Short Communication

The role of humic acid in Fenton reaction for the removal of aliphatic fraction of total petroleum hydrocarbons (diesel range) in soil

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Abstract

This study investigated the role of humic acid in Fenton reaction for the total petroleum hydrocarbons (TPH) (diesel) in soil. Batch reactions were conducted at varying humic acid dosages and pH. For the lowest molecular weight diesel contaminants, a humic acid dosage of 10 mg/l produced the favourable effect of reducing Fe$^{3+}$ to Fe$^{2+}$ which continued for higher humic acid dosages of 50, 100 and 150 mg/l. Conversely, for higher molecular weight diesel contaminants, the negative effect of hydroxyl radicals consumption by the humic acid was more significant than its reduction of Fe$^{3+}$ to Fe$^{2+}$. The positive role of humic acid on Fenton reaction increased with increasing humic acid dosage for the overall TPH, with an optimum dosage of 150 mg/l. At higher pH, the removal efficiencies increased or reduced depending on the molecular weight of TPH. The power law and pseudo-first-order kinetic models fitted the experimental kinetic data well.

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1. Introduction

The release of petroleum hydrocarbons and its derivatives, as external and non-natural solutes, to the environment is a source of pollution. These pollutants can be transported through the air, water and soil media. Mostly, soil will be the final sink for these pollutants and will remain as a permanent source of groundwater pollution. As such, remediation of petroleum hydrocarbons-contaminated soil has attracted a considerable amount of research.

Different processes have been applied for the remediation of petroleum hydrocarbons-contaminated soil, including physical, chemical, thermal and biological. Among these processes, Fenton reaction has been studied widely under the chemical remediation category. The overall concept of Fenton reaction is oxidizing the contaminants using one of the most reactive radicals, i.e. the hydroxyl radical (OH·), resulting from the reaction of hydrogen peroxide (H$_2$O$_2$) with iron (II) (Fe$^{2+}$).

A major obstacle in increasing the efficiency of the Fenton reaction is the short lifetime of OH·, and its faster destruction rate through consumption and wastage compared to its regeneration rate [1,2]. Proposed solutions for this problem include using the higher concentration of H$_2$O$_2$ and substituting a better form of a catalyst such as a chelating agent or another form of Fe salts. For instance, a study by Tsai et al. [3] examined the oxidation rate of diesel and fuel oil total petroleum hydrocarbons (TPH) by high H$_2$O$_2$ concentration (15 %) and waste basic oxygen furnace slag (100 g/kg) as the catalyst. The results showed that 76 % and 96 % of fuel oil and diesel oil TPH were removed after 40 h.

Relating to the efficiency of Fenton reaction for soil remediation, soil organic matter (SOM) is an important parameter. SOM is divided into different subgroups, including humic acid, fulvic acid and humin. The reactions of OH· with SOM are more complex than their reactions with inorganic anions [2]. In a study by Voelker et al. [4], the authors have studied the effects of different ligands on the rate of Fenton reaction. Carboxylate ligands, which can be found in abundance in fulvic acid, reportedly enhanced the Fenton reaction rate by forming complexes with Fe$^{2+}$ that had higher reactivity.

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potential in comparison with aqua complexes in increasing the oxidation rate. This effect was reported to be obvious at pH = 5, whereas no considerable changes at pH = 3 were observed. In another study by Goi et al. [5] on determining the effect of peat rich in organic matter on transformer oil destruction by H$_2$O$_2$, they reported that the optimum H$_2$O$_2$ to transformer oil weight ratio was 4:1. Increasing the ratio from 1:6.1 to 4:1 increased the removal efficiency from 22 % to 47 %, while increasing the ratio from 4:1 to 8:1 decreased the efficiency from 47 % to 0 %. In contrast, increasing the ratio in sand changed the efficiency marginally from 82 % to 87 %. Separately, Lim et al. [6] reported that SOM can contribute to increasing the removal efficiency of diesel fuel even to a greater degree than a chelating agent. Fan et al. [7] also reported a higher decomposition rate of H$_2$O$_2$ in the soil with higher organic matter in natural pH.

To date, there are no studies which report on the effects of humic acid, a constituent of SOM, in Fenton reaction on different aliphatic fractions of total petroleum hydrocarbons within the diesel range in soil. This study aims to address this by carrying out batch Fenton reactions to elucidate the effects of humic acid dosage in different pH conditions. The kinetics of the Fenton reaction are also determined.

2. Materials and methods

2.1. Materials

N-hexane (98.0 %) and silica gel 60 (0.063–0.200 mm) were obtained from Merck. R&M Chemicals supplied dichloromethane (DCM 99.5 %), iron (II) sulphate heptahydrate (FeSO$_4$·7H$_2$O), hydrogen peroxide (H$_2$O$_2$; 30 %) and sodium sulphate anhydrous. Diesel was supplied from a Shell gas station in Semenyih, Malaysia. Hydrochloric acid (HCl, 37 %), sodium hydroxide (NaOH, >97 %), potassium hydroxide (KOH, ≥85 %), mercury (II) chloride (HgCl$_2$, >99 %) and H$_2$SO$_4$ (95%–97 %) were supplied by Sigma Aldrich. Silica gel for column chromatography was pre-heated up to 160 °C before usage, and sodium sulphate was activated by heating up in a furnace at 420 °C. Standards n-hexadecane (C$_{16}$, 99.5 %) was bought from Merck while n-nonane (C$_9$, 99.5 %), n-docosane (C$_{22}$, 99.5 %), and n-octacosane (C$_{28}$, 99.5 %) were from Dr Ehrenstorfer GmbH Germany. The calibration standards were diluted to different concentrations in n-hexane.

Surface soil free from contamination was collected from Cameron Highlands, Malaysia and air-dried. The soil was then sieved through a 2-mm sieve (Endecotts Ltd., England) and stored at ambient temperatures (25–28 °C). Full characterisation of the soil has been reported previously [9]. The soil was categorised as sandy loam (68 % sand, 13.1 % silt and 18.9 % clay). The SOM was determined to be 10.32 ± 0.009 %. For the Fenton soil treatment, the soil was spiked with diesel in n-hexane to result in a contamination level of 5000 mg/kg. The n-hexane solvent was evaporated under the fume hood, and the soil was kept in a closed container before usage.

2.2. Extraction of humic acid

15 g of soil material was stirred in 100 ml of 0.1 M NaOH for 24 h. Subsequently, the slurry was centrifuged at 5500 rpm for 25 min to separate the supernatants containing the humic and fulvic acids fractions from the residue containing the humin fraction. 6 M HCl was applied to the supernatant to acidify it to pH < 2. After standing for 16 h, the suspension was centrifuged at 5500 rpm for 25 min to obtain the humic acid precipitate. To remove fine mineral particles such as clay silicates, the precipitate was further dissolved in 0.1 M KOH with periodic shaking for 2 h. By adding 6 M HCl to acidify the mixture to pH ≈ 1, and allowing the suspension to settle for 16 h, humic acid was re-precipitated. This precipitated humic acid fraction was separated by centrifuging at 5500 rpm for 25 min, freeze-dried for 16 h and finely ground.

2.3. Fenton soil treatment

All experiments were carried out batchwise in 50 ml beakers at fixed conditions of H$_2$O$_2$ = 0.5 M, Fe$^{2+}$ = 0.05 M, liquid to solid ratio (L/S) = 2, natural pH = 2.7. The experiments were conducted at an ambient temperature of 25 ± 3 °C to minimise costs associated with heating or elevated temperatures for the treatment process. Additionally, the kinetics of the treatment was shown to be fast, which allowed reasonably good removal efficiencies to be attained at ambient temperature. Since the same batch of contaminated soil samples was used for all the experiments in this study, the background SOM which included humic acid was assumed to be constant. To ascertain the effects of humic acid on the Fenton treatment, the humic acid dosage was varied (0, 10, 50, 100, 150 mg/l). FeSO$_4$·7H$_2$O was used as the source of Fe$^{2+}$, which was added by weighing and adding the required amount to provide the predetermined Fe$^{2+}$ molarity in the solution. The reaction was started by adding 5 g of 1-month aged contaminated soil to the solution, followed by the addition of 0.1 % HgCl$_2$ solution to stop biological degradation and then mixing the slurry with a magnetic stirrer (Cole-Parmer, USA) at a speed of 350 rpm. At predetermined times, the reaction was terminated by adding H$_2$SO$_4$ solution to bring the pH lower than 1. The solid phase was separated by centrifuging, and the amount of remaining diesel in soil was determined. Additional experiments were carried out at pH = 5.0, with and without the addition of humic acid at 10 mg/l.

2.4. Diesel extraction and analysis

A Soxhlet extractor (SOXThERM®, Gerhardt, Germany) was used to extract the total petroleum hydrocarbons (TPH) from the soil samples mixed with activated sodium sulphate using DCM. The extracts were purified using silica gel chromatography columns (5 g silica gel with 1 g of activated sodium sulphate at the top). 20 mL n-hexane was used as the eluting solvent, and the eluants were concentrated to less than 2 ml for gas chromatography (GC) analysis.

The aliphatic fraction of TPH in its diesel range was the targeted analyte in this study. A GC (PerkinElmer Clarus 680, Beacons Field, USA) equipped with a flame ionization detector (GC-FID), with an Agilent DB-TPH capillary column (30 m × 0.25 mm × 0.25 μm) was used. The GC oven temperature programme was an initial temperature of 35 °C, holding for 2 min, then an increase to 300 °C at a rate of 15 °C/min, and holding at 300 °C for 2 min. The detector and injector temperatures were 315 °C and 310 °C, respectively. Helium at 14 psi was used as the carrier gas. The injected volume into the GC was 1 μL. For the analysis, all peaks between C$_9$–C$_{28}$ range were divided into three fractions of C$_9$–C$_{16}$ (Fraction 1), C$_{16}$–C$_{22}$ (Fraction 2), and C$_{22}$–C$_{28}$ (Fraction 3). Fraction 1 consisted all peaks within the C$_9$–C$_{16}$ range plus the C$_9$ peak and half of the C$_{16}$ peak. All peaks between the C$_9$–C$_{22}$ range plus half of the C$_{16}$ peak and half of the C$_{22}$ peak made up Fraction 2. Fraction 3 consisted of all peaks between the C$_{22}$–C$_{28}$ range plus half of C$_{22}$ peak and peak of C$_{28}$. The TPH was the summation of the three fractions belonging to the aliphatic part of diesel between C$_9$ till C$_{28}$. 

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2.5. Kinetic modelling

Two kinetic models have been used for modelling the experimental kinetic data, i.e. the power law and pseudo-first-order. The power law is given by Equation (1), while the pseudo-first-order reaction is defined by Equation (2).

\[ q_t = K_p t^{-m} \]
\[ q_t = q_e + (q_0 - q_e) e^{-kt} \]

where \( K_p \) is the rate constant of the reaction, \( q_t (\text{mg}) \) is the amount of hydrocarbon in soil at time \( t \) (min), and \( m \) is a constant.

\[ k \] is the pseudo-first-order kinetic constant, \( q_e (\text{mg}) \) is the amount of hydrocarbon in the solid soil phase at equilibrium, \( t \) (min) is the time, and \( q_0 (\text{mg}) \) is the initial amount of hydrocarbon in the solid soil phase.

3. Results and discussion

3.1. Role of humic acid on EL-Fenton reaction

There are two opposing roles of humic acid on the Fenton reaction. The first lies in the consumption of \( \text{OH}^- \) by humic acid or SOM [7–8,10–11], which can reduce the reaction efficiency. The higher decomposition rate of \( \text{H}_2\text{O}_2 \) in soil with higher SOM at natural pH has been noted as evidence of this role [8]. The second role, which exerts contrary effects to the first, lies in the ability of humic acid to reduce \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) through binding with metals like metal chelates [10]. This leads to reactions with higher removal efficiency, as reported by Fan et al. [7] for methomyl degradation rate. The effect of humic acid dosage on the removal efficiency of the three fractions and TPH was monitored at 0, 10, 50, 100 and 150 mg/l at pH = 2.7. This dosage range of humic acid was decided based on the typical tested ranges in the literature [12,13]. Fig. 1 presents the changes in the removal efficiency versus time at different humic acid dosages. In general, the change in removal efficiency was rapid between 0 till 60 min. Between 60 till 120 min, there was a sharp decline in the rate of increase in removal efficiency. Finally, from 120 till 240 min, a plateau or minimal increase in removal efficiency was attained. The removal efficiencies obtained are comparable to those reported in the literature [5,14,15]. Noticeably, the removal efficiencies for Fraction 1 at a humic acid dosage of 10 mg/l was higher than no added humic acid, whereas the converse was true for Fractions 2, 3 and TPH. Additionally, the removal efficiencies at 10 mg/l were also lower than all other cases with higher humic acid dosages (50, 100, 150 mg/l). The observed results suggested that for Fraction 1, at 10 mg/l humic acid dosage, the favourable humic acid effect of reducing \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) was the dominant factor. The maximum removal efficiency attained after 4 h was 97.54% compared to 96.26% for no humic acid addition. For Fraction 1 too, by increasing the dosage of humic acid to 50, 100 and 150 mg/l, the role of humic acid in reducing \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) was again more significant than its consumption of hydroxyl radicals. As a result, the removal efficiencies increased though it should be noted that the removal efficiency differences between 50 and 100 mg/l were larger than the differences between 100 and 150 mg/l, which suggested the competitive edge provided by the humic acid diminished as consumption of hydroxyl radicals increased.

Contrastingly, for Fractions 2 and 3, the negative effect of hydroxyl radicals consumption by the humic acid appeared to be more significant than its reduction of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \). For Fraction 2, the removal efficiencies at all humic acid dosages except 150 mg/l were lower than no humic acid addition. Meanwhile, the removal efficiencies for Fraction 3 at all humic acid dosages, including 150 mg/l were lower than no humic acid addition though those at 150 mg/l were very close to no humic acid addition. The trends observed implied that with the increasing molecular weight across the three fractions, the role of humic acid as a hydroxyl radicals scavenger became more significant. This could be explained by higher molecular weight compounds being more tightly bound onto the soil matrix with more resistance towards Fenton treatment [16]. Additionally, due to the higher molecular weight, these compounds have higher chemical stability, which leads to lower oxidation efficiency by the hydroxyl radicals [17].

The TPH results reflected the net effect of all three fractions. At the highest humic acid dosage of 150 mg/l, the highest removal efficiencies were obtained. At 100 mg/l humic acid dosage and below, the removal efficiencies were lower than without humic acid addition. The overall TPH results indicated that the positive effect of humic acid on Fenton reaction increased with increasing dosage. Therefore, it could be deduced that there is an optimum humic acid dosage that exerts an overall positive effect on the Fenton reaction for diesel contaminated soil. In this study, the optimum humic acid dosage was 150 mg/l. Likewise to this study, the appropriate humic acid dosage would be beneficial to the efficacy of the Fenton treatment as reported in other studies, for instance Ref. [16].

3.2. Effect of pH

Fig. 2 illustrates the effects of humic acid on the removal efficiencies at pH = 5. It could be observed that the addition of humic acid at 10 mg/l led to increased removal efficiencies for Fractions 1, 2 and TPH, but resulted in decreased removal efficiencies for Fraction 3. Likewise to the cases at pH = 2.7, an increase in the molecular weight resulted in a decrease in the positive effect of humic acid through the reduction of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \). This was due to the higher molecular weight fraction being less susceptible to oxidation, as reported previously [16]. Comparing Figs. 1 and 2, for the case of 10 mg/l humic acid dosage, the removal efficiencies at pH = 2.7 were higher than at pH = 5 for Fraction 1. However, for Fractions 2, 3 and TPH, the converse was true. In general, a more active Fenton reaction with \( \text{Fe}^{2+} \) is enabled at a lower pH value because \( \text{Fe}^{2+} \) is soluble in an acidic medium and more likely to precipitate at higher pH [2]. Additionally, hydroxyl radicals generation is highest at approximate pH 3 and decreases at higher pH values [18]. For Fraction 1, which were more easily oxidised, it was likely that the availability of \( \text{Fe}^{2+} \) in soluble form and the presence of humic acid acting as chelating agent were the most significant factors which resulted in the higher removals at lower pH. However, for the more recalcitrant fractions, the reduced hydroxyl radicals generation at pH = 5 could have led to a reduced scavenging effect by humic acid. The chelating effect of humic acid became more dominant, which caused the higher removal efficiencies. This corresponded well to another study [12] which reported that humic acid increased the degradation of organic compounds in the range of pH 5–7.

3.3. Kinetic modelling

Table 1 and Table 2 lists the coefficients of the power law and the pseudo-first-order equations, respectively, as determined by curve-fitting. The coefficient of correlation \((R^2)\) values obtained were close to 1 (0.8350–0.9999), indicating a good fit of data to both models. As seen in Table 1, as humic acid dosage increased from 10 to 150 mg/l, the \( K_p \) values decreased for all fractions and TPH. Additionally, the \( K_p \) values decreased in the order of: Fraction
Fig. 1. Removal efficiencies for Fractions 1, 2, 3 and TPH at $H_2O_2 = 0.5$ M, $Fe^{2+} = 0.05$ M, L/S = 2, pH = 2.7.

Fig. 2. Removal efficiencies for Fractions 1, 2, 3 and TPH at pH = 5 with and without humic acid (10 mg/l) at $H_2O_2 = 0.5$ M, $Fe^{2+} = 0.05$ M, L/S = 2.
2 > Fraction 3 > Fraction 1. From Table 2, the $q_e$ values decreased while $k$ values increased for all three fractions and TPH by increasing the humic acid dosage from 10 to 150 mg/l. The $q_e$ values also followed a similar trend as the $K_p$ values whereby Fraction 2 was highest, followed by Fraction 3 and finally, Fraction 1. The converse was true for the $k$ values trend whereby Fraction 1 > Fraction 3 > Fraction 2. With decreasing $q_e$ values, the removal efficiency would be expected to increase, as shown in Fig. 1 whereby Fraction 1 removal efficiencies were highest followed by Fraction 3 and lastly, Fraction 2.

4. Conclusions

This study has investigated the role of humic acid on Fenton reaction of TPH diesel contaminated soil. For Fraction 1, the lowest molecular weight category, a humic acid dosage of 10 mg/l produced the favourable effect of reducing Fe$^{3+}$ to Fe$^{2+}$, which continued for higher humic acid dosages of 50, 100 and 150 mg/l. Conversely, for Fractions 2 and 3, the negative effect of hydroxyl radicals consumption by the humic acid appeared to be more significant than its reduction of Fe$^{3+}$ to Fe$^{2+}$, with a more pronounced effect for the highest molecular weight Fraction 3. The overall TPH results indicated that the positive effect of humic acid on Fenton reaction increased with increasing dosage. The optimum humic acid dosage, which exerted an overall positive effect on the Fenton reaction for TPH diesel contaminated soil was 150 mg/l. At higher pH, the removal efficiencies increased or reduced depending on the molecular weight of TPH. The power law and pseudo-first-order kinetic models fitted the experimental kinetic data well ($R^2 = 0.8350 – 0.9999$).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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