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Chemical oxidation of crude oil in oil contaminated soil by Fenton process using nano zero valent Iron

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***Abstract*—Hydrogen peroxide has been used to oxidize a sorbed petroleum hydrocarbons contaminant in a clay soil with 5000 gKg^{-1} of crude oil by using nano zero-valent iron as catalyst. Due to high buffering capacity of soil samples all experiments had been performed in neutral pH. From results, it was found that optimum molar ratio of H_2O_2:Fe0 was 33.7:1 with maximum TPH removal, 91%. Optimum reaction time was 4 hours. After 4 hours no H_2O_2 was detected in the slurry. Moreover, it was found that hydrogen peroxide was heterogeneously decomposed by the soil (due to its organic and/or inorganic components) and its decomposition rate decreases when the iron was previously precipitated–impregnated into the soil.**

Keywords: Fenton's reagent, soil remediation, TPH contamination, Neutral PH, Nano zero-valent iron

I. INTRODUCTION

Enormous effort has been made to find efficient and effective ways to remediate petroleum contamination in soil. Common method was excavation followed by land filling or incineration [2] Due to limitations and drawbacks of these methods, technologies such as bioremediation, soil vapor extraction, soil washing, thermal treatment and chemical oxidation…has been developed [2]. Chemical methods have been shown to oxidize and mineralize organics. Chemical oxidation may not only destroy target compounds, but also reduce toxicity associated with formulation ingredients and active agents [1-5]. Among different type of oxidation processes, Fenton's oxidation is of the most popular applied technology for site remediation, and it is recognized as one of the most powerful oxidizing reactions available and can be used to destroy a wide variety of biorefractory organic compounds in aqueous waste, soils, and ground water due to its high oxidative potential and its simplicity [1-4-7].

Fenton's oxidation, advanced oxidation catalyzed with ferrous iron [Fe^{2+}], is successful in removing organics from water[9,10] and also soils, but required the continuous addition of dissolved Fe^{2+}[4]. In lieu of Fe^{2+} a solid form of iron (zero-valent iron,Fe^0) would be advantageous because imprimis it could be attached to or coated on larger stationary soils like sand filtration materials and secondly mobilized in and attached to soil grains in contaminated aquifers[3]. Matheson and Tratnyek investigated application of Fe^0 in permeable reactive barrier walls instead of Fe^{2+} for dehalogenation of chlorinated organic contaminants [6].

The equations occurs in Fenton reactions are as follows; [3]

$$Fe^0 + H_2O_2 \longrightarrow Fe^2 + 2OH \qquad (1)$$

Fe2+ can then react with H2O2 in traditional Fenton's oxidation reactions [3-11]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} \quad H^+ \quad HO_2^{\bullet} \qquad (3)$$

Hydroxyl radicals (${}^{\bullet}OH$) generated in Fenton's reaction is the strongest oxidant leads to destruction and mineralization of organic contaminants [3].

Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems [8]. Nanoparticles show a higher catalytic activity because of their small size (10-100nm) and their large specific area [12]. The main objective of this research is to evaluate the application of Nano-zero valent iron (nZVI) as a catalyst for remediation of petroleum contaminated soil by Fenton's reaction.

II. MATERIALS AND METHODS

In this regard, clean soil samples were collected from a sampling depth of 10-30 cm at a relatively uncontaminated zone of Tehran refinery, nearby the petroleum contaminated Pond No.4. Initially, the soil was air dried at room temperature for about 3 days and then sieved through a US standard No.10 mesh (2mm) to remove large particles and provide a consistent surface area for sorption of crude oil. Physical and chemical properties of the soil are shown in table 1 and 2. Afterwards, the samples were held in oven at 550°c for about 3 hours to ensure no prior contamination in soil. Prepared samples were contaminated by crude oil (initial contamination was near 5000 ppm, 5 gram crude oil was spilled in 1kg soil). The tests were carried out after 3 weeks to be assured of crude oil sorption by soil.

Commercial hydrogen peroxide containing 30% by weight of H_2O_2, and sulfuric acid (H_2SO_4) were purchased from Merck. Concentration of residual H_2O_2 was analyzed by iodometric method [13]. Nano zero-valent iron (Particle size:8-18 nm, purity:85%, SSA:59-79 m^2/g, black, spherical) was obtained from Research Institute of petroleum Industry (Tehran, Iran) ,Crude oil was from Tehran refinery located in South of Tehran (Shahr - e - Rei) .

III. RESULTS AND DISCUSSIONS

A. *OPTIMIZATION OF THE RATIO OF H_2O_2/Fe_0*

The ratio of H_2O_2/Fe^0 is an important determinant in the efficiency of Fenton oxidation [1].In figure 1 the removal efficiency of TPH is presented. It is obvious that minimum TPH removal efficiency has been recorded when the ratio is 195.88:1. The highest efficiency in this stage is obtained with a H_2O_2/Fe^0 molar ratio 33.74:1(by 66.3 removal efficiency)

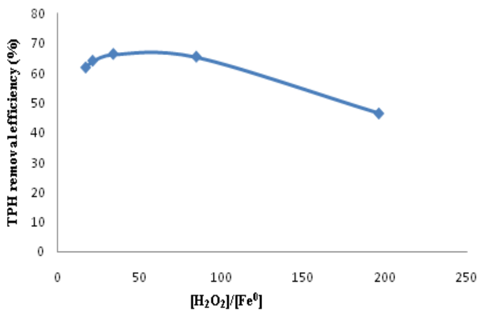

Figure 1. Optimum H_2O_2/Fe^0 molar ratio

B. *EFFECT OF HYDROGEN PEROXIDE DOSAGE*

The degradation of petroleum hydrocarbons are at variance with respect to dosage of hydrogen peroxide. High dosage of H_2O_2 is a remarkable source for $OH^{\cdot}$ Production, but as been shown in figure2 after a significant increase in removal efficiency the trend changed and declined by adding more volume of hydrogen peroxide.

Whereas Fenton's reaction with high dosage of hydrogen peroxide is plentifully exothermic, high temperature accelerates the decomposition of H_2O_2. Hence, this phenomenon leads reduction of H_2O_2 utilization. Other investigators also indicated this proof [17]. Moreover, inorganic reactants can also consume H_2O_2, and also when one of the reactants (H_2O_2 or Fe^0) is overdosed, both can react with hydroxyl radicals and inhibit the oxidation reaction [15, 16]. So usage of moderate volume of hydrogen peroxide is suggested in Fenton reaction, as been recommended by [14].

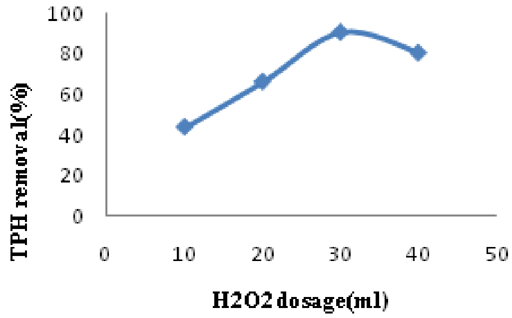

Figure 2. Effect of dosage of H_2O_2 on the degradation of TPH (irondosage = 0.5g, pH 7 and TPH concentration = 5000 ppm)

C. *EFFECT OF pH*

Figure 3 exhibits how the soil resisted to the change in pH. The soil pH was around 7 after addition of 10 mL H_2SO_4 (4M), and remained unchanged regardless of further addition of acid to acidify the soil. The strong buffering capacity that was manifested in this soil excluded the possibility of investigating pH effect on Fenton's reaction in this research.

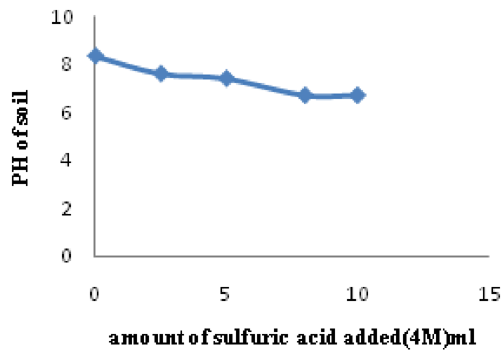

Figure 3. Buffering capacity of soil

IV. CONCLUSION

The degradation of total petroleum hydrocarbons (TPH) was investigated by Fenton reaction, using nano-zerovalent iron as a source of Fe^{2+}. Our recent work has demonstrated that 91% TPH removal efficiency has been achieved by Fenton's oxidation with 4 hours reaction time. In comparison with previous researches a few amount of nZVI was required to act as catalyst in Fenton reaction due to small particle size of Fe^0 and its high activity that leads to cost reduction. pH was an independent factor to be investigated in this research for soil remediation due to high buffering capacity of the soil; also pH adjustment is inoperative for site remediation. And finally, the prospect for successful exploiting the nanoscale technology for environmental applications appears very good.

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