Master Thesis

Activation of persulfate by Fe-bearing materials for remediation of diesel/biodiesel-contaminated soils and phenol-contaminated water

The Graduate School of University of Ulsan

Civil and Environmental Engineering Department

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Activation of persulfate by Fe-bearing materials for remediation of diesel/biodiesel-contaminated soils and phenol-contaminated water

Advisor: Seok-Young Oh

A Dissertation

Submitted to the Graduate School of Civil and Environmental Engineering

in partial fulfillment of the requirements for the degree of

Master of Science

by

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November 2017

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ACKNOWLEDGEMENTS

I would like to thank my advisor, Professor Seok-Young Oh, for his guidance and support throughout nearly two years of this research. His knowledge and serious research is a good mirror to me in the researching.

I am thankful my friends, lab-mates, Civil and Environmental Engineering Department for making my truly great experiences at University of Ulsan.

Finally, sending my thanks to my family!

ABSTRACT

In this research, batch experiments were performed to examine the remediation of organic pollutants using modified persulfate (PS) systems. Zero-valent iron [Fe(0)] and other iron-bearing materials were applied to activate the PS systems for treating diesel and biodiesel-contaminated soils and phenol-contaminated water. After 12 h, Fe(0)-PS, 82.6% and 85.3% of diesel and biodiesel in soils were removed, respectively. The optimal molar ratios of Fe(0)-to-PS and FeS-to-PS were 68.6:1 and 43.6:1, respectively. Biochar (BC) was proposed to combine with Fe(0) to enhance the oxidation of phenol by PS. BC could accelerate the oxidation of phenol by Fe(0)-activated PS probably due to surface functional groups and electron distribution in biochar. Controlling factors including pH, PS concentration, and various black carbon materials were also examined. Complete degradation of phenol was achieved in 330 min with 3000 mg of Fe(0), 2500 mg/L of PS, and 200 mg of biochar at pH 7. Our results suggest that the oxidation by PS activated with iron-bearing materials and biochar may be a viable option to treat organic pollutants in natural environments.

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CHAPTER 1. INTRODUCTION

1.1. Introduction

In modern society, organic contaminated soil and groundwater have been a significant problem after long industrialization period. Harmful chemicals are emitted to the environment through spillage or leakage from pipelines, storage tanks or industrial facilities which include highly water soluble and non-aqueous phase liquid (NAPLs) compounds, which are classified as fluids less dense than water (LNAPLs) or fluids denser than water (DNAPLs) [1, 2].

A variety of physical, chemical and biological technologies have been applied for contaminated site remediation. One such the prominent method is in situ chemical oxidation (ISCO) which is power system to decompose organic or inorganic compounds as catalyzed hydrogen peroxide (H_2O_2) propagations (CHP), permanganate or ozone [3]. However, above factors of ISCO have its limitation in reactivity, stability, and transport. CHP system has potential degradation in almost organic or inorganic contaminations. Nevertheless, the systems are unstable in the subsurface [4]. Permanganate also has persistence in the subsurface but it can remove narrow contaminated chemicals [5]. With ozone, there are several limitations such as lower solubility, unstable reactivity and hard to transfer the gas phase to aqueous phase [6].

Finding out a new system to remedy damages of previous ISCO had been done by Kolthoff and Peyton. After some decades from invented the PS, it has become increasingly popular oxidants with its strong point compared to H_2O_2 and O_3 [4]. Moreover, the studied investigation using PS was highly empirical and in consequence, a bases-tone study of activated PS processing in contaminated substances would highly enhance its strong sides in the field.

1.2. Persulfate chemistry

In situ chemical oxidation (ISCO) has been used for several decades for the remediation of contaminated groundwater and aquifer solids. Recently, PS ($S_2O_8^{2-}$), has become popular as an oxidant in ISCO systems due to its ability to oxidize a variety of contaminant. PS is the sulfate peroxide with the chemical structure $[O_3S\text{-}O\text{-}O\text{-}SO_3]^{2-}$ [7-9]. The effectiveness of ISCO depends on the rate of $S_2O_8^{2-}$ activation and the yield of $SO_4\bullet^-$ and other reactive radicals. Studies have shown that PS anions can be activated to emit sulfate radicals ($SO_4\bullet^-$) (E^o = 2.6 V), which are stronger oxidation compared to $S_2O_8^{2-}$ (E^o = 2.01 V) [7, 10-12].

The PS activation processing, sulfate, and hydroxyl radicals are formed. Sulfate radicals and hydroxyl radicals are very strong oxidants that potentially oxidize common groundwater or soil contaminants. The hydroxyl radical and sulfate radical reacts with most organic compounds, and chlorinated contaminants such as trichloroethylene (TCE) and tetrachloroethylene (PCE) [8] through three mechanisms: 1) hydrogen abstraction, 2) addition and substitution reactions with alkenes and aromatic compounds, and 3) electron transfer from carboxylate groups [8]. Reports expanded by Neta et al. (1977) indicate that the sulfate radicals have higher effective oxidant with organic compounds compare to the hydroxyl radicals because they are more selective to oxidation while $OH^\bullet$ may react rapidly by hydrogen abstraction or addition. The sulfate free radicals, $SO_4\bullet^-$, have been indicated to react with some aromatic compounds and benzene derivatives by electron transfer [12-15]. Furthermore, sulfate radicals have the ability to react with alcohols, hydrocarbons and ether compounds through hydrogen (H) abstraction by breaking the C-H bond. The reactions of aliphatic acids with sulfate radicals usually lead to carboxylation, but reactions with hydroxyl radical do not. Therefore, the reactions with sulfate radicals involve electron transfer for the $-COO^-$ group, whereas hydroxyl radical abstracts hydrogen atoms from an aliphatic C—H bond [12].

Up to date, the methods that have been widely used for generation of sulfate radical ($SO_4 \bullet^-$) include [8, 13-17]:

- Heat, light activation

- Metals activation using transition metals

- Gamma radiation activation`

- Metal-free carbon catalyst

The below reaction equations indicate the formation of sulfate radical ($SO_4 \bullet^-$) and hydroxyl radical ($OH^\bullet$):

$$S_2O_8^{2-} \xrightarrow{\text{Heat, h}\upsilon \text{ activation}} SO_4 \bullet^- \qquad (1)$$

$$M^{n+} + S_2O_8^{2-} \xrightarrow{\text{Metal activation}} M^{(n+1)+} + SO_4 \bullet^- + SO_4^{2-} \qquad (2)$$

$$SO_4 \bullet^- + OH^- \longrightarrow OH^\bullet + SO_4^{2-} \qquad (3)$$
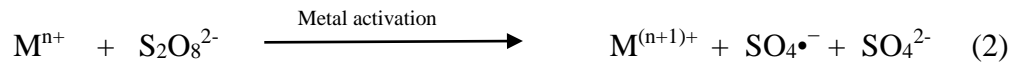
1.3. Persulfate activation by transition metal

Metal activation of PS is a prominent method for PS activation. Namely, Fe(0) and its other valences Fe^{2+}, which are inexpensive, nontoxic and recycled, are more commonly used metal activator. In the recent studies, PS system was activated by Fe(0) to remove polyvinyl alcohol (PVA), 2,4-dinitrotoluene, p-chloroaniline [14, 15, 18]. In addition, Cu^+, Co^{2+}, Ru^{3+}, Ag^+, Ce^{3+}, Mn^{2+}, Ni^{2+}, and V^{3+} were also used to activate PS [7]. Besides using convention metal to speed up the velocity of PS system, the recent reports indicate that applied natural ore or other materials combined with liked PS to accelerate to form radicals [15, 19], which can be formed by the following reaction:

$$Fe(0)_{(s)} + 2H_2O \longrightarrow Fe^{2+}_{(aq)} + H_2 + OH^- \qquad (4)$$

$$2Fe(0)_{(s)} + O_2 + 2H_2O \longrightarrow Fe^{2+}_{(aq)} + H_2 + OH^- \qquad (5)$$

$$Fe(0)_{(s)} + S_2O_8^{2-}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} \qquad (6)$$

$$\text{Fe}^{2+}_{(aq)} + \text{S}_2\text{O}_8^{2-}_{(aq)} \longrightarrow \text{Fe}^{3+}_{aq)} + \text{SO}_4^{\bullet-} + \text{SO}_4^{2-} \qquad (7)$$

$$\text{Fe}^{3+}_{(aq)} + \text{Fe}(0)_{(s)} \longrightarrow 3\text{Fe}^{2+}_{(aq)} \qquad (8)$$

In 2011, Oh et al., indicated that the heterogeneous activation of persulfate, involving direct electron transfer from Fe(0) or surface-bound (adsorbed or structural Fe^{2+} to persulfate, as shown in Equations 6 - 7:

$$\text{Fe}(0)_{(s)} + 2\text{S}_2\text{O}_8^{2-}_{(aq)} \longrightarrow \text{Fe}^{2+}_{(aq)} + 2\text{SO}_4^{2-}_{(aq)} + 2\ \text{SO}_4^{\bullet-}_{(aq)} \qquad (9)$$

$$\text{Fe}(0)_{(surf)} + 2\text{S}_2\text{O}_8^{2-}_{(aq)} \longrightarrow \text{Fe}^{3+}_{(surf)} + \text{SO}_4^{2-}_{(aq)} + \text{SO}_4^{\bullet-}_{(aq)} \qquad (10)$$
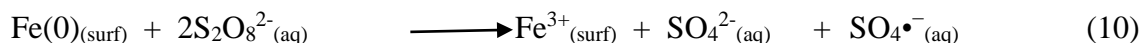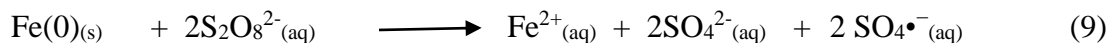
PS can be activated by Fe(0) because of its large surface area, tiny particle size, and high reactivity. However, Equations 3 - 4 showed that the rate corrosion of Fe(0) by H_2O, which may become the main reason to limit PS activation under anaerobic condition [20, 21]. The effect of micro-sized Fe(0) activate PS to a lesser extent than nano-sized Fe(0), where a larger surface area gives rise to an increased capability to emit Fe^{2+}. Nevertheless, the price of nano-sized Fe(0) and their beneficence are not similar. In order to overcome the problem, different types of supporting materials such as graphene, zeolite have been used to the better generate Fe^{2+} [15, 18, 22].

1.4. Persulfate activation by metal-free carbon

Carbon-based materials as adsorbent have attracted much attention such as activated carbon, car-bon nanotubes, porous carbon, graphene, reduced graphene oxide, nano-diamond and some kinds of biochars which made from the diversity of raw materials such as hardwood, rice hulls and bagasse. In recent years, a various of researcher groups announced the application of car-bon-based materials or modified carbon-based materials to degradation of pollutant because of nontoxic, recycled-agricultural waste, and high-efficiency treatment. The attraction features of carbon-based materials based on their physicochemical which including large surface area,

plentiful functional groups (quinone, ketone, carbonyl, and carboxyl). Besides, they have been used as an adsorptive support for metal catalysts to induce synergistic adsorption and decay of pollutants by radicals [22, 23]. Lee et al., showed that carbon nanotube could activate PS to oxidize phenol–contaminated water by radicals [24, 25]. PS activation on dimensional-structured nano carbons could remove phenols nearly 100% after 30 min, sulfamethoxazole (SMX) (initial concentration 5 mg/L) reached 99.9% removal in PS/ nitrogen-doped graphene and aminated graphene after nearly 3 h compared to 10% SMX decay in PS without modified graphene [16, 17]. Similarity, charge electrostatic and polar interactions on the surface nitrogen-doped reduced graphene oxide adsorbent remarkable the number of nitroaromatic compounds(NACs) and bisphenols has been removed by nitrogen-doped reduced graphene oxide [17, 26]. Using metals to modified carbon-based materials to enhance the adsorption, reduction and oxidation ability with PS, especially Fe(0) or nano-sized Fe(0) were performed to modify rich-carbon compounds which applied to activate PS to reduce U(VI), Co(II), Cr(VI) and organic-contaminated water [27-31].

In this study, interestingly, biochar (BC) is a form of biomass waste through modern pyrolysis processes under nitrogen gas which were used to investigate Fe(0)/PS to remove organic-contaminated water. The chemical and physical properties of bihar are similar above carbon-based materials such as porous structure, surface area with an abundant oxygen-containing functional group: example for carboxyl (-COOH), hydroxyl (-OH) depends on the pyrolysis conditions [32-34]. BC with its effective and low-cost adsorbents has been applied to remove polluted organic and heavy metal so they are the indispensable suggestion to improve the activation of PS activated with Fe(0) [32]. The effect of the kind of biochar to remove the pollutants depends on the raw materials and the conditions to make them. The char samples produced at high

pyrolytic temperatures (500-700 °C) were well carbonized and exhibited a relatively high surface area (>300 m^2/g), little organic matter (20% oxygen). By contrast, the chars formed at low temperatures (300-400 °C) were only partially carbonized, showing significantly different properties (< 200 m^2/g surface area, 40-50% organic carbon and >20% oxygen) [34]. Namely, three biochars, including pyrolyzed pine, wheat straw and maize needles at 300, 400 and 550 °C, which acts as an essential role to activate hydroperoxyl to reduce nearly 100% 2-Chlorobiphenyl (2-CB) after 120 min. Moreover, Fe^{3+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} with above biochars/PS or hydroperoxyl could be enhanced the removal rate of phenolic compounds [33, 35, 36].

1.5.   Objective of this study

-   Determine the effect of iron-bearing materials and PS on the degradation of total petroleum hydrarbons in diesel or biodiesel-contaminated soils.

-   Evaluate the effect of iron-bearing materials and biohar on the oxidation of phenol by PS.

-   Examine the effect of initial pH, PS concentration, and the amount of biochar on the PS system.

-   Suggest the possible mechanism on the activation of PS with iron-bearing materials and biochar.

CHAPTER 2. ENHANCED DEGRADATION OF PHENOL BY PERSULFATE ACTIVATED WITH IRON-BEARING MATERIALS AND BIOCHAR

2.1. Introduction

Industrial wastewater contains a huge of toxic chemicals such as phenol. With its toxic characteristics, the previous studies report some of the methods to enhance degradation of phenol. In the scope of this study, applying in situ chemical oxidation (ISCO) to solve phenol problem by using modified PS systems. Namely, using Fe(0) and AC, GR or BC to activate PS to degrade phenol.

2.2. Materials and methods

2.2.1. Materials

Phenol

Phenol (CAS: 108-52-2, extra pure, above 99%) was purchased from Dae Jung (Korea). Phenol also is known as carbolic acid, is an aromatic organic compound with the molecular formula C_6H_5OH. It is a white crystalline solid that is volatile. Solubility in water: 8.3 g/100 mL (20 °C). The molecule consists of a phenyl group (C_6H_5) bonded to a hydroxyl group (OH), which lead to weakly acidic of phenol ($K = 10^{-10}$). Phenol exhibits keto-enol tautomerism with unstable keto tautomer cyclohecxadienone, but only a tiny fraction of phenol exists as the keto form. The small amount of stabilization gained by exchanging a C=C bond for a C=O bond is more than offset by the large destabilization resulting from the loss of aromaticity. Phenol, therefore, exists essentially entirely in the enol form.

Other chemicals

Potassium persulfate (extra pure, ≥98%) was purchased from DC Chemical Co. Ldt (Korea). Sodium hydroxide (CAS: 1310-73-2, extra pure, 98%), sulfuric acid (CAS: 766493-9, extra pure, 95%), sodium chloride (CAS: 764-14-5, extra pure, 99%), hydrochloric acid (CAS: 7647-01-0, extra pure, 36.46%) were purchased from OCI Company Ltd (Korea). Iron (CAS: 7439-89-6, 99%, power, -70 mesh (<212µm)) was purchased from Acros. Methanol (CAS 67-56-1, HPLC grade) was purchased from Honeywell. All solutions prepared by deionized water.

Activated carbon and graphite

Graphite (CAS: 7782-42-5, power, <20 micro, synthetic) was purchased from Sigma Andrich. Graphite has a layered, planar structure. The individual layers are called graphene. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.

The two known forms of graphite, *alpha* (hexagonal) and *beta* (rhombohedral), have very similar physical properties, except for that the graphene layers stack slightly differently. The alpha form can be converted to the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated above 1300 °C. Graphite is applied in various technologies [37].

Activated carbon (AC) (CAS: 7740-44-0, untreated, granular, 8-20 mesh) was purchased from Sigma Andrich. AC composes of amorphous carbon and graphite layers with a complicated and heterogeneous structure. The pore distribution of AC can be categorised into three main groups, namely micropores ($d < 2.0$ nm), mesopores ($d = 2.0–50.0$ nm) and macropores ($d > 50.0$ nm). According to Yalçin and Sevinç, over 95% of the total surface areas of AC are commonly accounted by the presence of micropores distribution.

Biochar

BC is a form of black carbon which is synthesized through modern pyrolysis processes. All the biomass materials are the direct thermal decomposition of biomass in inner gas, which produces a mixture of solids (biochar), liquid (bio-oil), and gas (syngas) products.

Rice straw, taken in Ulsan city- South Korea, was clean, air dried and ground below 0.25 mm and kept in dark vials until further use. In this study, slow pyrolysis was applied to making BC. BC produced at different temperature levels of 250, 550 and 900 ^oC in 4 h under nitrogen gas (kept at 100 ^oC in 30 min before increasing the set temperature) were noted as RS250, RS550, RS900, respectively. Similarity, the Fe(0) embedded rice straw at 550 ^oC was conducted with rice straw and iron with the ratio of volume (95:5) under the above conditions.

With the surface BC coated Fe(0), the surface coating of BC by TA was performed in sorption experiments. Briefly, 7.5 g of BC was mixed with 500 mL of 5 g/L TA solution at 25 °C for 2 days. The mixture was centrifuged and the particles were washed repeatedly with deionized water under negligible detection of TOC in the supernatant. The particles were then freeze-dried. The coated TA was in the range of 51–140 mg/g depending on BC types.

Briefly, 25 g Fe(0) g and 400mL deionized water react with 10 mL Triton X-100 in the pressure reactions at 180 ^oC in 18 h, shaking 60-100 rpm. After that, the solution was filtered by 0.22 μm filter paper then washed with deionized water/ethanol (1:1, v/v) for 3 times. Solid was dried at 80 ^oC for 24 h. Ground rice straw mixed with above solid underwent the slow pyrolysis in the inert gas for 4 h at 550 ^oC.

All samples were stored in zipper bags, kept below 20 ^oC.

2.2.2. Batch experiments

The stock solution of phenol (100 mg/L) or PS was prepared in deionized water prior to each batch experiment. A sample contains 100ml of the PS/phenol stock solution (100 mg/L) and micrometer Fe (300 mg), the weight of activator (above synthesized materials) 100 mg. The initial pH was adjusted by NaOH (0.1 M) and H_2SO_4 (0.1 M) solutions. An aqueous solution (100 mL) was shaken at 180 rpm by water bath (HB-2053SW, Hanbaek, Kyunggi, Korea) at 22 ± 3^0C. All Erlenmeyer flasks were coved with tin foil. At selected time intervals (30, 60, 90, 120, 150, 210, 270 and 330 min), duplicate flasks were sacrificed. A 3 mL sample was collected and instantly separated from solution via filtration through a 0.45 μm membrane filter (Milipore, MA) for phenol analysis. For each experiment, controls with PS (or Fe(0), or synthesized materials) or oxidants were conducted in parallel under the same conditions.

In order to determine the effect of pH to degradation of phenol, the pH of the solution was controlled at the beginning of the reactions at 2.0, 3.0, 5.0, 7.0, 9.0, and 11.0, respectively. Additionally, pH experiments without Fe(0)/synthesized materials at 9.0 and 11.0 were prepared.

2.2.3. Analytical methods

The specific surface areas of BC were analyzed by Brunauer Emmett and Teller (BET) nitrogen adsorption technique at 77 K. Elemental C, N, O, and H contents of BC were determined using a VARIO MICRO elemental analyzer (Elementar, Germany). SU8010, HITACHI, Japan was applied to get SEM images of materials. pH was measured by pH meter (Orion 5star, Thermo Scientific, USA). 100mL of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH of the solution was adjusted from 2 and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.15 g of each BC or black carbon sample was added and the final pH was

measured after 48 h under agitation at room temperature. The pH_{pzc} is the point in the curve pH_{final} vs. pH_{inital} crosses the line $pH_{initial}=pH_{final}$.

With phenol, its concentration was determined by using high-performance liquid chromatography equipped with the ultra-violet detector (Ultimate 3000, DIONEX). The mobile phase used was 60% (v/v) methanol and 40% (v/v) ultrapure water. The flow rate 1.0 mL/min and the UV-VIS detector wavelength and the temperature of a pump were set at 224 nm, 25 ºC, respectively. Phenol was detected at retention time of 5.8 min.

2.3. Results and discussions

2.3.1. Properties of biochar and black carbon

Properties of five kinds of BC in different conditions (RS250, RS550, RS900, Fe(0) -embedded RS550 (5:95 v/v), RS550-coated Fe(0) (95:5 v/v)) and two kinds of black carbon (activated carbon, graphite) are summarized in Table 1.

Table 1. Properties of biochar, modified biochar, activated carbon and graphite

Type of biochar	pH	BET S.A. (m^2/g)	CEC (meq/100g)	PZC	Elemental content (%)			
					C	H	O	N
RS250	6.85	22.96	24.90	6.95	59.35	2.770	12.73	1.92
RS550	9.08	16.74	3.08	8.19	56.10	2.77	12.7	1.92
RS900	11.72	115.92	34.20	11.30	62.500	0.97	5.20	1.83
Fe(0)-embedded RS550 (Fe(0): biomass = 5: 95, v/v)	10.76	5.67	51.74	10.00	12.03	0.46	1.36	0.04
RS550-coated Fe(0) (Fe(0): biomass = 5: 95, v/v)	5.98	50.02		6.00				
AC	6.43	738.80	11.61	6.88	79.95	1.01	11.23	0.69
GR	3.75	11.60	5.40	4.86				

The results of basic characterization of RS biochar (Table 1 & Figure 1) show that content of C in RS900 is highest with 62.5%, BET S.A, pH, CEC, and PZC are 115.92 m^2/g, 11.72, 34.2 meq/100g, and 11.3, respectively. The elemental content of RS250 and RS550 is similar but pH, BET, CEC and PZC of them are slightly different.
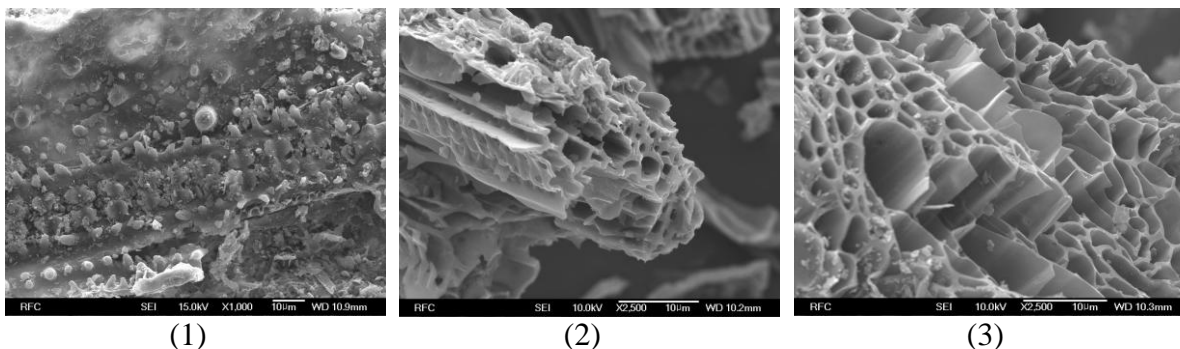
Figure 1. SEM images of (1) RS250, (2) RS550 and (3) RS900

2.3.2. Degradation of phenol by PS activated with Fe(0) and biochar.

The aim of these experiments is to evaluate the efficiency of various combinations (BC or AC or GR/Fe(0)) to activate PS for the removal phenol. Figures 2- 4 indicated the ability of degradation of phenol under different conditions. Without Fe(0) in PS, direct oxidation by PS or BC, RS550-coated Fe(0), RS550-embedded Fe(0)/AC, GR/PS did not result in the significant removal of phenol. Under 20% of initial phenol was removed in 340 min and the ratios depend on what kind of BC, modified BC, AC or GR presence in the reactions.

Over 30% phenol was decomposed with Fe(0)/PS, but the removal percentage were 82, nearly 49.2, 43.7, 89, 59.2, 58 and 80.1% in Fe(0) + AC + PS, Fe(0) + GR + PS, Fe(0) + RS250 + PS, Fe(0) + RS900 + PS, Fe(0) + RS550 + PS, Fe(0) + RS550-coated Fe(0) + PS and Fe(0) + Fe(0)-embedded RS550 + PS, respectively. PS by itself is unreactive towards with phenol because PS is unable to emit sulfate radical on its own. The degradation of phenol in BC, modified BC, AC or GR, and Fe(0) + PS are lower than the results in BC, modified BC or AC or GR/Fe(0)/PS. Adding a certain amount of BC, modified BC, AC and GR, the degradation of phenol speeds up which can be explained that BC, modified BC, AC and GR accelerate the degradation of a contaminated chemical. This phenomenon may be due to: i. oxygen-containing functional group on the surface of BC, modified BC, AC so may have acted as an activator of the electron-transfer mediator, decomposed persulfate to generate radical organics [34, 38-40] following below equations:

$$A_{surface} - OOH \ + \ S_2O_8^{2-} \longrightarrow \ A_{surface}\text{-}OO^{\cdot} \ + \ SO_4^{\bullet -} \ + \ HSO_4^{-} \quad (11)$$

$$A_{surface} - OH \ + \ S_2O_8^{2-} \longrightarrow \ A_{surface}\text{-}O^{\cdot} \ + \ SO_4^{\bullet -} + \ HSO_4^{-} \quad (12)$$

(A: activated carbon, biochar)

ii. The electron emitted follow the Equations 4 - 7 and exchange to PS to form radicals[23, 41-43]; iii. $\pi - \pi$ interaction on the surface of carbon compounds and their porous structure. The figures clear provided the detail efficiency in using various kinds of BC, modified BC, AC, GR to increase the removal rate of phenol because of their characteristics and properties.
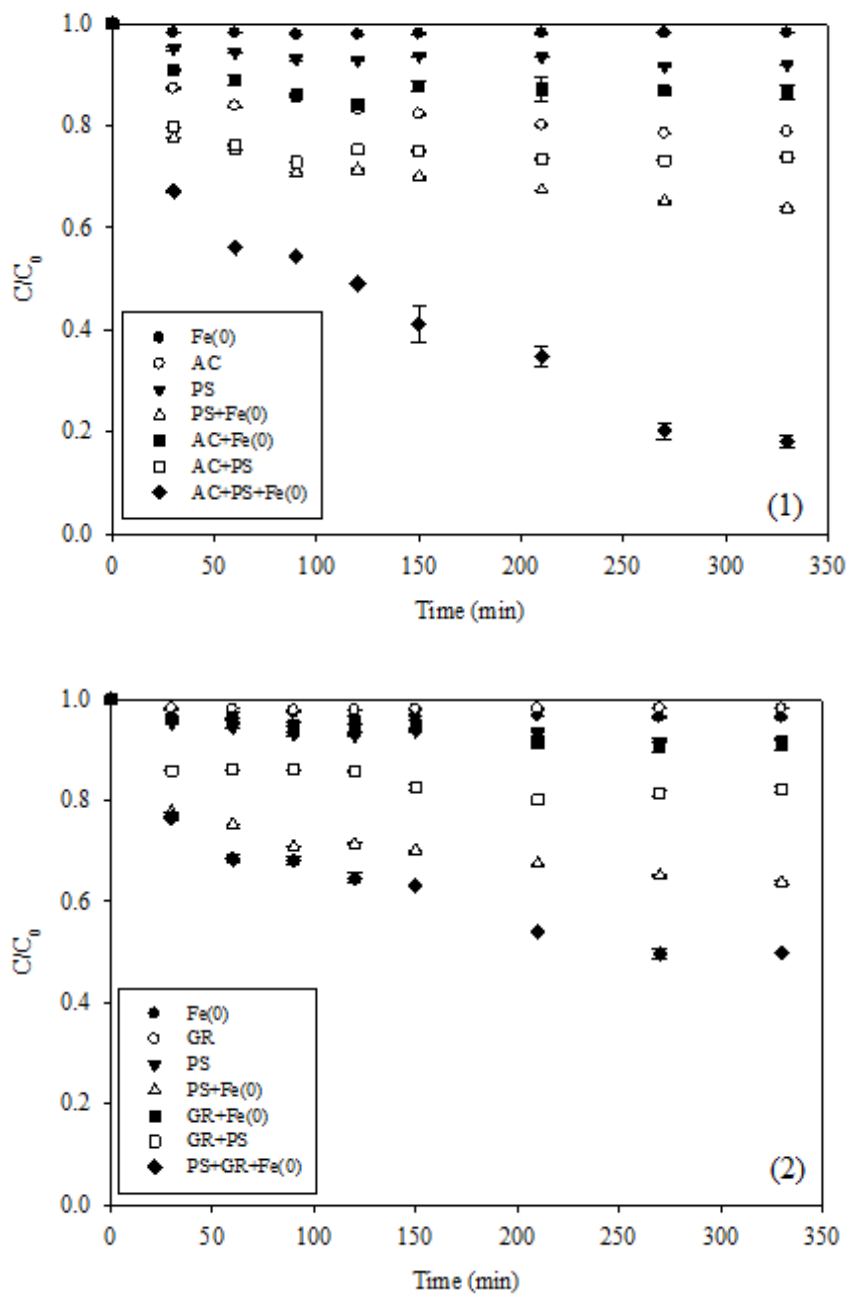
Figure 2. Phenol degradation by PS activated with Fe(0) and black carbon materials. Experiment conditions: pH = 7.0, [PS] = 100 mg/L, [Phenol] = 100mg/L, [Fe] = 300 mg:
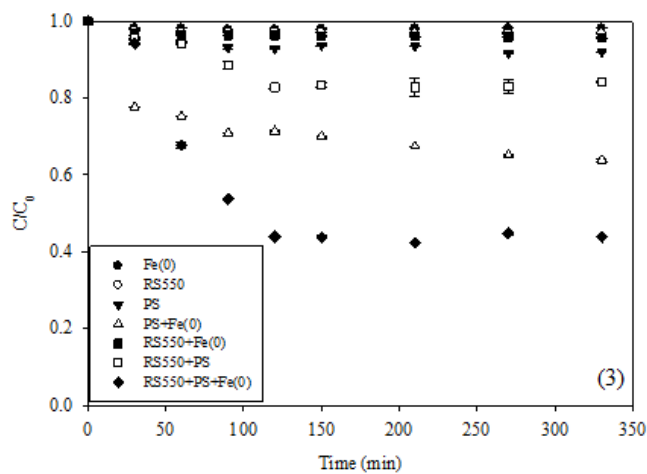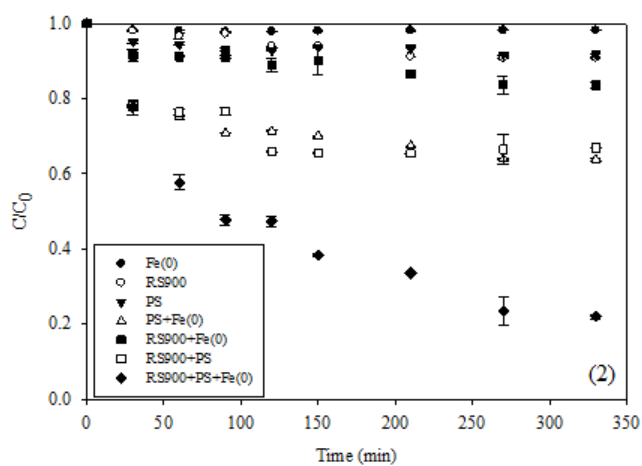**(1) [AC]=100 mg; (2) [GR]=100 mg**

Figure 3. Phenol degradation by PS activated with Fe(0) and black carbon materials.
Experiment conditions: pH = 7.0, [PS] = 100 mg/L, [Phenol] = 100mg/L, [Fe] = 300 mg:
(1) [RS250] =100 mg; (2) [RS900] =100 mg; (3) [RS550] = 100 mg

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Figure 4. Phenol degradation by PS activated with Fe(0)-embedded biochar and biochar-coated Fe(0). Experiment conditions: pH = 7.0, [PS] = 100 mg/L, [Phenol] = 100mg/L, [Fe] = 300 mg: (1) [Fe(0)-embedded RS550] = 100 mg; (2) [RS550-coated Fe (0)] = 100 mg

2.3.3. Effect of persulfate concentration

PS is the source of sulfate radical. The experiments emphasize the influence of PS content with concentration range from 1.06 x10^{-3} mM to 5.07 mM (10-1000 mg/L) to the phenol removal rate. PS mixed with Fe(0) and biochar or AC or GR at 300 mg, 100 mg, respectively. Figures 5- 7 shown the increasing percentage of phenol removal from 19 % to 81%, 31% to 59%, 9% to 91%, 27% to 61% and 31% to 62%, 84%, 87.9% under the AC/Fe(0)/PS, GR/Fe(0)/PS, RS900/Fe(0)/PS, RS250/Fe(0)/PS, RS550/Fe(0)/PS, RS550-coated Fe(0)/Fe(0)/PS, Fe(0)-embedded RS550/Fe(0)/PS respectively. At low PS concentration (PS $\leq$ 50 mg/L), increasing concentration of PS would lead to increase the sulfate radicals and enhance the degradation of contaminated compounds [23, 32, 44-47]. At higher initial PS concentration, according to Equations 4, 5, 9, and 10 showed that Fe^{2+} can be generated from the surface of Fe(0) lead to richer Fe^{2+} density in solution. Emitted Fe^{2+} react with $SO_4 \bullet^-$ until the Fe^{2+} reduced, which causes unable to produce sulfate radical by modified persulfate. Moreover, $SO_4 \bullet^-$ can be inhibited by Fe^{2+} (Equation 13). In the extremely PS concentration, however, the phenol degradation efficiency decreases. In the results of this part, the degradation of phenol depends on the activator because the influence of structure and surface chemistry of biochar, modified biochar, AC, GR (carbon material) and inhibition of sulfate radical in the presence of Fe^{2+} [13, 17, 45, 48]. Phenol degradation percentage is lowest with 10 mg/L PS, the optimum PS is 500 mg/L in the AC, RS900, RS550, RS250/Fe(0), the index is 1000 mg/L in GR/Fe(0).
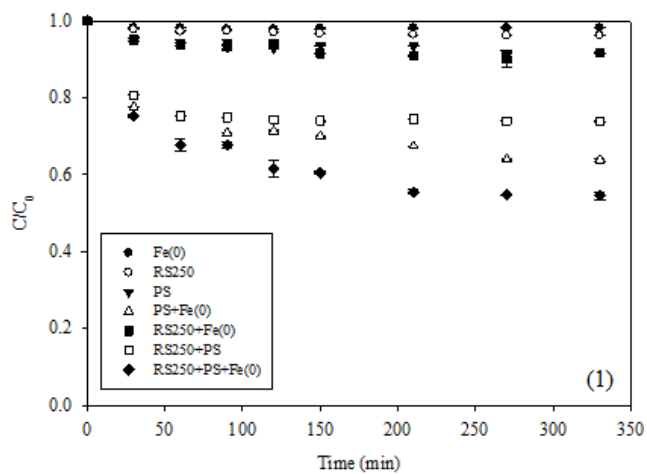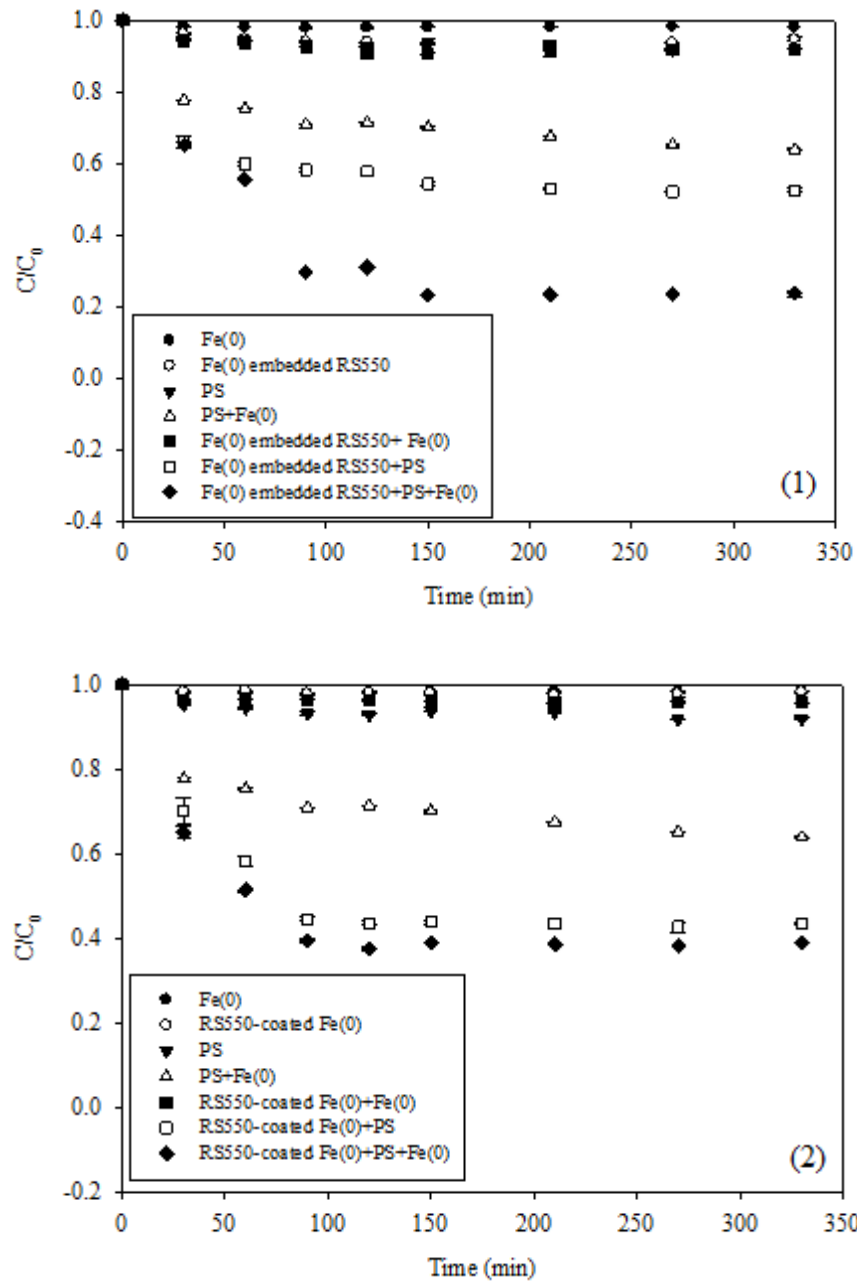
**Figure 5. Effect of PS concentration on Phenol degradation by
PS activated with Fe(0) and black carbon materials.
Experiment conditions: pH = 7.0, [Phenol] = 100 mg/L, [Fe (0)] = 300 mg:
(1) [AC] = 100 mg; (2) [GR] = 100 mg**

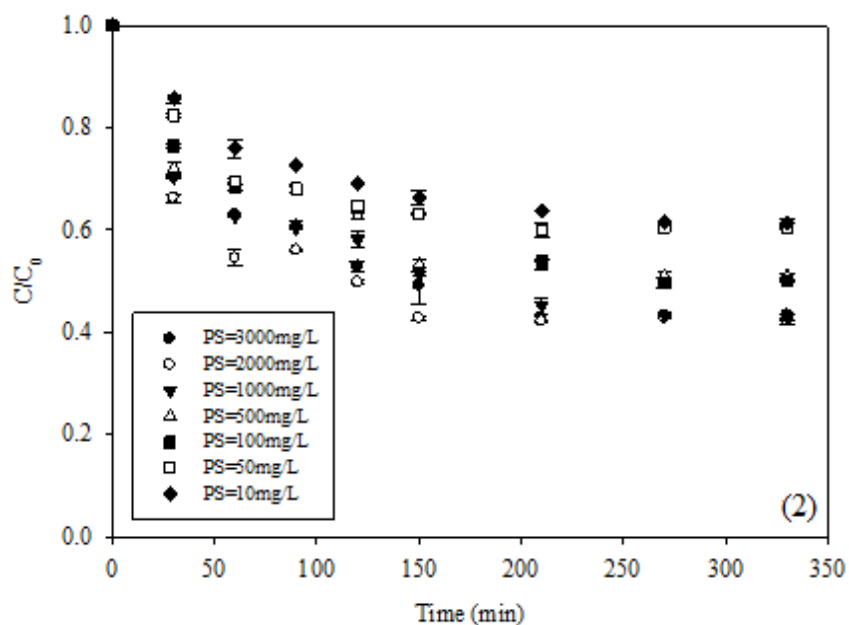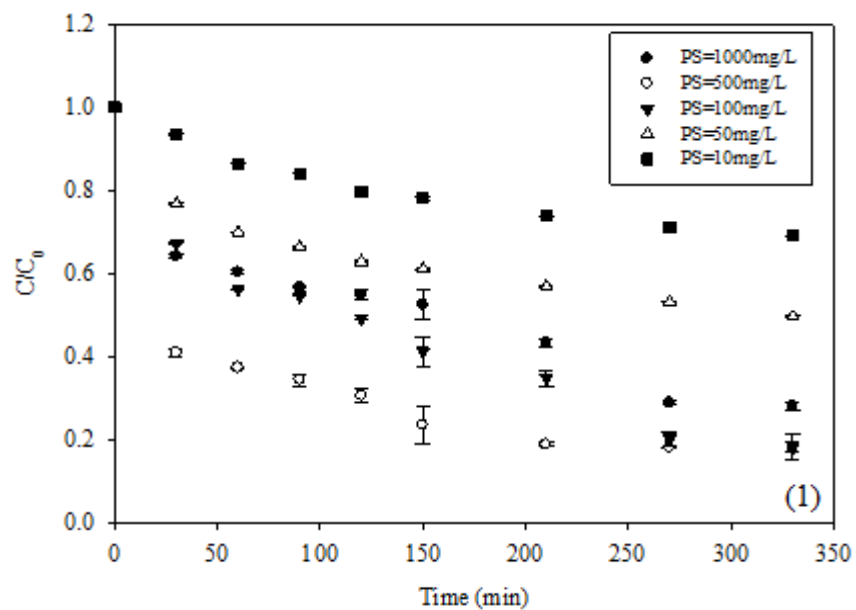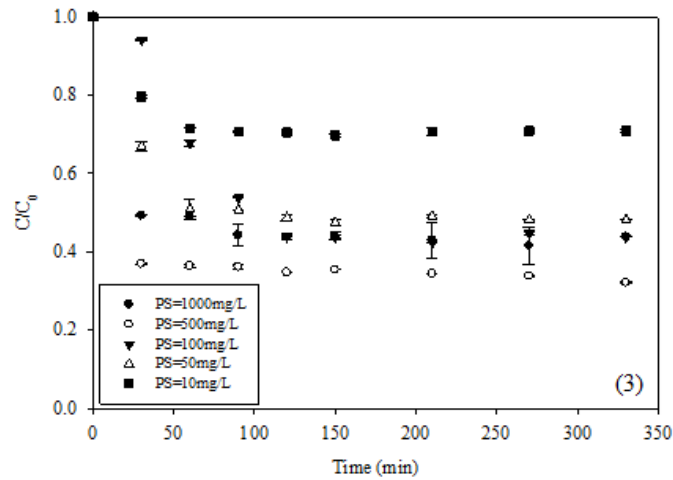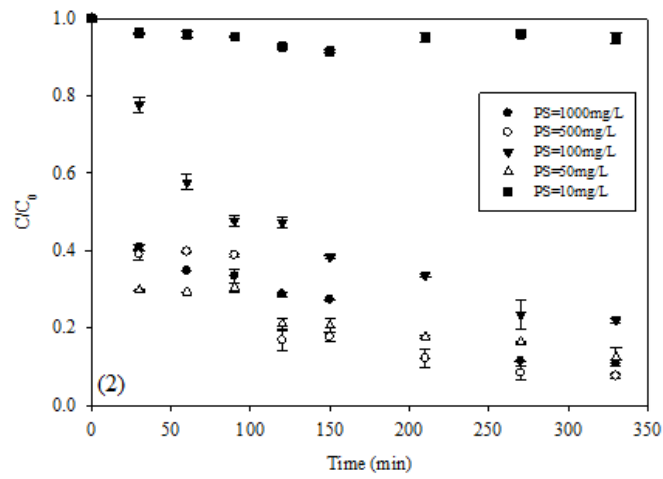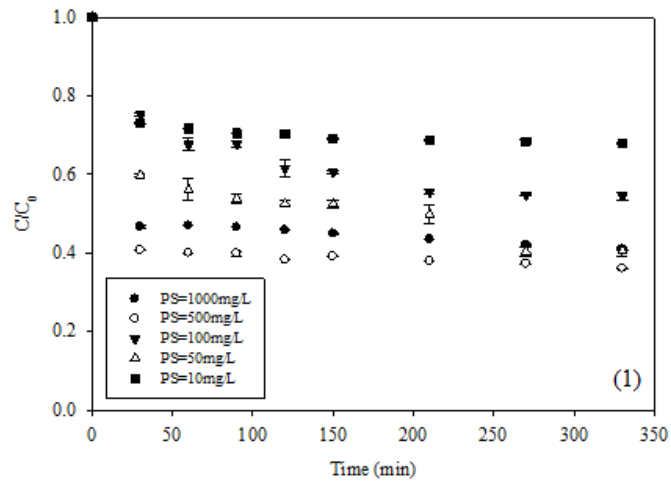**Figure 6. Effect of PS concentration on Phenol degradation by
PS activated with Fe(0) and black carbon materials.
Experiment conditions: pH = 7.0, [Phenol] = 100 mg/L, [Fe (0)] = 300 mg:
(1) [RS250] = 100 mg; (2) [RS900] = 100 mg; (3) [RS550] = 100 mg**
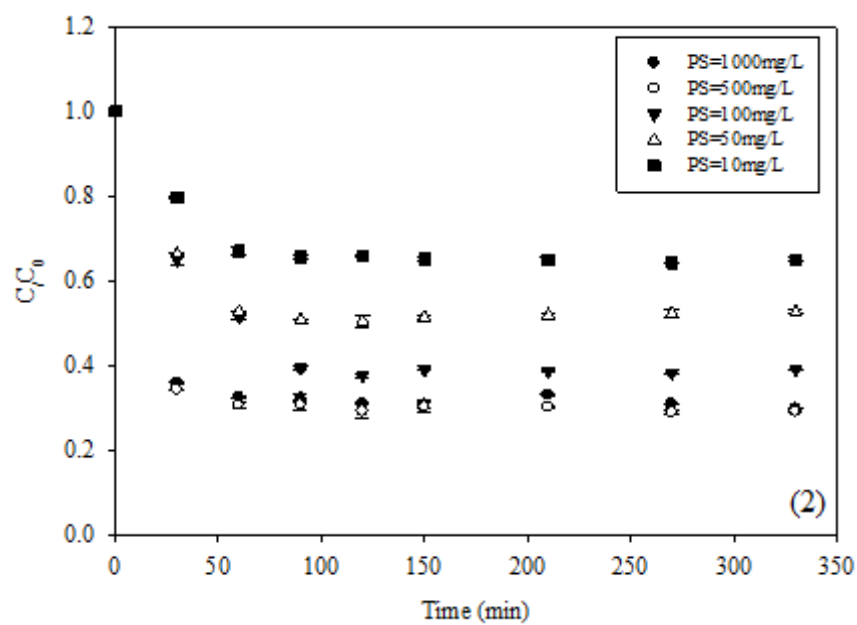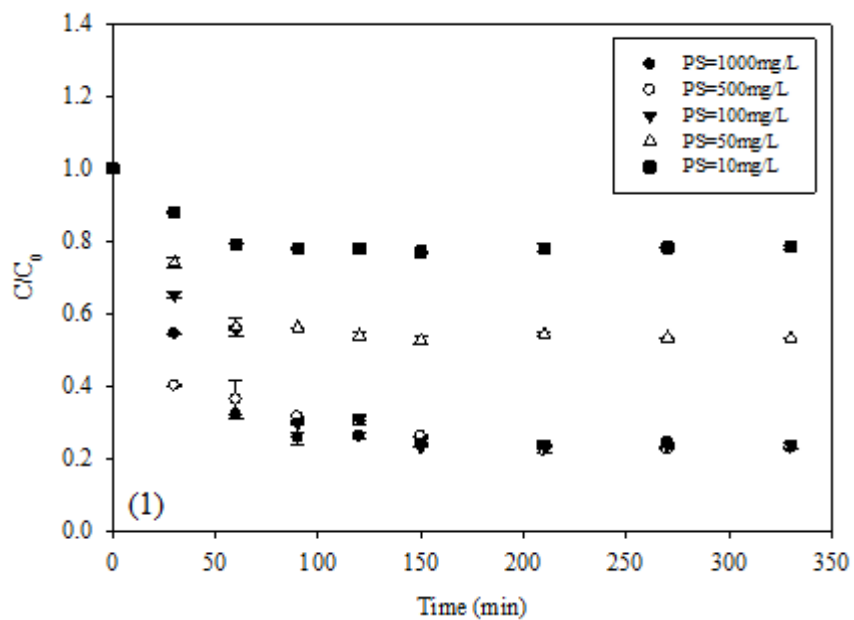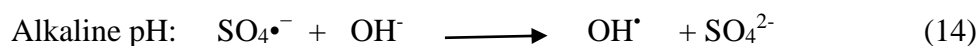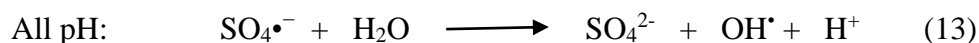
**Figure 7. Effect of PS concentration on Phenol degradation by
PS activated with Fe(0) and black carbon materials.**
Experiment conditions: pH = 7.0, [Phenol] = 100 mg/L, [Fe (0)] = 300 mg:
(1) [Fe(0)-embedded RS550] = 100 mg; (2) [RS550-coated Fe (0)] =100 mg
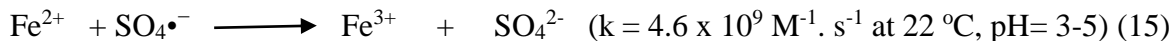
21

2.3.4. Effect of initial pH

The aim of all experiments in this part is finding the effect of pH range and optimal pH in the presence of different activators. The weight of biochar (RS250, RS550, RS900), modified BC, AC or GR mixed with Fe(0) is 100 mg and 300 mg, respectively; PS dosage is 1.0 mmol in 340 min reaction. The degradation of phenol was examined at pH range (2-11). Initial pH was adjusted by H_2SO_4 and NaOH and the results showed that the significant role of pH in phenol degradation with all activators which applied in this study. Figures 8- 10 indicated the variations in phenol removal rate efficiencies in all experiments under different pH. The pH increases from 2 to 11, PS was activated by biochar, modified BC, AC, or GR/Fe(0) to emit free radicals. To form $SO_4^{\bullet-}$ showed in the Equations 3 - 10, to form $OH^{\bullet}$ following Equations 13-14 [23, 44-46].

$$\text{All pH:} \qquad SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + OH^{\bullet} + H^+ \qquad (13)$$

$$\text{Alkaline pH:} \quad SO_4^{\bullet-} + OH^- \longrightarrow OH^{\bullet} + SO_4^{2-} \qquad (14)$$

The rate constants for Equations 11- 14 are of the orders of k $[H_2O] < 2.10^3$ s^{-1} [34] and $(6.5 \pm 1.0).10^7$ M^{-1} s^{-1} [35] respectively. In addition, Norman et al., concluded that the reaction rate constant of Equation 9 is small by comparison with those for the sulfate free radical reactions with organic compounds [34] $SO_4^{\bullet-}$ and $OH^{\bullet}$ is possibly responsible to decay contaminated-organics and either of radical may predominate over the other depending on pH conditions. All radicals react with organic compounds by three main pathways including hydrogen addition, hydrogen abstraction, and electron transfer. Although standard reduction potential of $SO_4^{\bullet-}$ is higher than its $OH^{\bullet}$ at neutral pH but all radical ability to degrade contaminated-organic or inorganic under different acidic conditions.

The results of all experiments indicated the optimum pH is 2, the percentage of phenol removal with the presence of AC/Fe(0)/PS, RS900/Fe(0)/PS, RS550-coated Fe(0)/ Fe(0)/PS, Fe(0)-embedded RS550/Fe(0)/PS are 81.5, 83.9, 74 and 78% respectively. These ratios with the presence of GR/Fe(0)/PS, RS550/Fe(0)/PS and RS250/Fe(0)/PS, are lower, which data are around 54, 40.1 and over 43%, respectively. The reason explains for the ability to degrade phenol is $SO_4{}^{•-}$ which emitted by activators and Fe^{2+} is the source of the electron, which exchanges PS to form sulfate radicals (Equation 7). But at the pH condition, Buxton et al., insisted the $SO_4{}^{•-}$ is a scavenger of Fe^{2+} following Equation 15 [46] lead to in some case phenol removal rate of pH 7 is lower than it is in pH 3 and pH 5.

$$Fe^{2+} + SO_4{}^{•-} \longrightarrow Fe^{3+} + SO_4{}^{2-} \quad (k = 4.6 \times 10^9 \text{ M}^{-1}.\text{ s}^{-1} \text{ at } 22 \text{ °C, pH= 3-5}) \quad (15)$$

At pH 9 and pH 11, the content of phenol in contaminated samples is lower than in acidic range because of Equation 13. $SO_4{}^{•-}$ can be change $OH^{•}$ in alkali condition (Equation 14). The percentage of phenol removal are around 43% in AC/Fe(0)/PS, GR/Fe(0)/PS, around 41% in RS250/Fe(0)/PS, RS550/Fe(0)/PS, RS900/Fe(0)/PS, RS550-coated Fe(0)/ Fe(0)/PS or Fe(0)-embedded RS550/Fe(0)/PS.

In the other hand, without Fe(0) and RS250, RS550, RS900, modified BC, AC or GR in the pH 9 and pH 11, the removal rate of phenol is lower than other conditions (around 5%). From results of all experiments, the report demonstrated the significant of Fe(0)/ BC, AC or GR micro-electrolysis in removal phenol in different pH.
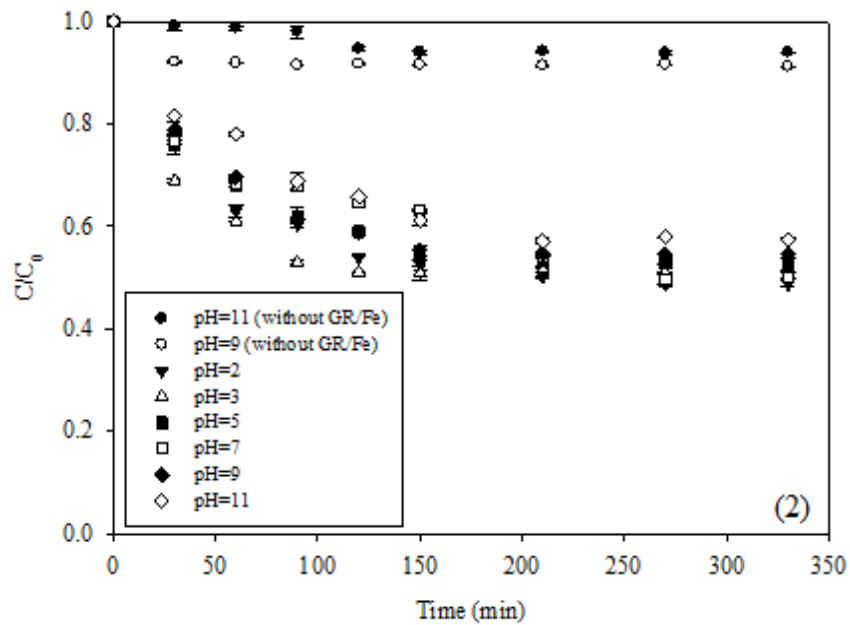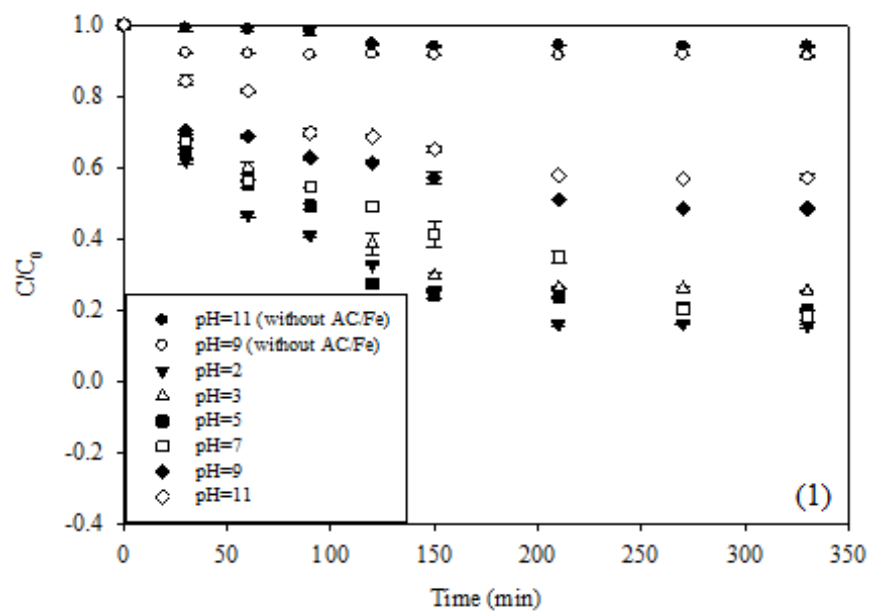
**Figure 8. Effect of initial pH on Phenol degradation by
PS activated with Fe(0) and black carbon materials.
Experiment conditions: [Phenol] = 100mg/L, [PS] = 100mg/L, [Fe (0)] = 300 mg:
(1) [AC] = 100 mg; (2) [GR] = 100 mg**
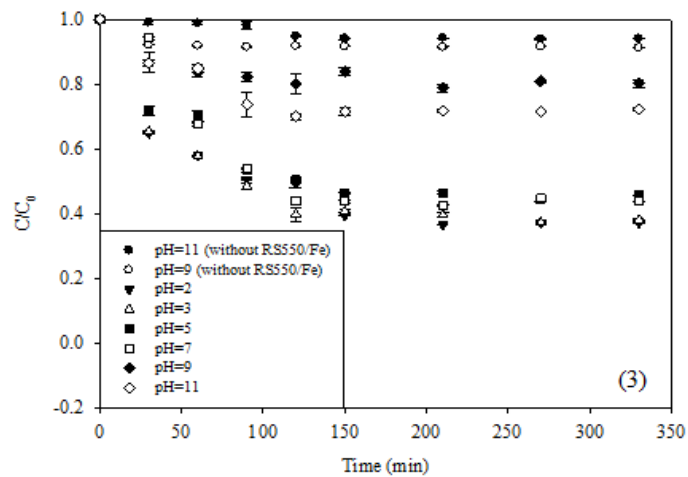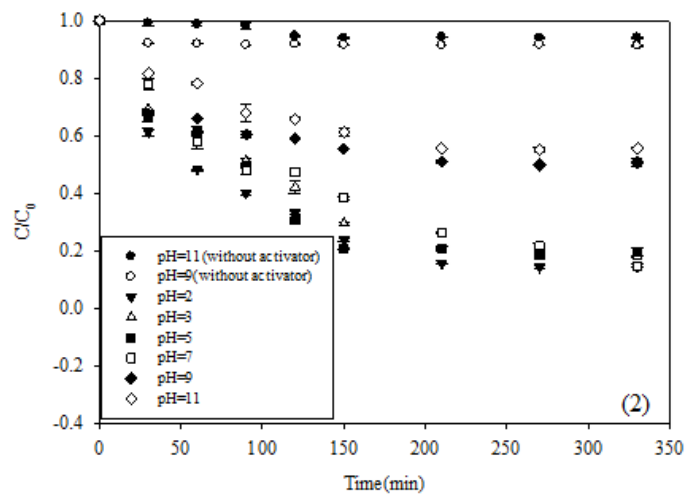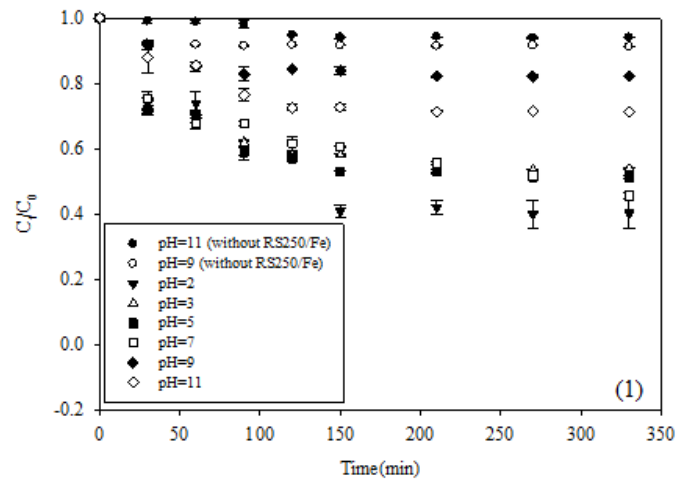
Figure 9. Effect of initial pH on Phenol degradation by PS activated with Fe(0) and black carbon materials.
Experiment conditions: [Phenol] = 100mg/L, [PS] = 100mg/L, [Fe (0)] = 300 mg:
(1) [RS250] = 100 mg; (2) [RS900] = 100 mg; (3) [RS550] = 100 mg
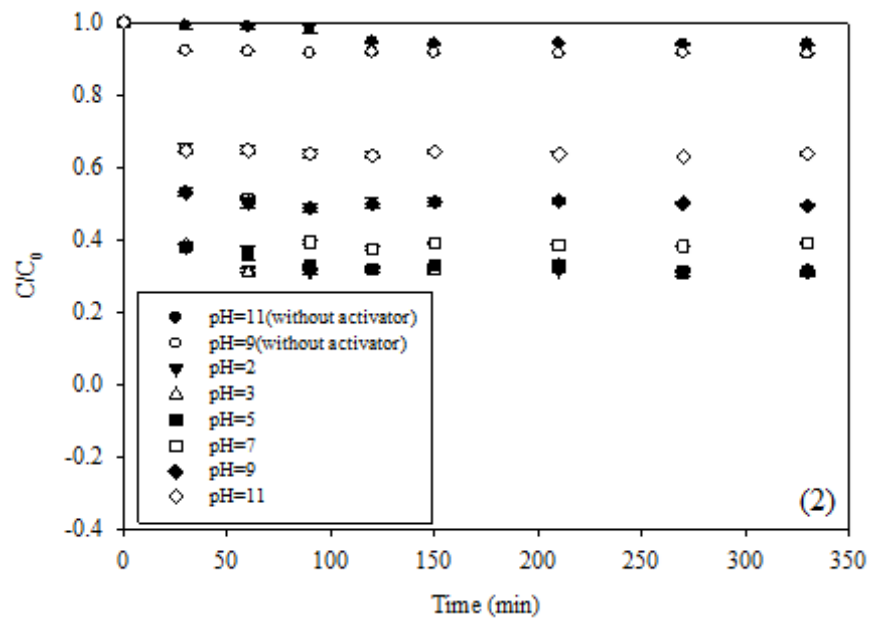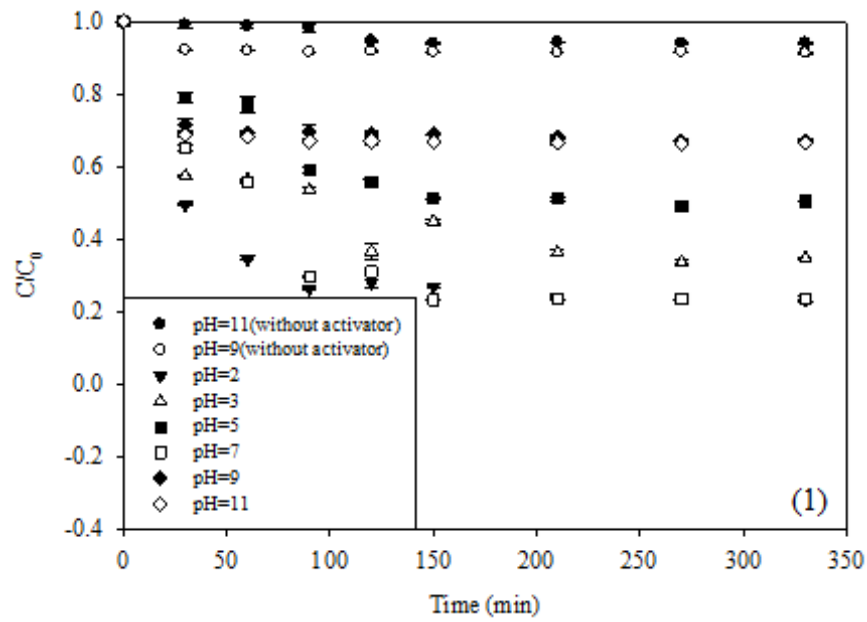
Figure 10. Effect of initial pH on Phenol degradation by
PS activated with Fe(0) and black carbon materials.
Experiment conditions: [Phenol] = 100mg/L, [PS] = 100mg/L, [Fe (0)] = 300 mg:
(1) [Fe(0)-embedded RS550] = 100 mg; (2) [RS550-coated Fe (0)] =100 mg

2.3.5. Effect of Fe(0), PS and BC dosage

All experiments, in this part, examined the effect of catalyst (including the weight of Fe(0), the weight of RS550 and the concentration of PS) to the phenol degradation. Figure 11 demonstrated the phenol removal rate with the presence of different weight of Fe(0). Phenol degradation efficiency was 63.7% with 300 mg Fe(0) in the PS system which is lower compared to 77, 81 and 78.5% phenol degradation with the 600 mg, 1200 mg, 1800 mg of Fe(0). Equations 4, 5, 9, 10 indicated that the presence of Fe(0) is more, the Fe^{2+} more which mean that more electron emits to the solution to exchange with sulfate ion and radicals were formed. In contrast, Equation 15 also showed that Fe^{2+} is an inhibiting factor to form sulfate radical in solution. Figure 12 provided the ratio of phenol removal with 100 mg, 200 mg, 400 mg, 600 mg of RS550. 200 mg RS550 in Fe(0)/PS removed nearly 76% phenol in contaminated-water. Similarity, the optimum PS concentration is 500 mg/L (Figure 13) with around 43% phenol removal compare to 51.2, 53, and 52% phenol removal with 100 mg/L, 2000 mg/L, 6000 mg/L PS, respectively. Explain the role of PS concentration in the oxidation reaction was shown in the effect of initial PS. In above experiments indicated that Fe(0) and PS could remove unremarkable phenol amount. The degradation efficiencies of phenol were 87, 95.2, 95, and 97.2%. for the Fe(0) (mg): PS (mg/L) of 1200 mg and 1000 mg/L, 1800 mg and 1500 mg/L, 2400 mg and 2000 mg/L, 3000 mg/L, and 2500 mg/L, weight of RS550 in all experiments is 200 mg, respectively (Figure 14). The results showed that Fe(0) and PS with RS550 could effectively activate PS to generate radical through Equations 4 - 5. Besides, hydroxyl radical can be formed in water to form hydroxyl radical, which inhibited the oxidation phenol [18, 49]. Figure 14 provided the optimum of Fe(0) and PS concentration with 200 mg RS550 is 3000 mg Fe(0) and 2500 mg/L PS.
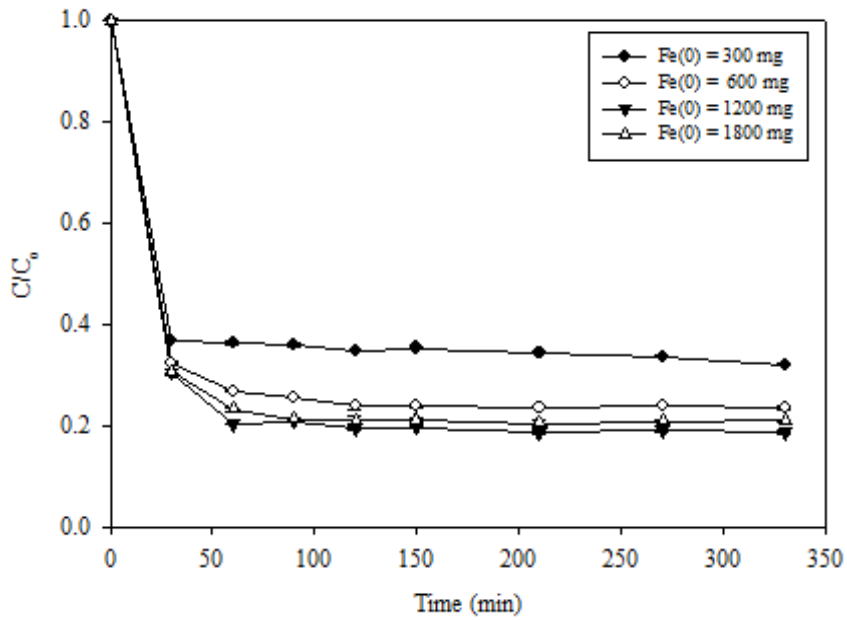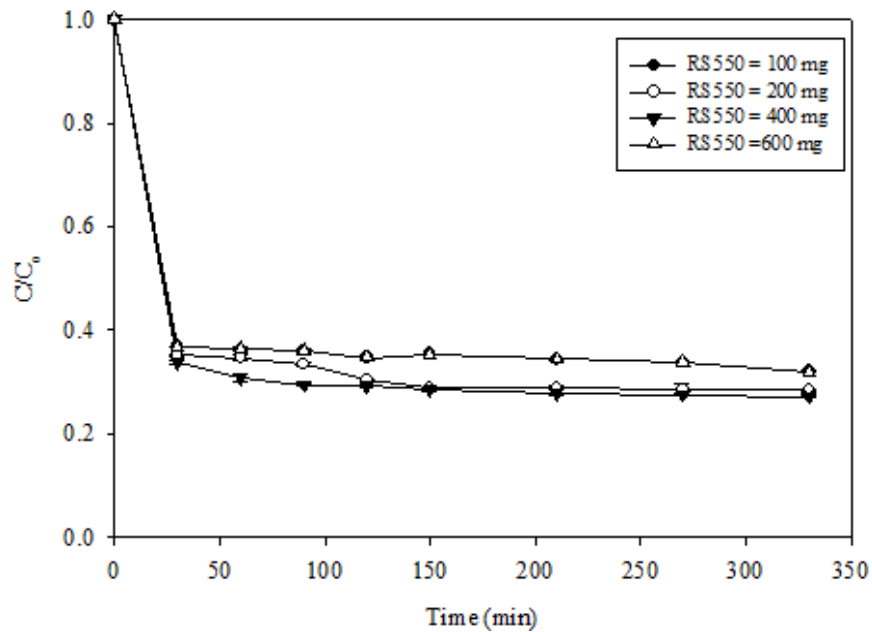
Figure 11. Effect of Fe(0) on phenol degradation by PS activated with Fe(0) and black carbon materials. Experiment conditions: initial pH:7.0, [Phenol] = 1.0 mM, [PS] = 2.5 mM, [RS550] = 100 mg.

Figure 12. Effect of biochar dosage on phenol degradation by PS activated with Fe(0) and black carbon materials. Experiment conditions: initial pH:7.0, [Phenol] = 1.0 mM, [PS] = 2.5 mM, [Fe(0)] = 300 mg.

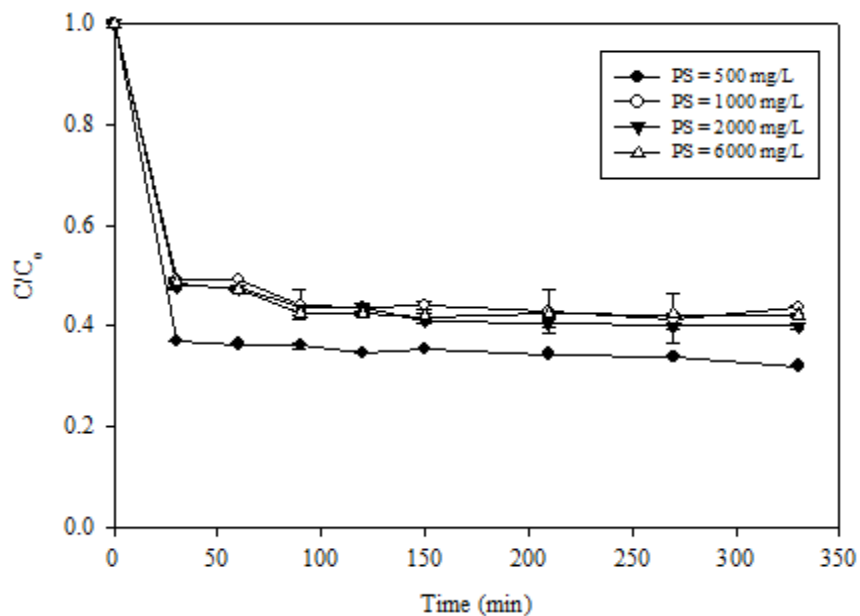**Figure 13. Effect of PS on Phenol degradation by PS activated with Fe(0) and black carbon materials. Experiment conditions: initial pH:7.0, [Phenol] = 1.0 mM, [Fe(0)] = 300 mg, [RS550] = 100 mg.**
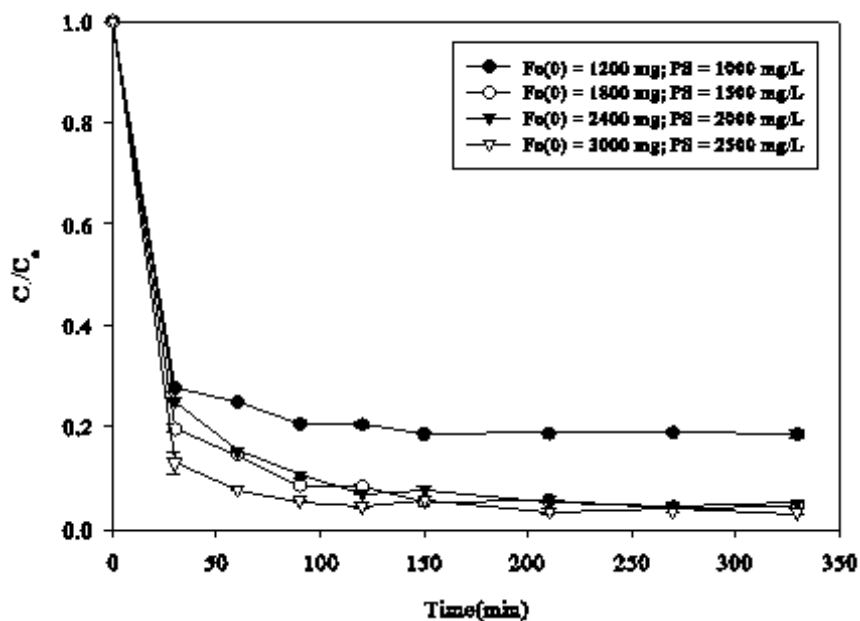
Figure 14. Effect of ratio of PS and Fe(0) on phenol degradation by PS activated with Fe(0) and black carbon materials. Experiment conditions: initial pH:7.0, [Phenol] = 1.0 mM, [RS550] = 200 mg.

2.3.6. Role of sulfate and hydroxyl radicals

Through the quenching experiments supported us to deeply understand the contribution and role of $SO_4\bullet^-$ and $OH\bullet$ in decay contaminated compounds. According to the reports of Neta et al., 1988 and Buxton et al., 1988, Anipsitakis et al., 2004 [12, 17, 50, 51]

MeOH and TBA are used to discriminate between $SO_4\bullet^-$ and $OH\bullet$ base on the their specific. MeOH, containing α-hydrogen, is considered as an examine quencher for both $SO_4\bullet^-$ (k_{11} = 1.1 x 10^7 $M^{-1}s^{-1}$) and $OH\bullet$ (9.7 x 10^8 $M^{-1}s^{-1}$). TBA, without containing α-hydrogen, is as a quencher for $SO_4\bullet^-$ (k_{21} = 4.0 x 10^5 $M^{-1}s^{-1}$, k_{22} = 6.0 x 10^8 $M^{-1}s^{-1}$). With addition 0.65 M MeOH, and 0.65 M TBA into reaction solution ($n_{Fe(0)}$ = 0.053 mol; n_{PS} = 0.0013 mol; $V_{solution}$ = 100 ml; pH= 7; $m_{BC; AC; GR}$ = 200 mg). All samples are shaking at room temperature, 180 rpm, 330 min. Solution was filtered by the 0.45μm membrane filter. Table 1 showed the results obtained for the phenol degradation with and without scavenging agents. The table also indicated the effect of alcohols is different with the different activators (BC900, BC550, BC250, AC, and GR). With the presence of MeOH, the phenol degradation in RS900, RS550, RS250, AC, GR are 10.3, 11.3, 15.1, 9.8, and 5.7%, respectively. The results with the presence of TBA are 20.25, 13.9, 16.5, 21.3, and 7.1%. The results revealed that MeOH and TBA could quench the removal rate of phenol and the effect of TBA to the degradation of phenol is lower than the effect of MeOH. In conclusion, the oxidation of persulfate radical ($SO_4\bullet^-$) is stronger than oxidation of hydroxyl radical ($OH\bullet$).

Table 2. Effect of MeOH and TBA on the degradation of phenol (1.0 mM) by PS(0.053mol) in the presence of Fe (0)/BC or AC or GR (initial pH = 7)

BC, AC and GR	Phenol degradation(%)		
	Blank	MeOH	TBA
RS900	98.5	10.3	20.2
RS550	97.3	11.3	13.9
RS250	92.3	15.1	16.5
AC	98.2	9.8	21.3
GR	87.1	5.7	7.1

*Blank: no alcohols

2.3.7. Role of BC, modified BC, AC and GR in phenol oxidation

With above the results, the role of BC, modified BC, AC, GR in phenol degradation is the simultaneous combination of two main activated persulfate ways: activated PS by heterogeneous transition metal catalysts and nonmetal carbon catalysts. Metal catalysts, namely, Fe(0) accelerate to generate electron which reacts with $S_2O_8^{2-}$ to form radicals (Equations 1-4 and Equations 6-8)- the results showed in Figure 1.

Non-metal carbon catalyst, in the research in 2004, Yuan et al., reported that on the surface of AC, GR, BC, and modified BC contain functional groups such as ⁻COOH, COO⁻, ⁻OH [34] which have a significant role to active PS directly as an electron-transfer mediator for emitting of $SO_4•^-$ [43, 52] and organic radicals $A_{surface}$-OO·, $A_{surface}$-O· (A: activated carbon, biochar) (Equations 11-12). Besides, AC, GR, BC or modified BC as PS activator depends on their impurities surface and mechanism reaction is similar to the AC activation of hydroperoxide as follow [12, 53, 54]

$$C-\pi + S_2O_8^{2-} \longrightarrow C-\pi^+ + SO_4^{2-} + SO_4•^- \qquad (16)$$

$$C-\pi^+ + S_2O_8^{2-} \longrightarrow C-\pi + SO_4^{2-} + SO_4•^- \qquad (17)$$
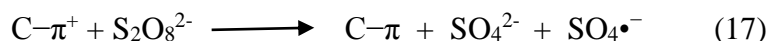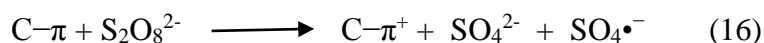
Moreover, AC, GR, BC, modified BC have been used as an adsorption to support metal catalysts to induce adsorption and accelerate to decay contaminated–water by $SO_4•^-$. With above

reasons, we infer that the RS250, RS550, RS900, modified BC, AC, and GR act a significant role to enhance the phenol degradation.

CHAPTER 3. DEGRADATION OF TOTAL PETROLEUM HYDROCARBON IN DIESEL OR BIODIESEL-CONTAMINATED SOILS BY PERSULFATE ACTIVATED WITH IRON-BEARING MATERIALS.

3.1. Introduction

Leakage and spills diesel, biodiesel from activities of human, technologies lead to polluted soil or sand. As we know petroleum diesel, also called petrodiesel, or fossil diesel is the most common type of diesel fuel. It is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 35 °C (662 °F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule, account for around 25% aromatic hydrocarbons, 75% saturated hydrocarbons and other elements [55].
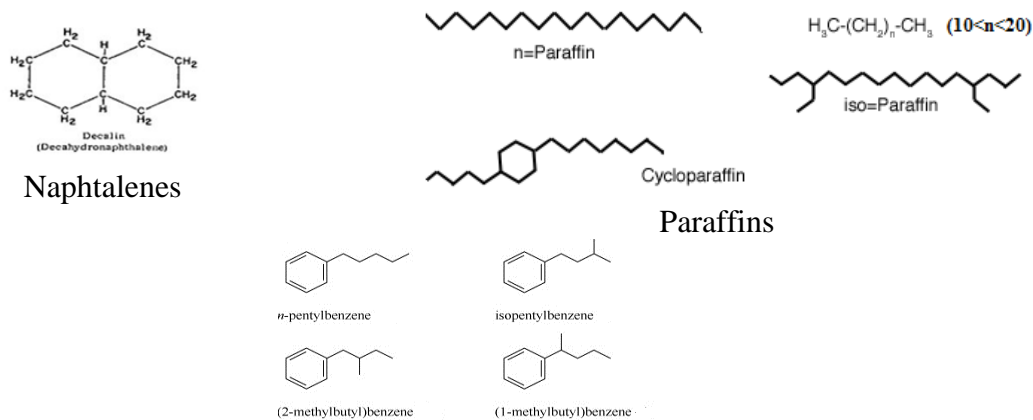
Figure 15. Alkylbenzenes

Biodiesel: known as fatty-acid methyl ester or biodiesel, is obtained from vegetable oil or animal fats (bio lipids) after the trans-esterified with methanol. It is the product of many types of oils, the most common being rapeseed oil (rapeseed methyl ester, RME) in Europe and soybean oil (soy methyl ester, SME) in the United State. Biodiesel contains over 96.5% ester and other addictive chemicals [56].
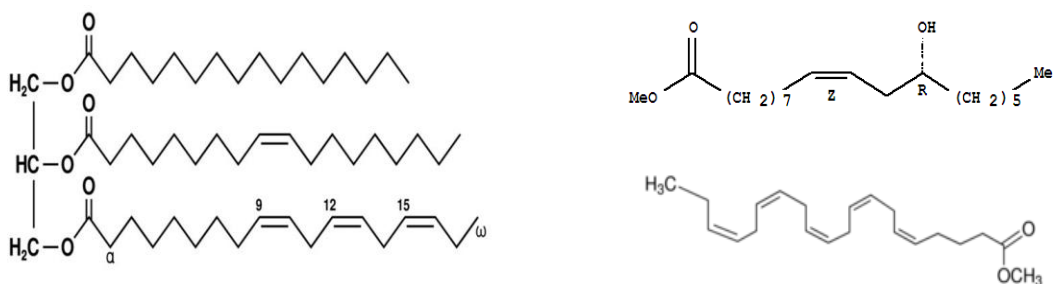
Figure 16. Some kinds of esters in biodiesel

With above component of diesel and biodiesel, finding a method to treat diesel and biodiesel

to limit disadvantage is important. Up to date, several treatment methods have been purposed

for the remediation of total petroleum hydrocarbon (TPH) contaminated soil or sand. The pre-

vious studies indicate a large of the method to TPH. However, each method has disadvantages

and advantages. In this study, activated PS by Fe(0) and iron compounds were applied to de-

grade diesel or biodiesel [57].

3.2. Materials and methods

3.2.1. Materials

Diesel and biodiesel were purchased from the gasoline in Ulsan city, South Korea. Character-

istics of the soil in this study and element contents which showed in the Tables 3-4.

Table 3. Characteristics of the soil used in this study

pH	Loss on ignition (%)	Particle size distribution			Minerals*
		Sand (%)	Silt (%)	Clay (%)	
6.3	2.5	20.0	75.1	4.9	Quartz, feldspar, kaolinite, goethite

* Identified by power X-ray diffraction analysis

Table 4. Elemental contents of the soil used in this study (unit: wt%)

Al	Ca	Cr	Fe	K	Mg	Mn	Na	P	Si	Ti
20.89	0.33	0.03	10.08	1.10	4.46	0.18	1.02	0.06	52.38	1.36

* Quantified by X-ray fluorescence spectrometer

Other chemicals: Potassium persulfate (extra pure, $\geq 98\%$) was purchased from DC Chemical

Co. Ldt (South Korea). N-hexane (CAS: 110-54-3, extra pure, 95%) were purchased from OCI

Company Ltd (South Korea). Dichloromethane (CAS: 75-09-2, 99.5%), acetone (CAS: 67-64-1, extra pure, 99.5%) were supplied by Samchun company (South Korea). Silica gel blue (CAS: 7631-86-9, medium granular) was provided by Dea Jung company. Iron (CAS: 7439-89-6, 99%, power, -70 mesh ($< 212\mu m$)) was obtained from Acros. The FeS (CAS: 1317-37-9, technical grade), the Fe_3O_4 (CAS: 1317-61-9, power, < 5 μm, 95%), the Fe_2O_3 (CAS: 1309-37-1, power, < 5 μm, $\geq 99\%$) were used for this study.

All solutions prepared by deionized water.

3.2.2. Batch experiments

To synthesized contaminated soil, a natural soil sample from Ulsan metropolitan city was collected, air dried and ground to pass through a 300 μm sieve. A pre-determined amount of diesel or biodiesel was mixed with the dried soil or sand to make 5000 mg/Kg of TPH. All artificial contaminated soil or sand was stored under 5 °C in the dark. Initial TPH concentration of soil or sand was periodically monitored before starting each batch experiment.

PS solution (250 mg/L) was prepared by deionized water before each batch experiment. 40 mL of the PS and 8.0 gram of contaminated soil or sand was added to a 100 mL brown glass vial with Teflon end caps. The vials were shaken sideways a 180 rpm in a sideways using a shaking water bath (HB-2053SW, Hanbaek, Kyunggi, Korea) at 22 $\pm 3^0$C. To examine the effects of Fe(0) and iron compounds on the oxidation-reduction of TPH in soil or sand. The weight of Fe(0) and iron compounds doses in the fix amount of PS 250 mg/L were: 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 gram per vial. At the selected time intervals: 1, 2, 3, 5, 7, and 12 h, duplicate vials were sacrificed and each soil sample was immediately separated from solution through filter paper 0.47 μm (Glass microfiber filters-Whatman). For each experiment, controls without Fe(0) or iron compounds or without PS and oxidant were conducted in parallel under identical conditions.

3.2.3. Analytical methods

The TPH of soil and sand were determined following the Korean standard method for analysis. The collected soil samples were extracted two times with 80 mL of dichloromethane using a sonifier (Model 450, Branson Ultrasonics Co., Danbury, CT, USA) set at duty cycle 50%, pulse mode 1 second for 3 min. After filtration with filter paper 0.47 µm (Glass microfiber filters-Whatman), moisture in the extract was removed by adding 20 gram Na_2SO_4 and the extract was again with filter paper 0.47 µm (Glass microfiber filters-Whatman) and condense to 2 mL using evaporator (HS-2050S, Hahnshin Scientific, Co, Kyunggi, Korea). The extracted sample (1 µL) was injected into gas chromatography (GC, Model 1000, Dani, Italy) equipped with a flame ionization detector and HP-5 capillary column (0.25 µm, 0.32 mm x 30 m, Agilent Technologies, Santa Clara, CA, USA). The carrier gas was ultrapure helium and injector volume was 2 µL. The injector and detector temperature were programmed to increase from 50 ^{o}C (2 min) to 320 ^{o}C (10 min) at 10 ^{o}C/min. The separated solution was also extracted with n-hexane/acetone (1:1 v/v) using vortex shaker for 3 min and the TPH of extract was determined using GC to add up the TPH concentrations.

3.3. Results and discussions

3.3.1. Treatment diesel/biodiesel-contaminated soil by Fe(0)-activated persulfate

To evaluate the ability of Fe(0)/PS system to remove TPH in diesel in contaminated soil and sand, the Figure 17 indicated that the removal rate of TPH on soil is over 80% compared to 52.8% on sand after 12 h. The main reason which explains this diversity is component of sand and soil.

Similarity, the ability of Fe(0)/PS to degrade biodiesel soil and sand show in Figure 17. The TPH removal is depending on the ratio of catalyst (Fe(0)) in PS. The figures demonstrate the highest removal. The of TPH is nearly 70% on the presence of 5.0g Fe(0)/PS. However, the

ratios can be changed following the contamination highest TPH removal rate is 72.8% with

the presence of 2.0 g Fe(0) and 250 mg/L PS.
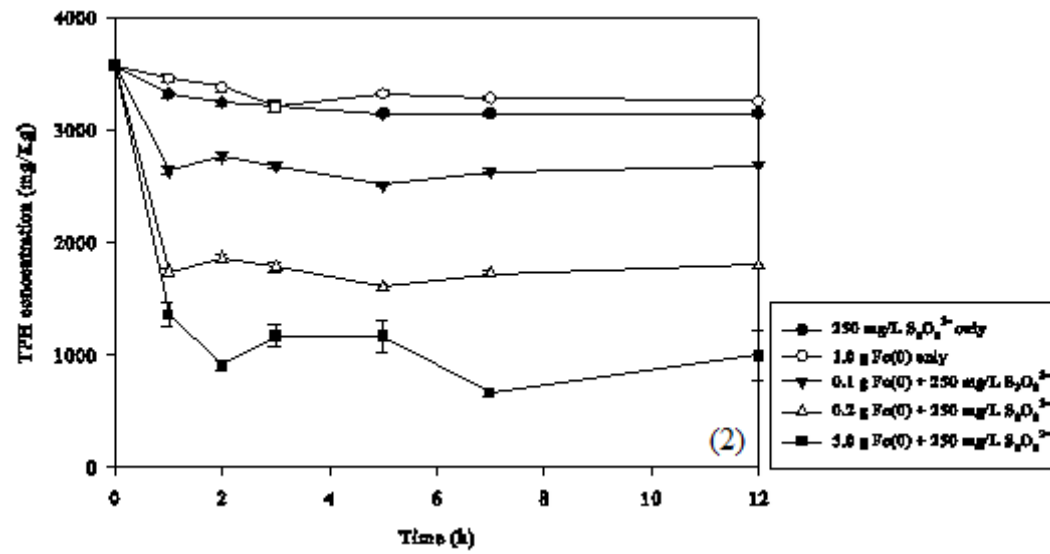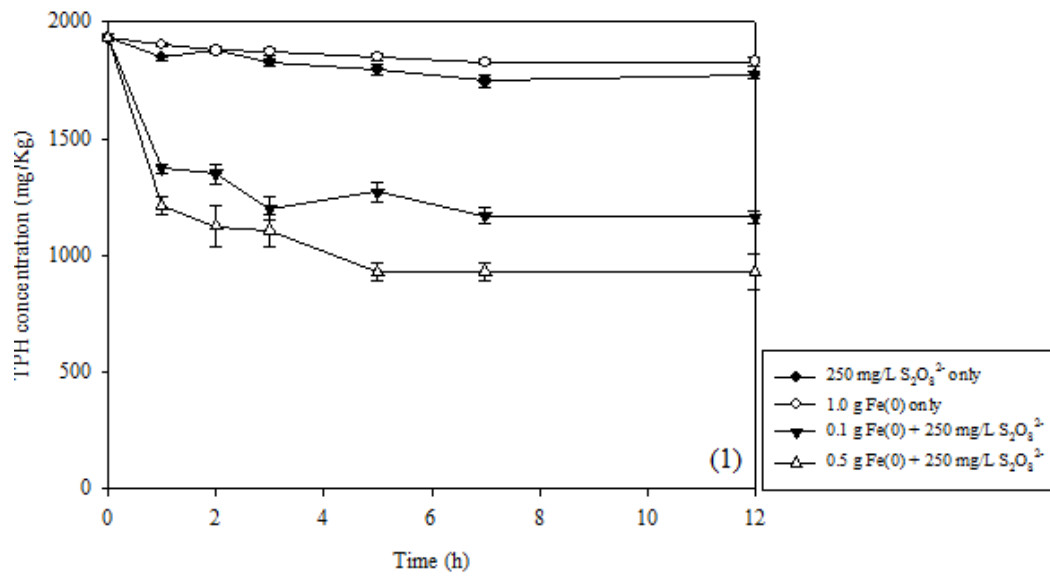
Figure 17. TPH concentration during the treatment by PS activated with Fe(0):
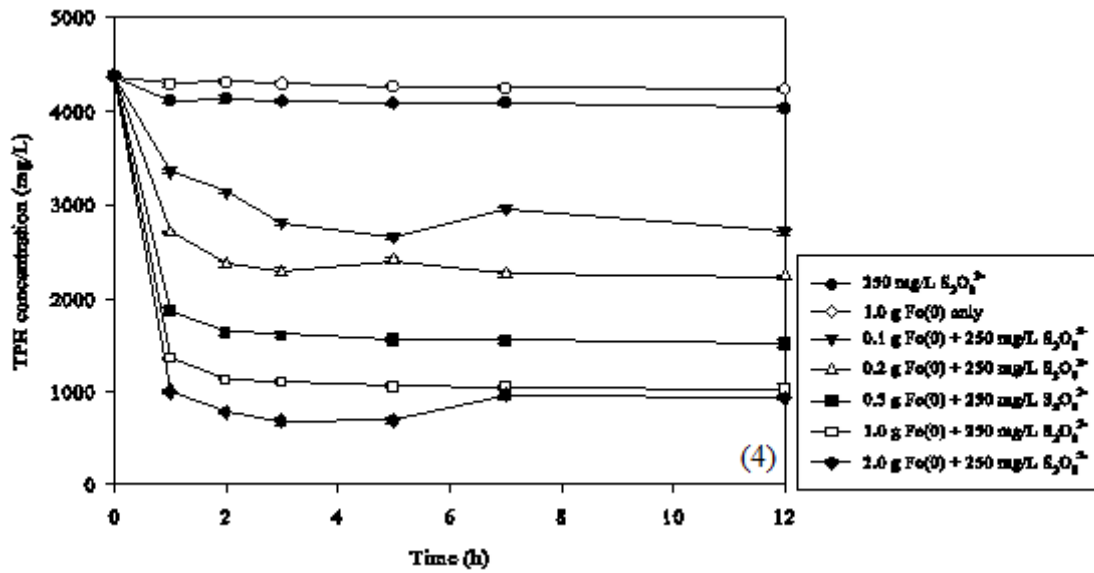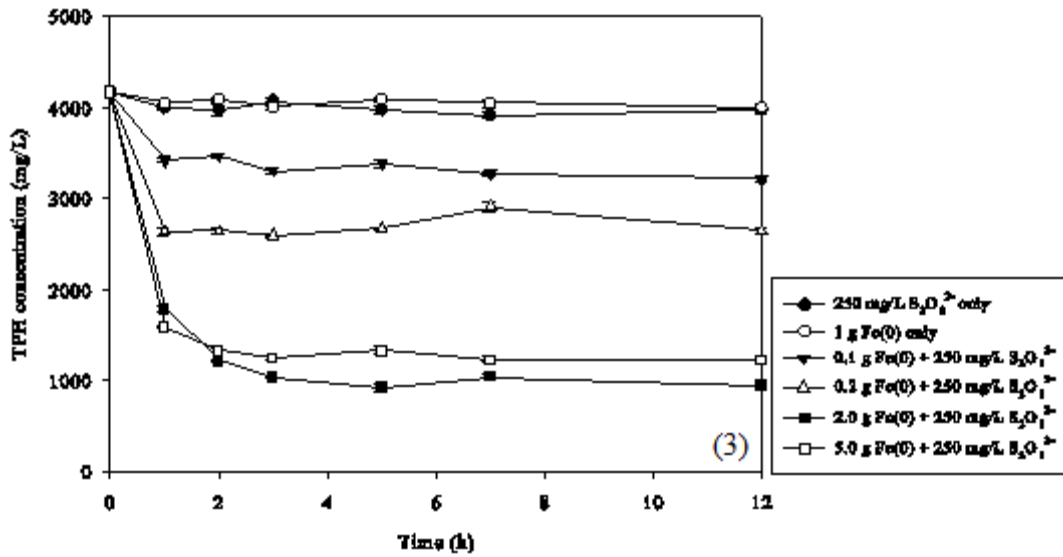**(1): diesel-contaminated sand; (2): diesel-contaminated soil;**
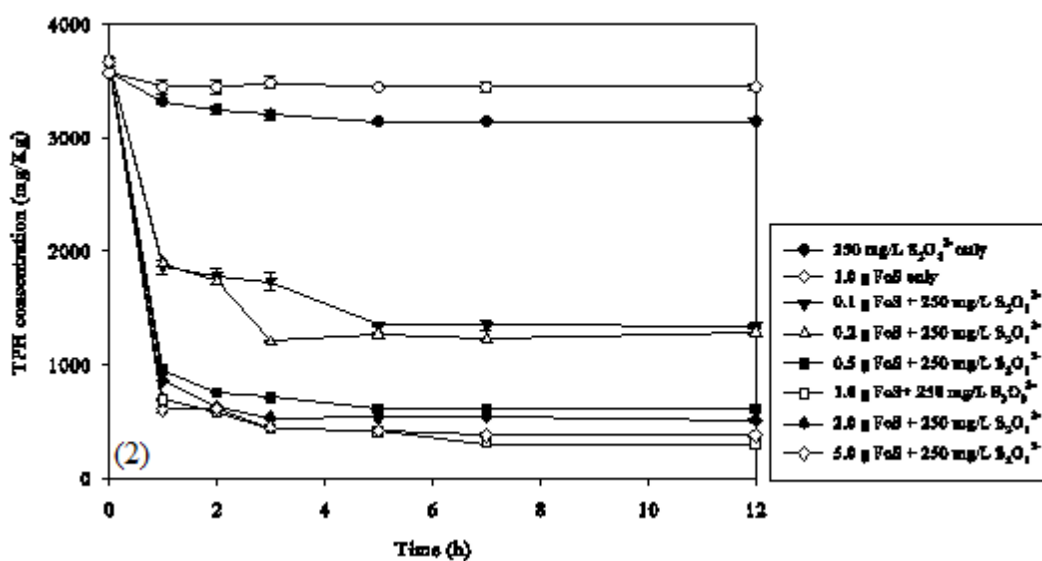**(3): biodiesel-contaminated sand (4): biodiesel-contaminated soil**

3.3.2. Treatment diesel/biodiesel-contaminated soil by FeS-activated persulfate

In all experiments, diesel and biodiesel were collected to evaluate the effectiveness of PS for the removal of petroleum hydrocarbons. Figure 18 presents the results of TPH oxidation by modified PS system and FeS could activate PS and the removal of TPH was enhanced. Namely, Figure 18 shows the effect of FeS/PS to degrade of diesel in sand or soil. Biodiesel in the polluted soil whose percentages of removal rate was 92.1%, the TPH removal ratio of the polluted sand was nearly 5% less. The amount of diesel removal in contaminated soil was 91.3%, which was 14.6% more than the percentage in the contaminated sand. The difference in efficiency reactions depends on contaminated soil or sand. So the component in soil and sand acts an important role in the reactions.

Moreover, the results not only indicate the removals rate of TPH but also indicate the interdependent of ratio FeS: PS. Evidently, the optimum molar ratio of FeS-to-PS is 43.6:1 with almost contaminated soil or sand. Nonetheless, each modified PS system, the degradation of TPH is not directly proportional to the weight of catalyst (FeS). In the biodiesel contaminated sand, an evident, the removal rate of TPH with 1.0 g FeS is lower compared to the ratio of 0.5 g FeS.

Compare to Fe(0)/PS, the degradation of TPH with the presence of ferrous ion and PS is lower. The results indicate that persulfate can be activated by ferrous ion (Equation 3), however, free sulfate radical is scavenged by ferrous iron throughout Equation 18 [57].

$$SO_4 \bullet^- \ + \ Fe^{2+} \ \rightarrow \ \ Fe^{3+} \ + \ SO_4^{2-} \ \ (18)$$
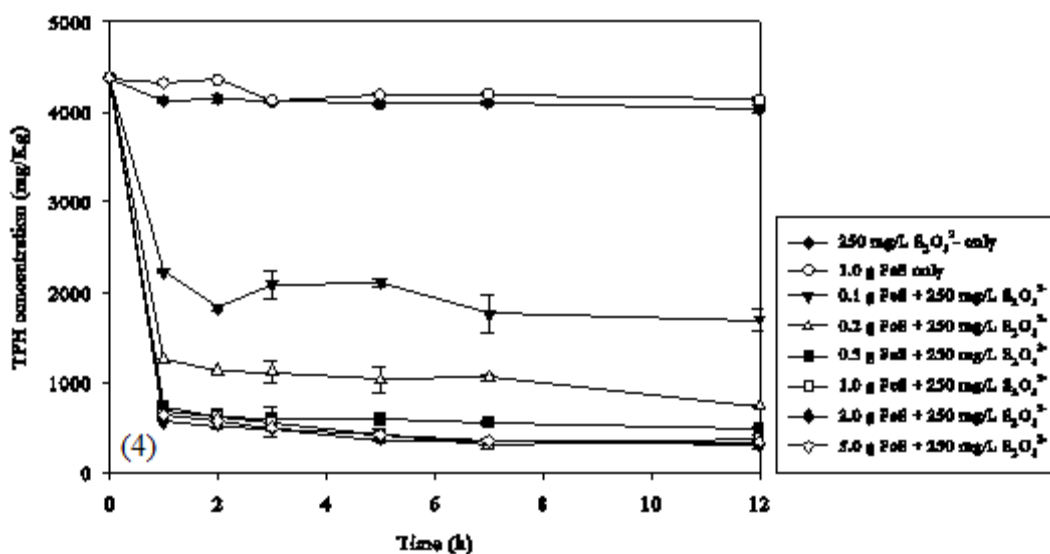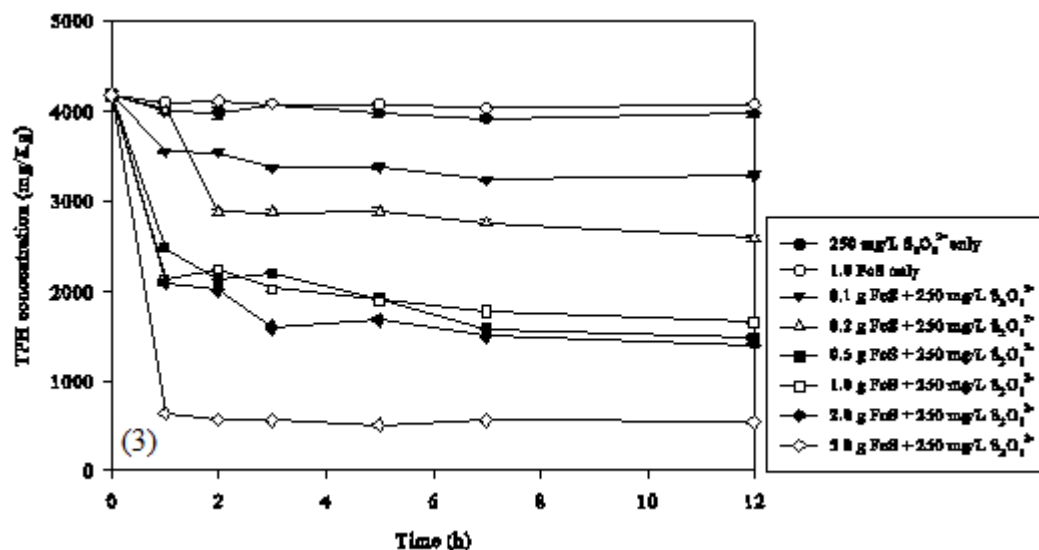
Figure 18. TPH concentration during the treatment by PS activated with FeS:
(1): diesel-contaminated sand; (2): diesel-contaminated soil;
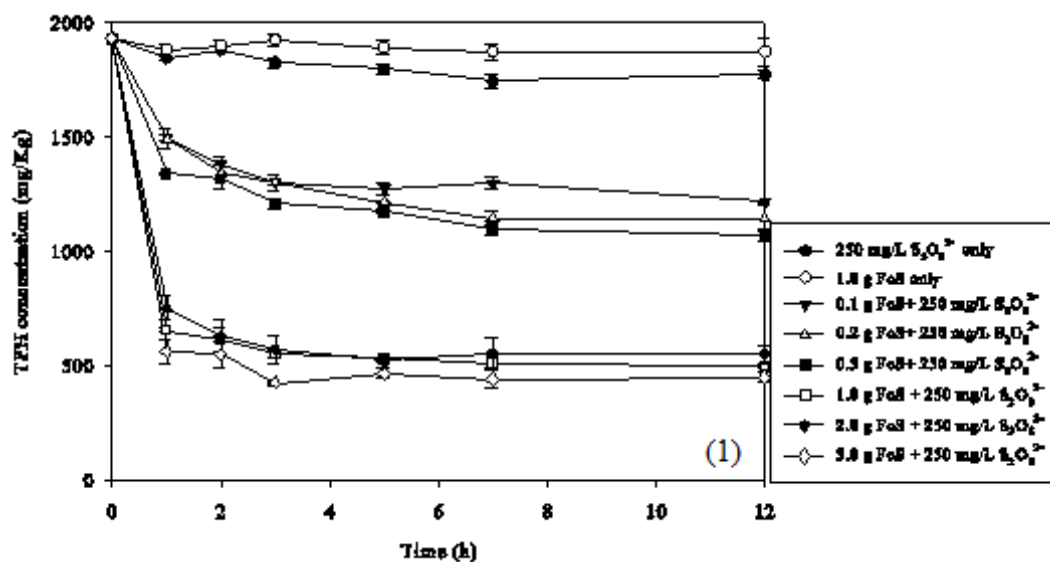**(3): biodiesel-contaminated sand (4): biodiesel-contaminated soil**

CONCLUSIONS

1. The results of this study indicate that diesel and biodiesel in soils can be degraded by Fe(0)-activated PS and FeS-activated PS.

2. BC, AC, and GR can accelerate the activation of Fe(0)-activated PS to enhance the phenol degradation. AC and RS900 are prominent activators because of their effect on the phenol degradation, resulting in 83.5 and 89% with AC and RS900, respectively.

3. The removal rate of phenol is influenced by reaction conditions: initial pH, PS concentration, and the amount of BC.

4. MeOH and TBA could quench the removal rate of phenol, indicating that the persulfate radical ($SO_4\bullet^-$) is dominant oxidant compare to the hydroxyl radical ($OH^\bullet$).

5. The results suggest that persulfate oxidation in the presence of Fe-bearing materials and BC may be a promising option to remediate organic contaminants in water and soils.

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