ORIGINAL RESEARCH PAPER

Remediation of total petroleum hydrocarbons using combined in-vessel composting and oxidation by activated persulfate

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ABSTRACT: This study was investigated the efficiency of activated persulfate and in-vessel composting for removal of total petroleum hydrocarbons. Remediation by activated persulfate with ferrous sulfate as pre-treatment was done at batch system. In the chemical oxidation, various variables including persulfate concentrations (10-3000 mg/g as waste), pH (3-7), ferrous sulfate (0.5-4 mg/g as waste) and temperature (20-60°C) were studied. In the biological system, premature compost was added as an amendment. The filter cake to compost ratio were 1:0 (as control) and 1:5 to 15 (as dry basis). C: N: P ratio and moisture content were 100:5:1 and 45-60%, respectively. The results showed that acidic pH (pH=3) had high efficiency for the removal of total petroleum hydrocarbons by activated persulfate. Temperature had the significant effect during the persulfate oxidation. When ferrous sulfate was used as an activator for degradation at acidic condition and 60°C, removal efficiency increased to 47.32%. The results of biological process showed that the minimum total petroleum hydrocarbons removal in all reactors was 62 percent. The maximum and minimum removal efficiency was obtained at 1:5 (69.46%) and 1:10 (62.42%) mixing ratios, respectively. Kinetic study showed that second order kinetic model ($R^2 > 0.81$) shows the best agreement with the experimental data and the rate of TPH degradation at low mixing ratio (1:3) was faster than high mixing ratio (1:15). Therefore, according to the results, in-vessel composting after pre-treatment by activated persulfate is suggested as an efficient process for degradation of total petroleum hydrocarbons.

KEYWORDS: *Activated persulfate (APS); Biodegradation; C:N:P ratio; In-vessel composting (IVC); Persulfate oxidation; Total petroleum hydrocarbons (TPH).*

INTRODUCTION

According to studies, less than 10% of engine oils is additive materials and 90% oil. One of the main use of this lubricant is gas and diesel engines (Thavasigamani, 2008). Oil usually degrades and ruins its original quality during the vehicles working and therefore should be replaced (Caetano *et al.*, 2017). Used oil management is done with collecting from production center and conceded to the bigger installations which called off re-refineries. Because of mismanagement and lack of supervisor and authority for control of used oils, these wastes have a negative effects on the environment and human bodies (El-Fadel and Khoury, 2001). Final product of facilities is hydraulic and flux oil, lubricants, engine oils and some wastes like acidic sludge and filter cake. Many

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technologies have been taken for recycling of these wastes that include high concentration of hazardous materials (Guerin, 2008). In Iran, acid-clay treatment is the conventional method which have been employed in re-refinery industry since 40-year age. This method is used to treat more than 950000 tons per year of wastes. However, 15-25% acidic sludge and filter cake are produced during this process (Jafari *et al*., 2016). Total petroleum hydrocarbon (TPH) and some pollutants like metals are the main component of these waste which its concentration is high (Sood *et al*., 2010; Nouri *et al.,* 2013; Hoseini *et al*., 2015; Pazoki and Hasanidarabadi, 2017), but there is no standard limitation in Iran about the TPH concentration. TPH obtained from filter cake of re-refinery industries consists of non-hydrocarbon matters such as phenol, organic acids, ketone alkane, pyridine and aromatic hydrocarbons (Wu *et al*., 2016a, Mazloomi *et al*., 2016). Biochemical degradation of lower-range hydrocarbons which generates at petroleum industry such as diesel and fuel oil are more difficult than higher range petroleum hydrocarbons due to lower pH, mobility, volatility, biodegradability and high viscosity (Oh and Shin, 2014). Accidental or intentional releases of this type of hazardous waste from equipment and facilities (such as storage and tanks pipelines) into water and soil environments are caused negative effects for human bodies and environments (Hu *et al*., 2013). Chemical oxidation at site method is a technology that applied for mineralization and degradation of pollutants contain high organic compounds has been largely applied for the decomposition of TPH from polluted environments (Abdel-Ghani *et al.,* 2016, Karbassi *et al.,* 2015, Sivakumar 2015, Baciocchi, 2013, Wu *et al*., 2016a). Some physical and chemical processes have been used for the removal of organic materials (Bazrafshan *et al*., 2012, Mahvi *et al*., 2010). Sodium persulfate ($Na_2S_2O_8$) and other oxidants have been widely used as a strong agent (E_0= 2.01V) and very water-soluble (560 g/L) oxidant and the persulfate ion ($S_2O_8^{2-}$) is a very strong oxidant when converted to $SO_4^{·-}$ (E_0 = 2.4V) and ·OH (E_0 = 2.8V) by activation with UV light, bases, heat, H_2O_2, promoting acidic pH, ZVI, hydroxide or transition metal ions (Me^{n+}) such as Fe^{2+}, Cu^{2+}, and Co^{2+} (Mazloomi *et al*., 2016, Pardo *et a*l., 2015, Wu *et al*., 2016a). pH is the most important factor for the type of radical so that in the basic conditions hydroxyl radicals are predominant while under acidic conditions sulfate radicals are more dominant (Karbassi and Heidari, 2015; Liang *et al*.,

2008). Biological treatment processes like composting have been recommended as a low cost, efficient and environmental friendly method for biodegrading of some wastes in the last years (Sarkar *et al*., 2005). In-vessel composting (IVC) has been widely used for degradation of hydrocarbon and co-composting of acidic and sludge oil. Environmental parameters like oxygen demand, ambient air temperature, nutrients, pH, moisture amount and mixing ratio could be easily controlled during the in-vessel technology (Koolivand *et al*., 2013b). Therefore, present survey was done to evaluate the combination of persulfate and compost process to remediation of high concentrations of TPH. For this reason, first a pre-treatment stage using APS was performed with iron and then IVC process in several different ratios were used for finally purification of TPH. This study has been carried out in Alborze Province of Iran in 2016.

MATERIALS AND METHODS
Sampling

The samples of filter cake have been taken from Eshtehard (Alborz Province) industrial city (re-refinery units). The immature compost samples were also obtained from aeration unit of Tehran composting plant. The samples were picked up from the first week composts and different depths (3 points). All samples were thoroughly agitated together to achieve the unify samples and additional materials like glass, sand and plastic were taken apart from mixed samples. All mixed samples were passed through 2 cm mesh and finally agitated to amendment (dry manure (5% w/w)) to provide the microorganisms.

Reactor features

The experiments were done as a bench scale study. Glass vials (80mL) was used to perform the chemical section of the study. In this stage, 2g of filter cake samples was added to the vials. In addition, IVC was done in plastic containers (1000 mL). Oxygen demand for microorganism activities as provided by an oxygen supply system at the bottom of each container and some orifice was placed at the above of each container for discharging odors and air. In addition, each container was equipped to thermometer and water supply systems. Diaphragm pumps (Model ACO 5505, Hailea, Guangdong, China) was used for aeration of samples and distribution system was employed to provide the same amount of oxygen for

each container. It merits to mention that the rate of entrance air to containers was 20 mL/min.

Chemical conditions and procedures

Na$_2$S$_2$O$_8$ was used to provide the persulfate (PS) radicals and oxidation agent. The activation of PS was done with ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O). Sodium hydroxide (NaOH, 0.1N) and nitric acid (HNO$_3$, 0.1N) was employed for adjusting the initial pH (3, 5, and 7). The initial pH of filter cake was 4.21±0.08. The chemical oxidation with persulfate was done as a primary process at different initial PS concentrations (10–3000 mg/g as waste) and constant concentration of ferrous ions (2 mg/g as waste). In oxidation process, the solution of PS and Fe^{2+} (10 mL) was added into each vials which contain 2 g of filter cake. It was performed at 2 hours of reaction time and 150 rpm (New Brunswick Innova 4048; Eppendorf, New York, USA). Also, the activation of soluble persulfate and iron was carried out for one time at the initial time. The best Fe^{2+} concentration in this study was 0.5–4 mg/g as waste at optimum PS concentration (Mazloomi *et al*., 2016). The pH effect on the oxidation of TPH was performed at various initial pH (3-7) and natural pH of filter cake in the optimal PS/Fe^{2+} ratio. In addition, the temperature effect on the oxidation process was carried out with increasing temperature from 20 to 60 °C at the optimal PS/Fe^{2+} ratio and pH.

Biological conditions and procedures

Firstly, various ratios of the filter cake (pretreated by PS) to compost were provided (1:3, 1:5, 1:8, 1:10 and 1:15). Secondly, two reactors that consist of only compost materials (filter cake to compost was ratio 1:0) were considered as a control container. In addition, HgCl$_2$ (2%) was used as a biocide agent to determine the effect of other factors like volatilization on the TPH removal (Koolivand *et al*., 2013b) it should be noted that other reactor has no additive. Control containers were used to evaluate the degradation or removal of TPH via volatilization. Also, to prevent the toxic shock for microorganism, the total adaptation time (20 days) was considered. To ascertain the effectively of biological process on the TPH removal, the filter cake which was degraded with APS, was gradually increase to the all reactors at various four phases (each 5 days). The time of biological process was 70 days after adaptation period. The concentration of nitrogen

and phosphorus during the biological process after a period of adjustment was analyzed in each reactor. To adjust of nitrogen was used ammonium chloride as a source of nitrogen and potassium dihydrogen phosphate as a source of phosphorous. C: N: P ratio in all reactors was adjusted about 100:5:1. Duration of the composting process, the moisture content was 45 to 60%.

Analytical methods

All chemicals used in this study were analytical degree and purchased from Merck Company, Darmstadt, Germany. The solvent of *n*-hexane (CH$_3$(CH$_2$)$_4$CH$_3$) was used for extracting the TPH samples. Before the sampling, the reactor contents of IVC system were thoroughly agitated and sampling was obtained from various depths. For analyzing TPH, the sample was prepared with addition of 4 mL of n-hexane to 1g of dry sample. Subsequently, the mixture was agitated at 300 rpm for 1min. The concentration of TPH was determined by GC-FID (Model CP-3800, Varian, Belrose, Australia) (Koolivand *et al*., 2013b). Moisture content of the samples were measured with digital hygrometer (Model pH-Moisture Meter, China) and dried with oven (Model tactical 308, Gallenkamp, Loughborough, UK) at 105^{0}C for 24 h. The pH and temperature of samples were determined through pH meter (Model, Portable Meter, Germany) and mercury thermometers, respectively. In addition pH was directly detected through pH meter (Model pH Meter, Combi-Tester, TFA, Germany). For preparation of sample to determine the pH at the laboratory conditions, 1gr of dried filter cake and sample were solved in deionized water (5mL) and was mixed at 200 rpm for 1min and supernatant of the mixture was separated to detect the pH solution. Organic carbon was measured with in furnace equipment (Model Muffle Furance, England) through loss-on-ignition procedure. In order to preparation pf the samples, a certain amount of dried sample (1g) was heated at 600°C for 2 h. Method 4500-N$_{org}$ was used to analyze the total Kjeldahl nitrogen. To determine the total Kjeldahl nitrogen, first 1gr of dry sample was completely mixed with 250 to 300 mL of distilled water and 3 mL of 0.1 M sulfuric acid to hinder abscond the ammonia. Total Phosphorus was determined with addition of 1gr of dried sample to 50 mL of distilled water (4500-C, standard methods) (Apha, 2012). ICP device (Model ARCOS FHE12, Spectro, Kleve, Germany) was used for determination

of metal concentration using digestion method with nitric acid digestion. The amount of organic carbon, TPH, nitrogen and phosphorus were weekly determined and the reactor and ambient temperature were measured as daily. pH solution was measured during the reaction time and subsequently daily.

GC procedure

GC-FID with CP-Sil8CB column (length: 30m, diameter: 0.32mm and thickness: 0.25μm) was employed for determination of TPH. Carrier gas was helium and inlet pressure of helium was 11 Psi at a spilt ratio 25% and velocity of carrier gas at column was 2.9 mL/min. The temperature of oven was 35 ^{0}C isothermal for 3 min, 15°C/min until 300 $^{\circ}$C, then also isothermal for 5 min and final temperature of 310 $^{\circ}$C with a rate of 200°C/min for 3 min. The detector and injection port temperature were 325°C and 280°C, respectively. The flow rate of hydrogen, nitrogen and air at flame ionization detector (FID) were 40, 30 and 450 ml/min, respectively. C_6–C_{35} were measured in this study and total run time was 29 min.

Kinetic study

Kinetic study is considered as a practical factor for analyzing the decomposition of TPH in different processes. In this study, the most popular kinetic models (first and second order models) were investigated for degradation of TPH using in-vessel reactors (Agarry *et al*., 2015, Nwankwegu *et al*., 2016, Shirmardi *et al*., 2012). Kinetic study could be carried out to identify the residual concentration of pollutant as well as prediction of the process. In addition, the Eqs. 1 and 2 used to calculate the kinetic model were:

$$LnC_t=LnC_0-k_1t \qquad \text{for first order reaction and} \qquad (1)$$
$$1/C_t=k_2t+1/C_0 \qquad \text{for second order reaction} \qquad (2)$$

Where, k_1 and k_2 refer to first and second order constant and C_0 and C_t represent the initial and certain

time(t) of TPH concentration, respectively. The $t_{1/2}$ is defined as the required time for degrading half amount of pollutant at time t which calculated for first order and second orders reactions according to Eqs. 3 and 4.

$$t_{1/2}=Ln2/k_1 \qquad (3)$$
$$t_{1/2}=1/k_2C_0 \qquad (4)$$

Statistical methods

In this study, all chemical experiments were done at triplicate. Kruskal–Wallis test was employed to determine the interactions between independent variables (pH and temperature on TPH degradation). In addition, ANOVA test was applied to investigate the effect of the mixing ratios in 10 weeks of IVC. It should be mentioned that SPSS software (Version 24) was used for data analysis.

RESULTS AND DISCUSSION
Filter cake and immature compost characteristics

Table 1 shows the physiochemical properties of the immature compost and filter cake used in this study. According to the results, the most portions of filter cake (>50%) was TPH which represents the waste petroleum compounds is the main concern for the environment. It was found that TPH contents of oily sludge were 5% to 86.2% by mass (more frequently between 15% to 50%) (Jasmine and Mukherji, 2015, Asgari *et al*., 2017). In addition, the C: N ratio of filter cake and immature compost was 50.96:1 and 52.63:1, respectively. Also, C: P ratio was 375.67:1 and 114.55:1 for the filter cake and immature compost, respectively. High amount of C: N ratio for the immature compost indicates that nitrogen sources such as vegetables and plants are available in the municipal solid waste of Tehran.

Table 2 illustrates the concentration of various elements which exists in the filter cake. As seen in the Table 2, the concentration of different elements (Fe, Zn, Cu, Mn, Mo, Ba, B, and Al) in the filter cake

Table 1: Physicochemical properties of the filter cake and compost

Parameter	Unit	Filter cake	Immaturated compost
Organic carbon	g/kg	537.22	240.55
TKN	g/kg	10.54	4.57
TP	g/kg	1.43	2.10
pH	-	4.21	7.28
Moisture content	%	5.78	45.27
TPH	g/kg	504.16	ND*

ND: Not detectable

Table 2: Elemental analysis of the filter cake used in this study
(Units are expressed as mg/kg)

Element	Concentration	Element	Concentration
Fe	12308.70	As	20.72
Mn	2288.06	Cr	14.45
Ba	2269.25	Ag	10.61
Zn	1854.95	Be	6.57
Al	5188.34	Co	5.29
Cu	4880.21	V	5.17
B	3392.10	Hg	4.81
Mo	2318.32	Tl	4.01
Pb	128.49	Se	0.16
Li	83.64	Sb	0.06
Ni	38.51	Cd	0.01
Sn	22.24		

exceeds of 1000 mg/kg. Also, lead concentration was higher than 100 mg/kg. Ag, Cr, As, Sn, Ni and Li concentration were low (10 to 85 mg/kg) and Be, Co, V, Hg, Ti, Se, Sb and Cd had low concentration less than 10 mg/kg. It was due to the interaction between main source of oil and engine oil. High amount of metals in filter cake showed this type of waste are placed in hazardous waste. It was reported in the previous studies (Koolivand *et al*., 2013b, Asgari *et al*., 2017)

Pre-treatment

Due to high concentration of TPH (504.16±13.78 g/kg) minimum and maximum removal efficiency for 10 to 3000 mg (PS)/g (filter cake) were about 8.46 to 54.36 %, respectively. Based on the analysis of result the removal efficiency of TPH can be increased by increasing the persulfate dose (P<0.05), and the interaction between the concentration of 750 (47.84±3.86%) to 3000 mg/g (54.36±5.26%) was not significant. Then, concentration of 750 mg/g PS was considered as the optimal value for the next steps. The result of removal efficiency for determining the optimal concentration of Fe^{2+}(mg/g as waste) were as follows: 44.42±0.66%, 43.13±0.93%, 44.04±0.73%, 44.45±57% and 44.04±0.47% for 0.5, 1, 2, 3 and 4 mg/g Fe^{2+}, respectively. Then the best molar ratios of PS/Fe^{2+} about 250:1 was selected for next steps. However, non-parametric test results to determine the optimal concentration of iron as activators showed that the mean difference is equal (P=0.069). In fact, increasing the iron concentration had no effect on removal efficiency based on previous studies, the excess ferrous ions could be act in the role of scavenger for free radicals of the sulfate (Matzek and

Carter, 2016, Mazloomi *et al*., 2016). The pH effect on the TPH decomposition was investigated. The performance of PS/Fe^{2+} Systems was studied at various pH (3-7). Based on result, TPH removal was high at acidic condition (pH=3) which removal efficiency was 47.19±0.46%. It was found that sulfate radicals prevail at acidic condition (low pH) that removal efficiency of TPH was greater than high pH (Xie *et al*., 2012, Mazloomi *et a*l., 2016). Lower efficiency of TPH degradation at pH 7 (39.60±0.53%) might be due to the variation of metals speciation (Fe^{2+} to Fe^{3+}) or self-decomposition of oxidation agents (i.e. HSO_5^-) at low pH. However, non-parametric test results to determine the optimal pH showed that the mean difference is equal (P=0.07). The influence of initial pH (pH = 3), temperature (20-60°C) at the optimum PS: Fe^{2+} ratio (250: 1) on TPH removal was examined. Result showed that the increasing the temperature from 20(47.15±0.88%) to 60°C (49.97±0.52%) led to increasing TPH removal and this increase is significant (P=0.015). In addition, it was reported that oxidant consumption rate, redox potential (Eh), oxidative potential of PS and heat-activated PS increased at high temperature (Matzek and Carter, 2016, Mazloomi et al., 201). Also, generation of the sulfate radicals at pH: 2-7 were increased in heat-activated PS system (Olmez-Hanci *et al*., 2013). The remaining TPH after this step was about 238.50±10.02 g/kg. Therefore, the use of persulfate can be used as an oxidizer for initial reduction of high concentration of TPH.

Biodegradation of TPH during the composting reactors

Table 3 presents the TPH remain after adjustment period in each reactor (with different mixing ratios) after pre-treatment of TPH with APS at the optimum

PS: Fe^{2+} ratio (250: 1), pH=3 and T=60°C. According to the results, the highest and lowest concentration of TPH obtained at adaptation time and the filter cake to compost ratio of 1:3 and 1:15 were 79.50 and 15.90 g/kg, respectively. In addition, TPH removal after ten weeks was 40.40 and 12.29 g in the filter cake to compost ratio of 1:3 and 1:15, respectively. Also, the lowest removal efficiency of biodegradation after a period of 10 weeks was more than 62 percent in all reactors and the maximum removal efficiency compared to the initial amount was obtained at the initial three weeks that indicates a further degradation of the organic matters (especially saturated hydrocarbons) (Wang *et al*., 2011). Reducing in the biodegradation speed after this time could be related to increasing the fraction of non-biodegradable TPH (Koolivand *et al*., 2013b). Fig.1 shows the fluctuation of TPH removal during the composting process. The maximum and minimum TPH removal efficiency were obtained at mixing ratio

of 1:5 (69.46%) and 1:10 (62.42%).

According to the results, the effects of mixing ratio on the removal of organic compounds and TPH was significant. In addition, the analysis of one-way ANOVA represents that the effect of average removal efficiencies of TPH were significant (P<0.05). These results are similar to previous studies. According the previous study, TPH removal was more than 65% (Koolivand *et al*., 2013b, Koolivand *et al*., 2013a). However, according to the results, the mixing ratios of more than 1:8 needed further compost to decrease the contamination and in the mixing ratio of less than 1:8 the removal efficiency also were not considerable augmented. While, it was previous stated that with increasing organic amendment led to reduce the removal efficiency of TPH (Asgari *et al*., 2017).

Trend of organic carbon (OC) consumption
Fig. 2 shows the alteration of OC parameter in

Table 3: TPH removal efficiency during IVC period

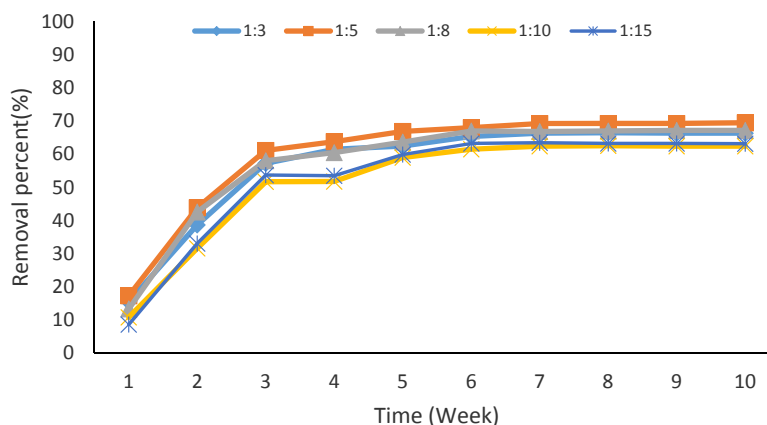| Time(week)	Residual TPH (g/kg)				
	1:3 ratio	1:5 ratio	1:8 ratio	1:10 ratio	1:15 ratio
Adjustment period	79.50	47.60	29.75	23.80	15.90
0	67.18	39.36	25.79	21.23	14.53
2	48.77	26.75	17.09	16.28	10.65
3	34.00	18.50	12.49	11.50	7.36
4	30.65	17.25	11.76	11.48	7.40
5	29.86	15.77	10.82	9.77	6.38
6	27.56	15.24	9.82	9.17	5.84
7	26.76	14.62	9.87	8.94	5.82
8	26.67	14.62	9.82	8.92	5.84
9	26.76	14.62	9.77	8.94	5.84
10	26.78	14.54	9.77	8.94	5.86

Fig. 1:Trend of the TPH removal during IVC period

all reactors studied in this study during the reaction. Decreasing the organic carbon in all reactors more likely was due to biological degradation (Wu *et al.*, 2017b). As seen in the Figs. 1 and 2, alteration of TPH in the reactors was similar to OC. It should be considered that OC supply as an amendment in the reactors must not be consumed as carbon source to provide energy. Based on the results OC: TPH ratio showed that the carbon consumption was carried out slower than TPH removal (Fig. 3).

The effect of monitoring factors

The profiles of monitoring factors (temperature and pH) during the composting for degradation of TPH from Filter cake (at 10 weeks) are shown in Figs. 4 and 5. According to the results, the reactor temperature were always higher than the ambient temperature during the initial 42 days (week 6). It could be predicate that the activity of microorganisms during the composting

process and degradation of TPH can lead to increasing the reactor temperature. In addition, reducing the amount of biodegradable materials after 6 weeks could result in decreasing the reactor temperature (An *et al.*, 2012, Asgari *et al.*, 2017). It should be mentioned that small reactors used in this study also led to high temperatures. The maximum and minimum temperatures in the composting reactors during the experiments were 28°C and 23°C in comparison with ambient air that were 26.5°C and 23°C. As Figs. 1 and 4 show, when the reactor temperature was lower than the ambient temperature, the removal efficiency of TPH was very slow. It was reported that the reactor temperature should be considered as an effective factor for degradation of TPH (Koolivand *et al.*, 2013b). In addition, another environmental factor that influence on the biodegradation rate and microorganism bacteria is pH. According to the Fig. 5, at initial stages of the process, pH fluctuated between 6.6 to 7 and
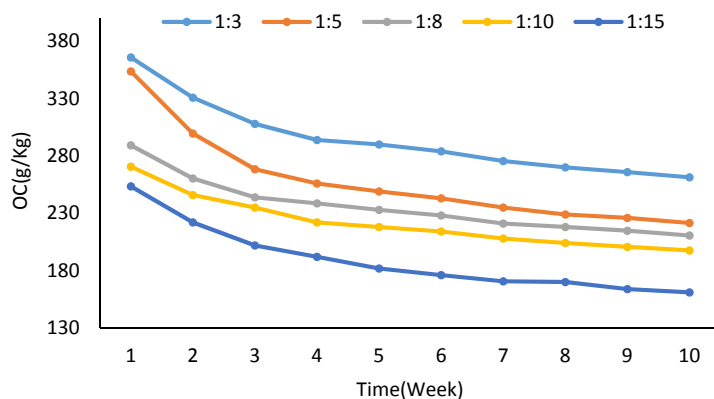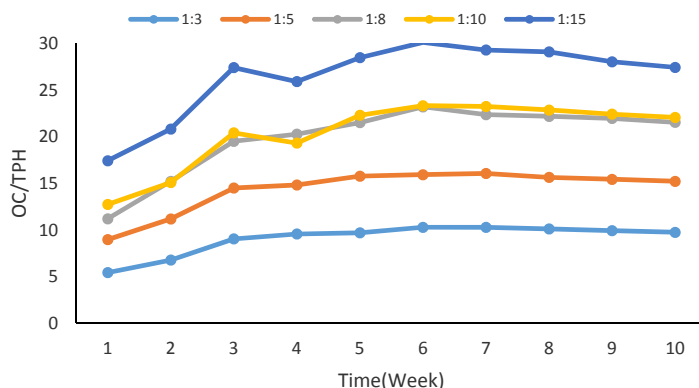

Fig. 2: Trend of OC consumption during IVC period

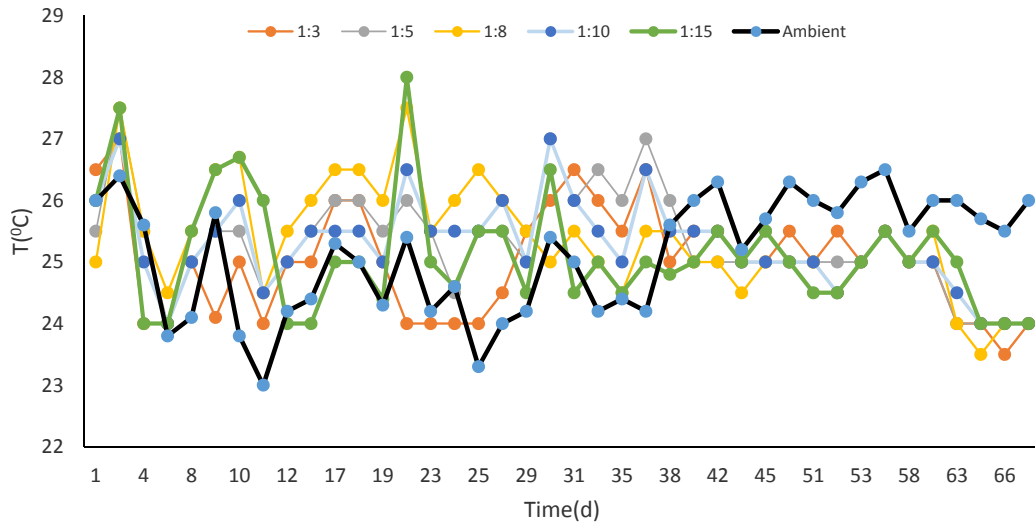Fig. 3: Trend of OC: TPH changes during IVC period

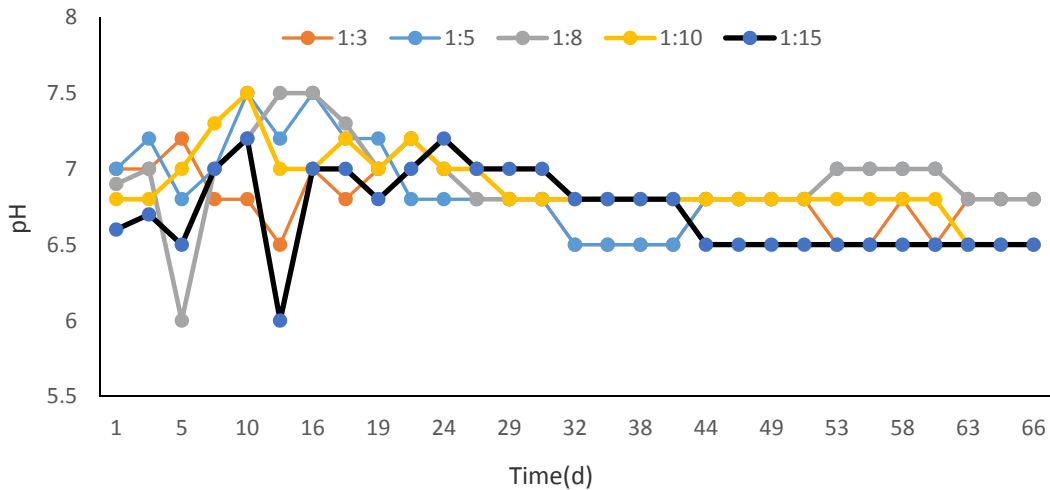Fig. 4: Temperature profile during IVC for removing TPH

Fig. 5: pH profile during IVC for removing TPH

subsequently reduce to 6 at 1th and 2th week. It should be due to organic acids and carbon dioxide production during the microorganism activities and biodegradation process (An *et al*., 2012). Final pH was in the range of 6.5 to 6.8 after four weeks (Fig. 5).

Study of other factors in biodegradation process

The biodegradation rate of TPH during the composting process depends on the amount of carbon, nitrogen and phosphorous in the raw material. Also, number of bacteria population which decompose

the biodegradable materials via the composting process can be affected by the amount of nutrient elements (carbon, phosphorus and nitrogen). Fig.6 represents the variation trend of TKN, TP, C: N and C: P during the biodegradation of TPH at composting process. According to the results, N and P contents in all reactors decreased during the composting and the trend of decreasing was in the similar way. The consumption of nutrient materials (N and P) were reduced during the composting, as the rate of nitrogen and phosphorous consumption and TPH degradation
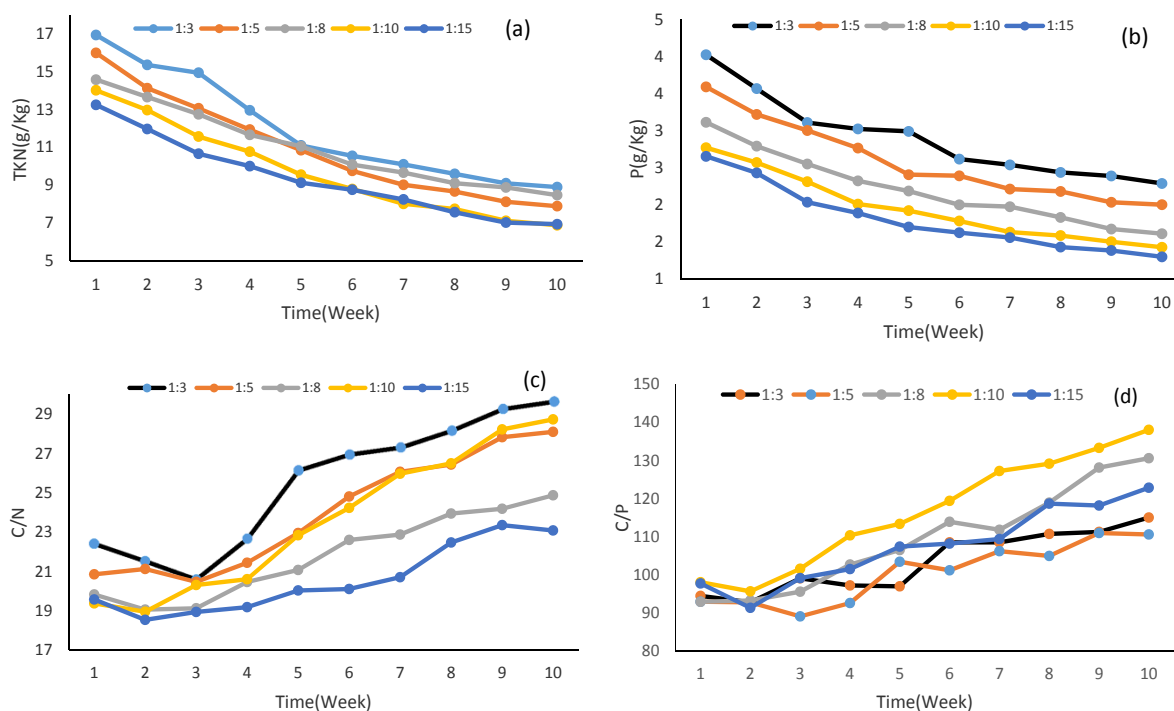
Fig. 6: Trend of (a) the TKN, (b) TP, (c) C: N and (d) C:P changes during the IVC process

Fig. 5: pH profile during IVC for removing TPH

Mixing ratio	First order rate constant, k_1(1/d)	Half-life, $t_{1/2}$(d)	R^2	Second order rate constant, k_2(g/mg.d)	Half-life, $t_{1/2}$(d)	R^2
1:3	0.0455	15.23	0.7556	0.0026	4.84	0.8167
1:5	0.0486	14.26	0.7444	0.0049	4.29	0.8138
1:8	0.0464	14.94	0.7529	0.0072	4.67	0.8202
1:10	0.0430	16.12	0.7979	0.0076	5.53	0.8492
1:15	0.0440	15.75	0.7760	0.0117	5.38	0.8268

in the initial process was faster than final stages. Therefore, it can be implied that the degradation of petroleum hydrocarbons has been done by biological activity. Also, increasing the C: N and C: P ratio during the degradation process might be presented that the rate of nitrogen and phosphorus consumption was higher than organic carbon (Figs. 6 (c) and (d) (Koolivand *et al*., 2013b, Asgari *et al*., 2017). According to the previous studies, the maximum removal efficiency of TPH during the biodegradation of oily sludge at C: N: P ratio of 100:1.74:0.5 was about 51% (Roldán-Carrillo *et al*., 2012). But C: N: P ratio in this research were 100: 5: 1 and the highest and lowest of TPH removal efficiency were 69.46% (1:5 mixing ratio) to 62.42 % (1:10 mixing ratio), respectively.

Abiotic degradation and volatilization

The results of this study showed that total volatilization loss were 1.46 and 1.57 % with and without $HgCl_2$ respectively. Therefore, it shows that the role of volatilization and abiotic parameters for removal of TPH during the composting was negligible. In addition, the temperature used in this study was in the range of mesophilic range, thus volatilization process could have no significant effect on the TPH removal. The results obtained in this section, confirming the results of previous studies on the TPH removal by in-vessel composting (Koolivand *et al*., 2013a, Asgari *et al*., 2017). Therefore, it can be derived that the main mechanism for TPH removal was microbial activity.

Kinetic analysis of TPH removal

Table 4 presents the results of kinetic models and half-life. The results of first order kinetic model showed that the rate constant of biodegradation of TPH at mixing ratio 1:3 (k_1=0.0455 1/d; $t_{1/2}$=15.23 d) was similar to the mixing ratio of 1:15 (k=0.0440 1/d, $t_{1/2}$=15.75 d). In addition, the results of second order model showed that the rate constant at mixing ratio of 1:3 (k_2=0.0026 g/mg.d; $t_{1/2}$=4.84d) was faster (about 11%) than mixing ratio of 1:15 (k_2=0.0117 g/mg.d; $t_{1/2}$=5.38 d). Also, the results of kinetic study showed that second order model had the best agreement with the experimental data (higher R^2) (Table 4). Therefore, high R^2 values and short half-life (less than 7.53 d) showed that the decomposition of TPH was so fast. It was reported by previous studies associated with biodegradation of TPH (Nwankwegu *et al*., 2016, Asgari *et al*., 2017).

CONCLUSION

The results of present study discloses that combination of filter cake and composting materials can appropriately reduce the TPH resulted in re-refinery industry after pre-treatment by APS. As in this study, TPH concentrations of about 500 g/kg to less than 27 g/kg reached. Microbial activity is main factor for reduction of TPH. Based on the results, filter cake to compost ratio lower than 15: 1 can be significantly degraded the TPH (more than 62%). Nevertheless, the residual TPH after IVC is higher than existing environmental standards, but the combination system of chemical pre-treatment and IVC could be considered as an efficient method for reducing the TPH in high concentrations.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

ABBREVIATIONS

%	Percent
% w/w	% mass/mass
APS	Activated persulfate
C	Carbon
°C	Degree Celsius
C_0	The initial concentration
C_6–C_{35}	Petroleum hydrocarbon ranges
$CH_3(CH_2)_4CH_3$	*n*-hexane
°C/min	Degree Celsius per minute
C: N	Carbon/ Nitrogen ratio
C: N: P	Carbon/ Nitrogen /Phosphorus ratio
Co^{2+}	Cobaltous ion
C: P	Carbon/ Phosphorus ratio
C_t	Concentration as a function of time
Cu^{2+}	Cupric ion
d	Day
E_0	Standard Potential
Eh	Redox potential
Eqs	Equations
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
$FeSO_4 \cdot 7H_2O$	Ferrous sulfate heptahydrate
g	Gram
GC-FID	Gas Chromatography -Flame Ionization Detector
g/kg	Gram per kilogram
$HgCl_2$	Mercuric chloride
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
IVC	In-vessel composting
k_1	First order rate constant
k_2	Second order rate constant
Ln	The natural logarithm
M	Molar
Me^{n+}	Transition metal ions
mg/g	Milligram per gram

min	Minute
mL	Milliliter
mL/min	Milliliter per minute
N	Nitrogen
NaOH	Sodium hydroxide
$Na_2S_2O_8$	Sodium persulfate
OC	Organic carbon
OC: TPH	Organic carbon/ Total petroleum hydrocarbon ratio
·OH	Hydroxyl ion radical
P	Phosphorus
p	p-value
PS	Persulfate
PS/Fe^{2+}	Persulfate / Ferrous ion ratio
R^2	Regression Coeficient
rpm	Revolutions per minute
$S_2O_8^{2-}$	Persulfate ion
$SO_4^{·-}$	Sulfate ion radical
$t_{1/2}$	Half-life
TKN	Total Kjeldahl nitrogen
TPH	Total petroleum hydrocarbon
UV	Ultraviolet
V	Volt
ZVI	Zero valent iron

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