Treatment of petroleum-hydrocarbon contaminated soils using hydrogen peroxide oxidation catalyzed by waste basic oxygen furnace slag

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ABSTRACT

The contamination of subsurface soils with petroleum hydrocarbons is a widespread environmental problem. The objective of this study was to evaluate the potential of applying waste basic oxygen furnace slag (BOF slag) as the catalyst to enhance the Fenton-like oxidation to remediate fuel oil or diesel contaminated soils. The studied controlling factors that affect the removal efficiency of petroleum hydrocarbons included concentrations of H_2O_2, BOF slag dosages, types of petroleum hydrocarbons (e.g., fuel oil and diesel), and types of iron mineral. Experimental results indicate that oxidation of petroleum hydrocarbon via the Fenton-like process can be enhanced with the addition of BOF slag. Results from the X-ray powder diffraction analysis reveal that the major iron type of BOF slag/sandy loam system was iron mineral (e.g., α-Fe_2O_3 and α-FeOOH). Approximately 76% and 96% of fuel oil and diesel removal were observed (initial total petroleum hydrocarbon (TPH) concentration = 10,000 mg kg^{-1}), respectively, with the addition of 15% of H_2O_2 and 100 g kg^{-1} of BOF slag after 40 h of reaction. Because BOF slag contains extractable irons such as amorphous iron and soluble iron, it can act as an iron sink to supply iron continuously for Fenton-like oxidation. Results demonstrate that Fenton-like oxidation catalyzed by BOF slag is a potential method to be able to remediate petroleum-hydrocarbon contaminated soils efficiently and effectively.

1. Introduction

Accidental releases of petroleum products from pipelines and storage tanks are among the most common causes of soil contamination [1,2]. Petroleum hydrocarbon pollution is one of the main environmental problems, not only by the significant amounts released but also by their toxicity. Among those petroleum hydrocarbons, fuel oil and diesel are more difficult to treat compared to gasoline due to their characteristics of lower volatility, lower biodegradability, higher viscosity, and lower mobility [3–5].

In situ chemical oxidation (ISCO) is a promising innovative technology of degrading an extensive variety of hazardous wastes for the remediation of soils at waste disposal and organic contaminant spill sites [6,7]. ISCO is based on the delivery of chemical oxidants to contaminated media to destroy contaminants to end products or to convert them into more biodegradable compounds allowing them to be degraded biologically. Chemical oxidation with hydrogen peroxide (H_2O_2) involves the generation of free radicals. The injected H_2O_2 decomposes to hydroxyl radical ($^{\bullet}$OH), which is strong, nonspecific oxidant that reacts with most organic compounds at near-diffusion controlled rates [8,9]. There are two categories of Fenton processes [10,11]. One is the standard Fenton reaction, which utilizes soluble ferrous iron (Fe^{2+}) as the catalyst, and the other is the so-called modified Fenton or Fenton-like process, which includes the use of ferric iron (Fe^{3+}), iron oxides such as magnetite (Fe_3O_4) [12], goethite (α-FeOOH) [13], α-Fe_2O_3 [14] and iron chelates.

The removal efficiency of contaminants by iron oxide catalyzed Fenton-like reaction is influenced by parameters such as types and concentrations of iron oxides, H_2O_2 concentration, the presence of other oxidant-consuming compounds and pH. Watts and Dilly [3] applied the monobasic potassium phosphate to enhance the mineral catalyzed Fenton-like remediation of diesel contaminated soils, but resulted in only 40% diesel loss. Kong et al. [12] reported that iron mineral catalyzed H_2O_2 system would have a promising application to petroleum-hydrocarbon contaminated site remediation since natural soils generally contain 0.5–5 wt% (5–50 g kg^{-1}) of iron minerals. In addition, Fenton-like oxidation technology has been studied by numerous groups for remediation of organic contaminated soils and other solid matrices. These researchers have shown that hydroxyl radicals generated through Fenton-like reaction are capable of oxidative degradation of numerous organic pollutant, including diesel [3,12,15], chlorinated ethylenes [11], aromatic hydrocarbons [13,16], 2,4-dichlorophenol [17], and 4-chlorophenol [18,19]. However, there is a lack of information about its effectiveness for the direct oxidation treatment of fuel oil in the subsurface.

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Table 1
The major compositions of BOF slag.

Compositions	SiO_2	Al_2O_3	CaO	MgO	Total iron	Extractable iron	Amorphous iron	Free iron	Fe_o/Fe_d	pH
	wt%				$g\,kg^{-1}$					
Value	32.6	13.7	40.9	6.5	52.8	45.2	14.7	26.4	0.33	12.1

Fe_d, extractable iron; Fe_o, amorphous iron.

Basic oxygen furnace slag (BOF slag) is a final waste material in the basic oxygen furnace steel making process. In blast furnace iron making, limestone (as fluxes) is added to react with the gangue minerals (iron ore and coke) to form iron slag. Slag is separated from the molten iron owing to the different specific gravity of molten iron and slag. In a basic oxygen furnace, the molten iron is converted into steel with oxygen, which also requires some flux materials to react with gangues. The slag formed in the BOF, after being solidified, is called BOF slag [19–22]. In recent years, the management of BOF slag has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints [21,23]. BOF slag is heterogeneous oxide material which is compounded by some main oxides such as FeO, Fe_2O_3, CaO, SiO_2, SO_3, Al_2O_3, and MgO due to their mass percentage [24,25]. There is 5–20% of FeO and 1–8% of Fe_2O_3 present in the BOF slag [18,20,21]. Furthermore, FeO and Fe_2O_3 can be dissociated to produce Fe^{2+} and Fe^{3+} in aqueous solution.

The objective of this study was to evaluate the potential of applying BOF slag as the catalyst to activate the Fenton-like oxidation process for the remediation of petroleum-hydrocarbon contaminated soils. The studied controlling factors that affect the removal efficiency of petroleum hydrocarbons included concentrations of H_2O_2, BOF slag dosages, types of petroleum hydrocarbons (e.g., fuel oil and diesel), and types of iron mineral (e.g., magnetite, hematite, and goethite).

2. Materials and methods

2.1. Chemicals and soil samples

The fuel oil (no. 6 fuel oil) and diesel used in this study were purchased from Chinese Petroleum Corp. (Taiwan) and used as received. The H_2O_2 (30%) was purchased from Merck KGaA Chemicals (German) and used as received. The BOF slag was obtained from China Steel Corp., Taiwan, and it was sieved with a no. 100 mesh sieve to remove large slag. BOF slag was collected and placed in a desiccator after washing with distilled water, and dried at $200\,^\circ$C in an oven. BOF slag was washed by DI water (with pH of 6–7) for approximately 5 min before use. Because the purpose of BOF slag washing was to remove dirt and impurity on it, only a short and gentle wash process was applied, and therefore, the irons, which were extracted by DI water would not be significant. The main constituents of BOF slag are SiO_2, Al_2O_3, CaO, MgO, total iron, extractable iron, amorphous iron, free iron, and pH as shown in Table 1. Magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and goethite (α-FeOOH) were obtained from Fluka Chemical Co. (USA).

In this study, both the sandy loam and silica sand were used as the media in oxidation experiments. The sandy loam was sampled from a background and uncontaminated area (15–30 cm below land surface) of a petroleum-hydrocarbon spill site in Taiwan. The collected soils were air dried, passed through a 2-mm sieve, and kept refrigerated at $4\,^\circ$C until analyzed. The natural silica sand was imported from Vietnam and washed with distilled water prior to use. Soil samples were analyzed to determine their characteristics including parameters of particle size, pH, soil organic matter, redox potential, total iron, extractable iron, amorphous iron, and free iron. Particle size distribution was determined by the pipette methods

[26]. The soil pH was measured using a mixture of soil and deionized water (1:1, w/v) with a glass electrode (TES 1380, Taiwan). The Walkley–Black wet oxidation method was used to measure the organic matter in soil [27]. Redox potential was measured by an ORP meter (ORION Model 250A+, Thermo, USA). Total iron concentration was measured by AA (Atomic Adsorption, Hitachi Z6100) with a Fe hollow cathode lamp. Extractable iron (Fe_d) determination, using 0.25 M of hydroxylamine chloride solution as an extract, followed the procedures described by Hesse [28]. Amorphous iron (Fe_o) concentration was quantified by ammonium oxalate extraction [29]. Free iron was extracted by the dithionite–citrate–bicarbonate method [30]. These soils were named silica sand, and sandy loam, respectively, and their characteristics are shown in Table 2.

2.2. Experimental conditions and procedures

Collected soils were mechanically homogenized in a stainless steel container. The soil was spiked with petroleum hydrocarbons (e.g., fuel oil and diesel) dispersed in 1.5 L of a 1:1 (v/v) n-hexane/acetone solution. The soil was then further homogenized. The solvents were allowed to evaporate from the soils by placing the container of spiked soil in a fume hood, thus leaving behind the petroleum hydrocarbon in the soil at a theoretical initial total petroleum hydrocarbon (TPH) concentration of approximately 10,000 mg kg^{-1} of soil. The initial TPH concentration was confirmed by the analyses of triplicate soil samples. Less than 1% of variation was observed from the triplicates analyses (data not shown). The operating parameters included concentration of H_2O_2, BOF slag dosage, types of soils, types of petroleum compounds (e.g., fuel oil and diesel), and types of iron mineral (e.g., magnetite, hematite, and goethite). All batch experiments were performed in duplicates. The batch oxidation reaction was conducted in 100-mL glass tubes with Teflon caps. Each batch contained 50 g of fuel oil or diesel contaminated soils (silica sand or sandy loam) with initial TPH concentration of 10,000 mg kg^{-1}, 30 mL of H_2O_2 solution, and other additives (e.g., BOF slag and iron mineral). The experiment was conducted at room temperature, and soil samples were collected at different time points (e.g., 0, 5, 10, 20, 30, and 40 h) for the analysis of TPH, H_2O_2, temperature, soluble iron, and X-ray powder diffraction (XRD) during the reaction.

Samples were spun on a Hettich-Zentrifugen EBA 21 centrifuge for 30 min at 10,000 rpm, and stored until analysis at $4\,^\circ$C in the

Table 2
Properties of the tested soils.

	Silica sand	Sandy loam
Sand (%)	100	68
Silt (%)	ND	22
Clay (%)	ND	10
pH	6.9	5.8
SOM (%)	ND	0.5
ORP (mV)	–	267
Total iron (g kg^{-1})	0.09	33.6
Extractable iron (g kg^{-1})	0.06	12.1
Amorphous iron (g kg^{-1})	ND	2.9
Free iron (g kg^{-1})	ND	8.4
Fe_o/Fe_d	–	0.24

ND, not detected; –, not available; Fe_d, extractable iron; Fe_o, amorphous iron.

dark. Removal of TPH was monitored by shake-extracting the vial contents for 24 h with mixture of *n*-hexane/acetone (1:1, v/v). Analysis of TPH extract was performed using a Hewlett-Packard 6890 gas chromatography (GC) equipped with a flame ionization detector and a DB-1 (HT) capillary column (0.32 mm × 30 m). The injector temperature was 300 °C and the detector temperature was 350 °C. The oven temperature was programmed to increase from 50 (5 min) to 350 °C (10 min) at 10 °C min^{-1}. Hydrogen peroxide concentrations were determined by iodometric titration method [31]. Soluble iron concentration (only with 15% H_2O_2 and BOF slag after 40 h) was measured by AA (Atomic Adsorption, Hitachi Z6100) with a Fe hollow cathode lamp.

To verify the crystal structure of minerals, solid samples were analyzed by XRD. The XRD data of solid sample such as BOF slag, magnetite, hematite, goethite, and tested soils (e.g., silica sand and sandy loam) were collected with a Rigaku Rint-2000 (Japan) diffractometer using Ni-filtered CuKα radiation generated at 30 kV and 10 mA. The XRD patterns were recorded over the range 0–40°(2θ) with a scanning speed of 1.0°(2θ)/min [32].

3. Results and discussion

3.1. Characteristics of tested soil and BOF slag

Results from the particle tests reveal that the natural silica sand had a silica sand texture (100% sand), and the collected site soils had a sandy loam texture (68% sand, 22% silt, and 10% clay). Furthermore, the extractable irons (Fe_d) were approximately 0.06 (silica sand) and 12.1 g kg^{-1} (sandy loam) (Table 2). In Table 1, the measured amorphous iron (Fe_o), and extractable iron in BOF slag were approximately 14.7 and 45.2 g kg^{-1}, respectively. Results also indicate that the Fe_o/Fe_d value of sandy loam and BOF slag were 0.24 and 0.33, respectively. Results show that the BOF slag contained significant amounts of iron to enhance the reaction of Fenton-like oxidation [3,10,33]. Fig. 1 presents the variations in the value of pH versus BOF slag dosage without H_2O_2 addition. Results show that the soil pH increased after the addition of BOF slag. The more the BOF slag added, the more increased pH was observed. Results show that the soil pH value increased from 5.8 to 6.7 after 100 g kg^{-1} of BOF slag was added to sandy loam. According to the pH–pE speciation diagram [33], the dominant form of extractable iron was Fe^{3+} in the tested soils.

3.2. Experiments without BOF slag

Fig. 2 presents the efficiencies of TPH (initial TPH of fuel oil = 10,000 mg kg^{-1}) removal versus reaction time with different initial H_2O_2 concentrations (0%, 1%, 3%, 7%, 10%, 15%, and 30%)

Fig. 1. Variations in the value of pH versus BOF slag dosage; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; $[H_2O_2]_0$ = 0%.
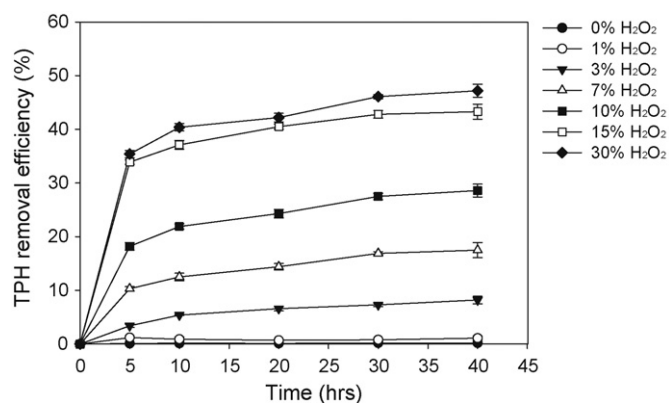
Fig. 2. Efficiency of TPH removal versus reaction time with different initial H_2O_2 concentrations; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; BOF slag initial dosage, 0 g kg^{-1}; soil type, sandy loam; initial pH 5.8.

without BOF slag addition (Fe_o/Fe_d value = 0.24) in sandy loam system. Less than 1.1% of TPH removal efficiency was observed in experiment with low H_2O_2 concentration (1%). In the experiment with 1% of H_2O_2, the TPH concentrations dropped from 10,000 to 9,890 mg kg^{-1} (1.1% of TPH removal) after 40 h of reaction.

Although H_2O_2 can be used as an oxidant alone, the oxidation reaction is not kinetically fast enough to degrade many hazardous organic contaminants with low H_2O_2 concentration [6,7]. Thus, previous researchers reported that high concentration of H_2O_2 (generally above 1%) is required for site application since various organic matters in soils could quench H_2O_2 [6,35]. Contaminants in soils exist as particulate and sorbed conditions, and a strong oxidizing condition is required to degrade contaminant efficiently. Results indicate that TPH removal can be significantly increased with increased H_2O_2 concentration. Approximately 43% and 47% of TPH were removed in experiments with H_2O_2 concentrations of 15% and 30%, respectively, after 40 h of reaction. This indicates that the TPH oxidation can be enhanced under conditions of higher H_2O_2 concentration. In a future practical application, a sequential addition of high concentration of H_2O_2 can be conducted to provide a stronger oxidizing power. Although 15% of H_2O_2 shows less removal efficiency than 30% of H_2O_2, it was selected in the following batch study of Fenton-like oxidation experiments because of the cost and safety reasons.

3.3. Effect of soil types on the treatment efficiency without BOF slag addition

Fig. 3 presents the effect of soil types on the removal of TPH with 15% of H_2O_2 concentrations and 10,000 mg kg^{-1} of TPH (fuel oil). This study explored the Fenton-like oxidation of TPH in silica sands (extractable iron = 0.06 g kg^{-1}) and sandy loam soils (extractable iron = 12.1 g kg^{-1}). Results indicate that TPH removal can be significantly increased with increased extractable iron concentration. In the presence of H_2O_2 and tested soils (e.g., silica sand and sandy loam) only, the TPH removal efficiencies were 20% (silica sand) and 43% (sandy loam), respectively, after 40 h of reaction. This could be due to the fact that the sandy loam had a higher concentration of extractable iron, which helped to catalyze oxidation reaction. Thus, under the same conditions, the sandy loam soils caused higher TPH removal efficiency than silica sands. The results imply that the concentration of extractable iron played an important role in the TPH removal efficiency. Results from this study are in agreement with those from other study [10].
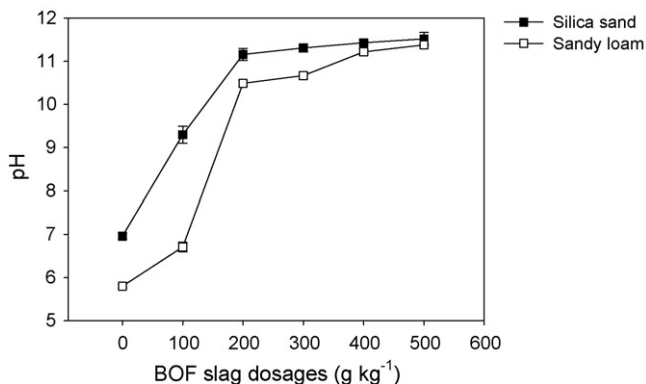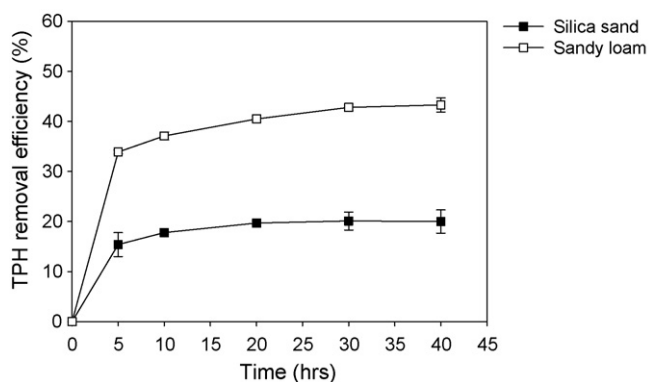
Fig. 3. Variations in the percentage of TPH removal efficiency versus reaction time with varied soil types; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; BOF slag initial dosage, 0 g kg^{-1}.
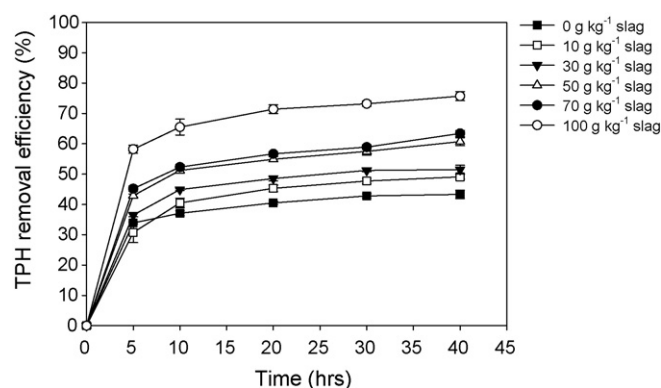
3.4. Effect of BOF slag dosage on the treatment efficiency

Fig. 4(a) presents the effect of BOF slag dosage on TPH removal efficiencies. Fig. 4(b) presents the decay of H_2O_2 in tested soil (sandy loam) versus reaction time with different initial BOF slag dosage. Fig. 5 presents the efficiency of TPH removal versus reaction time with different initial BOF slag dosages in sandy loam system. Results indicate that the increased BOF slag dosage from 0 to 100 g kg^{-1} caused the increase in the removal efficiency of TPH after 40 h of reaction (Figs. 4(a) and 5). Fig. 6(a) and (b) presents the variations in Fe$_o$/Fe$_d$ value and soluble iron concentration versus reaction time with 15% of H_2O_2 and different initial BOF slag dosage. In the presence of sandy loam soils, the efficiencies of TPH removal were

Fig. 4. (a) Effect of BOF slag dosage (0, 100, 200, 300, 400, and 500 g kg^{-1}) on the efficiency of TPH removal with the addition of 15% H_2O_2; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; reaction time, 40 h. (b) Decay of H_2O_2 in tested soil (sandy loam) versus reaction time with different initial BOF slag dosage (0, 100, 200, 300, 400, and 500 g kg^{-1}); conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%.

Fig. 5. Efficiency of TPH removal versus reaction time with different initial BOF slag dosage (0, 10, 30, 50, 70, and 100 g kg^{-1}); conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; soil type, sandy loam.

found to be 43% and 76% with the initial BOF slag dosages of 0 and 100 g kg^{-1}, respectively, while the Fe$_o$/Fe$_d$ value increased from 0.24 to 0.27 (Fig. 6(a)). On the other hand, the efficiencies of TPH removal were 20% and 49%, in the presence of silica sands for two different BOF slag dosages (e.g., 0 and 100 g kg^{-1}). Results show that the efficiency of TPH removal increased with increased BOF slag (from 0
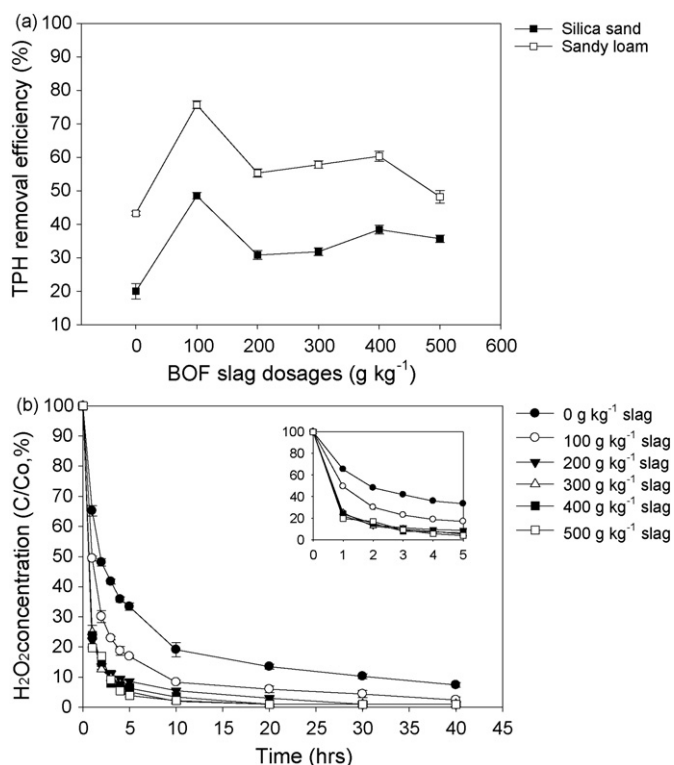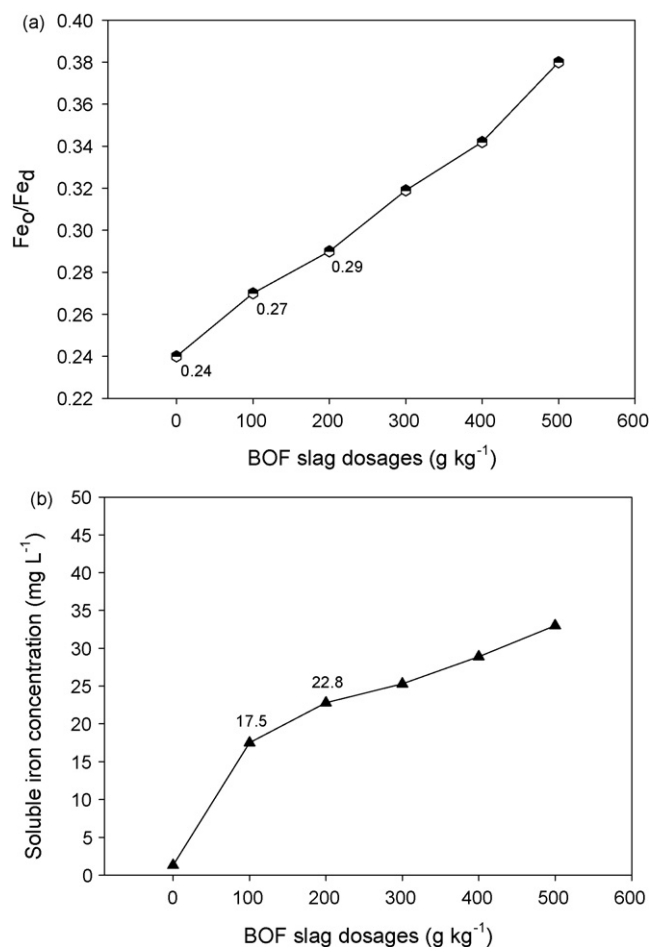

Fig. 6. (a) Variations in Fe$_o$/Fe$_d$ value versus reaction time with 15% of H_2O_2 and different initial BOF slag dosage (0, 100, 200, 300, 400, and 500 g kg^{-1}); conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; reaction time, 40 h. (b) Variations in soluble iron concentration versus reaction time with 15% of H_2O_2 and different initial BOF slag dosage (0, 100, 200, 300, 400, and 500 g kg^{-1}); conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; reaction time, 40 h (only with 15% H_2O_2 and BOF slag).
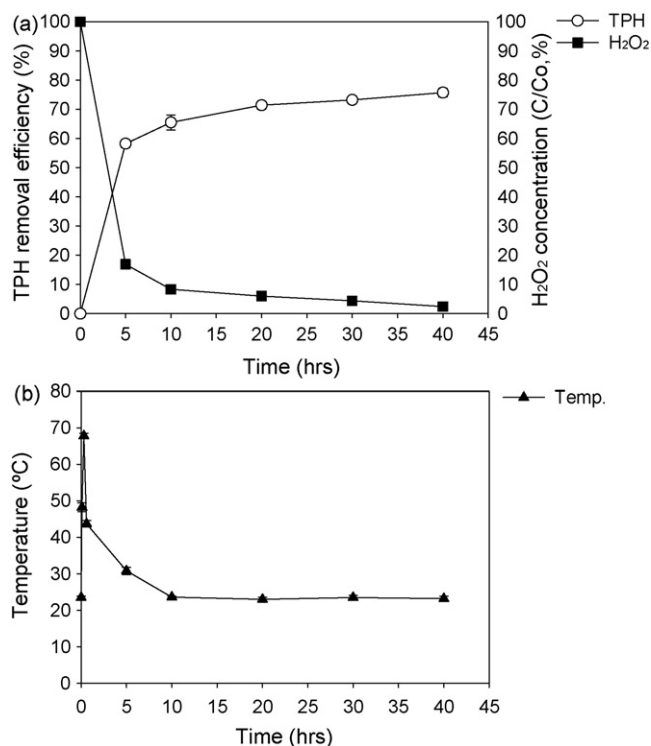
Fig. 7. (a) Variations in TPH, and H_2O_2 concentrations versus reaction time with 15% of H_2O_2 and 100 g kg^{-1} BOF slag; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; BOF slag initial dosage, 100 g kg^{-1}; soil type, sandy loam; initial pH 6.7. (b) Variations in temperature versus reaction time with 15% of H_2O_2 and 100 g kg^{-1} BOF slag; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; BOF slag initial dosage, 100 g kg^{-1}; soil type, sandy loam; initial pH 6.7.

to 100 g kg^{-1}) in different soil systems. This indicates that BOF slag addition would accelerate TPH removal. The produced extractable iron (e.g., Fe^{3+}) could catalyze the Fenton-like reaction, and generate $^{\bullet}$OH for TPH oxidation.

Fig. 4(a) also reveals that TPH removal was significantly decreased with BOF slag dosage increased from 100 to 200 g kg^{-1}, while the Fe_o/Fe_d value increased from 0.27 to 0.29 (Fig. 6(a)). Furthermore, results from Fig. 4(b) indicate that H_2O_2 concentration was significantly decreased with BOF slag dosage increased from 100 to 200 g kg^{-1} during the first 5 h of reaction. This might be due to the phenomenon that higher BOF slag dosage (>100 g kg^{-1} in this study) would cause the consumption of H_2O_2 for water production [36]. Thus, increased BOF slag dosage would not produce more $^{\bullet}$OH, but cause superfluous fresh iron surfaces. The extra iron surfaces would also cause the consumption of oxidants (e.g., H_2O_2 and $^{\bullet}$OH) rapidly, and thus, lead to significant decline of TPH removal efficiency [17,19]. Other researchers indicate that more efficient Fenton-like reaction would occur under acidic or neutral conditions [13,17]. Results from this study show that pH values increased from 6.7 (100 g kg^{-1}) to 10.5 (200 g kg^{-1}) (Fig. 1). The increased pH value might cause the decrease in TPH removal efficiency. Therefore, the dosage of BOF slag was fixed at 100 g kg^{-1} for Fenton-like oxidation experiments.

Fig. 7(a) and (b) presents the variations in TPH, consumption of H_2O_2, and variation in temperature versus reaction time with 15% of H_2O_2 and 100 g kg^{-1} of BOF slag. Results from Fig. 7(a) reveal that approximately 83% of H_2O_2 was depleted after 5 h of oxidation reaction. The consumption of H_2O_2 also caused the leveling off of the TPH removal curve after 5 h of operation. Results depict that TPH concentration dropped from 10,000 to 4,200 mg kg^{-1} (approximately 58% of TPH removal), and temperature increased from 23.5
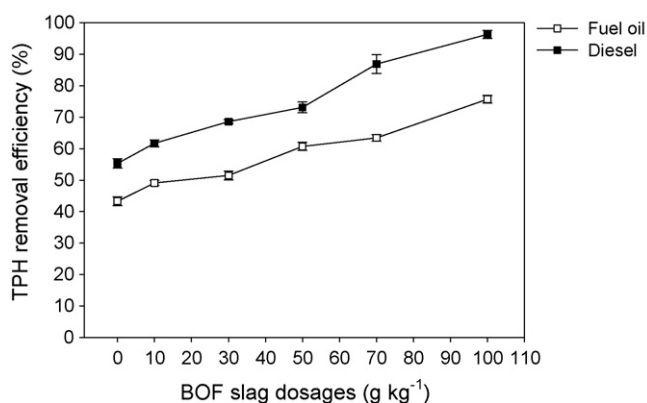

Fig. 8. Variations in the percentage of TPH removal efficiency versus reaction time with varied petroleum types; conditions: petroleum initial concentration, 10,000 mg kg^{-1}; [H_2O_2]$_0$ = 15%; soil type, sandy loam; reaction time, 40 h.

to 30.8 °C (up to 67.8 °C during the first 0.3 h of reaction) with the presence of 100 g kg^{-1} BOF slag and 15% of H_2O_2 after 5 h of oxidation (Fig. 7(b)). The increase in soil temperature is usually observed immediately after the injection by H_2O_2 solution [37,38]. The optimal temperature for ISCO treatments with H_2O_2 injection is generally within the interval of 35–41 °C [6]. Fenton-like reactions in the subsurface are in fact highly exothermic, and can lead to a significant increase in soil temperature [7]. Excessive heat generation and gas formation are dangerous because they can lead to undesired soil sterilization, instability of reactants, and explosions. Thus, for safety reasons, site temperatures should be closely monitored in the field application.

3.5. Comparison between diesel and fuel oil with the addition of BOF slag and H_2O_2

Fig. 8 presents the variations in TPH concentrations versus time with the addition of 15% H_2O_2 and 100 g kg^{-1} of BOF slag in different petroleum types system. Similar to the results of fuel oil oxidation, diesel removal was significantly enhanced with the presence of both H_2O_2 and BOF slag. Lower diesel TPH removal efficiency was observed in experiment with H_2O_2 addition only (without BOF slag addition). This also indicates that BOF slag was used as the catalyst for the activation of Fenton-like oxidation. Results show that approximately 55% of diesel TPH removal was observed in experiments with H_2O_2 addition only (without BOF slag addition) after 40 h of reaction (Fig. 8). However, approximately 96% of diesel TPH removal was observed with both H_2O_2 (15%) and BOF slag (100 g kg^{-1}) addition after 40 h of reaction. Results from the fuel oil oxidation experiments show that about 76% of TPH was removed with both H_2O_2 (15%) and BOF slag (100 g kg^{-1}) addition after 40 h of reaction. The different TPH removal efficiencies between the diesel and fuel oil experiments might be due to the fact that fuel oil has larger size of molecules and larger molecular weight than diesel. Thus, fuel oil is less degradable via the oxidation process [3,12]. Experimental results demonstrate that BOF slag enhanced the oxidation of petroleum hydrocarbons (e.g., fuel oil and diesel) in soils by Fenton-like reaction.

3.6. Comparison between BOF slag and iron mineral system

Fig. 9 presents the effect of BOF slag and iron mineral types on the removal of TPH with the presence of 15% of H_2O_2. Results show that the experiment with 100 g kg^{-1} of BOF slag (58%) had the most significant TPH removal efficiency during the first 5 h of reaction compared with the degradation trends with magnetite (48%), hematite (42%), goethite (41%), and sandy loam only (34%).
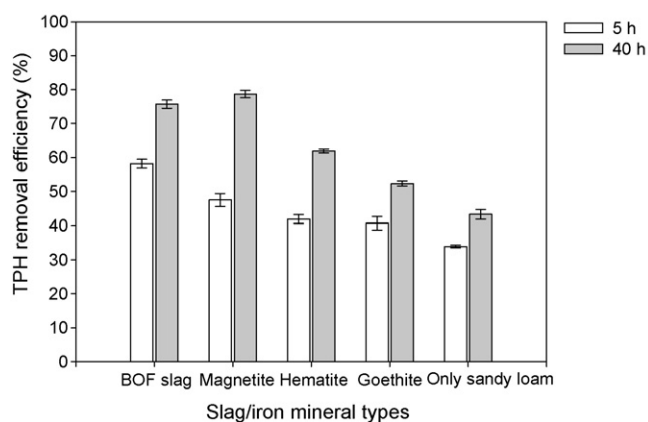
Fig. 9. Variations in the percentage of TPH removal efficiency versus reaction time with varied iron mineral types and BOF slag; conditions: fuel oil initial concentration, 10,000 mg kg^{-1}; [H$_2$O$_2$]$_0$ = 15%; soil type, sandy loam; slag/iron mineral dosage, 100 g kg^{-1}; initial pH 6.7.

The TPH removal efficiency was in the order of 100 g kg^{-1} of magnetite (79%) > 100 g kg^{-1} of BOF slag (76%) > 100 g kg^{-1} of hematite (62%) > 100 g kg^{-1} of goethite (52%) > only sandy loam (43%) after 40 h of reaction.

Kong et al. [12] reported that the naturally occurring iron minerals, goethite and magnetite, were used to catalyze H$_2$O$_2$ and initiate Fenton-like reaction of silica sand contaminated with diesel and/or kerosene in batch systems. Their results show that the magnetite system provided stronger oxidation condition than goethite system due to the amount of soluble iron, while the concentration of soluble iron was from 0.7 to 8.2 mg L^{-1} with different initial pH, and different dosages of magnetite and H$_2$O$_2$ (15%) after 120 h of reaction.

Results show that BOF slag system had similar effect on the activation of Fenton-like reaction in the system with magnetite, but was much more effective than systems with hematite and goethite as the catalysts. This might be due to the fact that BOF slag contains significant amounts of extractable iron such as amorphous iron and soluble iron (e.g., 17.5 mg L^{-1} of soluble iron produced in reaction with 15% of H$_2$O$_2$ and 100 g kg^{-1} of BOF slag after 40 h of reaction) (Fig. 6(b)) in the reaction system. Therefore, BOF slag catalyzed H$_2$O$_2$ system would cause more effective oxidative reaction than the system using iron mineral (e.g., hematite and goethite) as the catalyst for the activation of Fenton-like reaction.

3.7. XRD patterns showing the identified irons

The XRD patterns of six solids containing Fe are shown in Fig. 10(a). On the basis of the positions of the main diffraction peaks in the XRD patterns, different crystallites in the catalysts were identified. The patterns show the main diffraction peak of sandy loam (tested soil) at 2θ = 26.1 and 33.2. Clearly, pattern of sandy loam shows a typical broad peak, indicating that the iron phase is an iron oxide hydroxide α-FeOOH. Results also show that the main diffraction peaks of BOF slag appeared at 2θ = 33.2 and 35.9, which could be the characteristics of α-Fe$_2$O$_3$. Results indicate that the BOF slag/sandy loam or BOF slag/iron minerals systems would have significant oxidation capacity for TPH oxidation. Because significant amount of crystalline iron (e.g., α-Fe$_2$O$_3$ and α-FeOOH) and extractable iron (e.g., amorphous and soluble iron) is present in the BOF slag (Fig. 6), the BOF slag is able to cause high treatment efficiency of TPH, and can be used repeatedly as shown in Fig. 10(b). Results from this study demonstrate that the combination of Fenton-like with a proper type of iron minerals can improve the efficiency of contaminant oxidation in situ. This indicates that
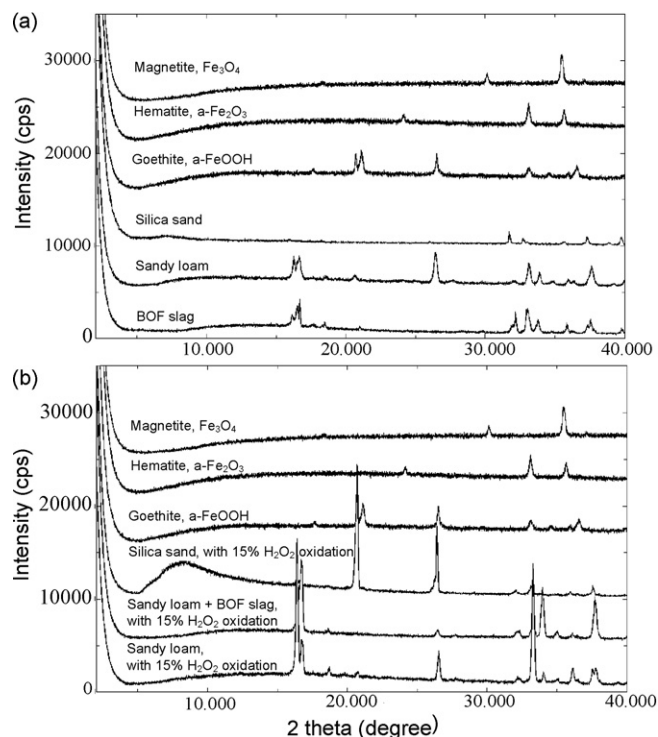

Fig. 10. XRD diffraction patterns of the soil/BOF slag (a) before of oxidation reaction and (b) after of oxidation reaction.

combining BOF slag enhanced Fenton-like oxidation is a promising technology to remediate petroleum-hydrocarbon contaminated soils.

4. Conclusions

In this study, BOF slag was applied to activate Fenton-like oxidation to remediate petroleum-hydrocarbon contaminated soils. Conclusions obtained from this study include the following:

(1) Results suggest that addition of BOF slag is able to catalyze the Fenton-like oxidation process and improve the removal efficiencies of petroleum hydrocarbons. Approximately 96% and 76% of TPH removal efficiencies (initial TPH = 10,000 mg kg^{-1}) were observed in diesel and fuel oil oxidation experiments, respectively, with both H$_2$O$_2$ (15%) and BOF slag (100 g kg^{-1}) addition after 40 h of reaction.
(2) Based on the results from XRD analysis, the major iron types in the BOF slag/sandy loam system were iron minerals such as α-Fe$_2$O$_3$ and α-FeOOH. Results also indicate that the BOF slag is able to cause high treatment efficiency of TPH, and can be used repeatedly without significant loss of the crystalline and extractable iron in the BOF slag.
(3) BOF slag system was much more effective on the activation of Fenton-like reaction than systems using hematite and goethite as the catalysts. This is due to the fact that BOF slag system contains extractable and amorphous irons as well as some soluble irons.
(4) BOF slag can act as an iron sink to supply iron continuously for Fenton-like oxidation.

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