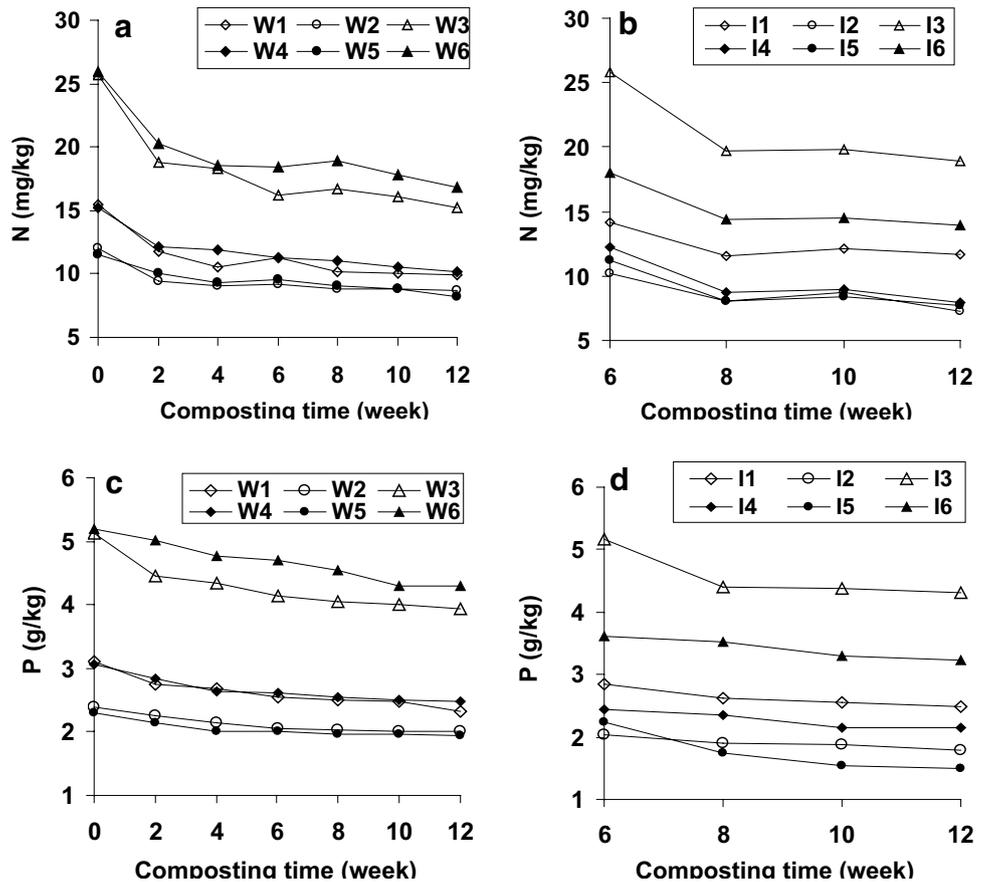
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