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## Effects of soil organic matters on Fenton reaction

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### Abstract

Heterogeneous Fenton reaction has been widely known to destruct organic contaminants, in its basic application definition, by applying one or more Fe<sup>2+</sup> or Fe<sup>3+</sup>-containing source(s) with hydrogen peroxide for producing the strong hydroxyl radicals. Comprehensive experiments in the Fenton reaction area have been done for over 100 years, and considerable progress has been achieved. Achieved removal efficiency by Fenton reaction is usually studied by evaluating the effects of parameters such as initial reagents concentrations, pH, and soil organic matter (SOM). Among them, the results related to the effect of SOM sometimes seem conflicting, as its effects are reported either promoting or inhibiting and sometimes both. Reaction parameters such as initial reagents and pH are the most studied and effective ones in evaluating the effects of SOM on Fenton reaction for organic pollutants. This review intends to give a comprehensive survey of the impact of SOM on the Fenton reaction, with the focus on the heterogeneous Fenton reaction in the soil and solid. For this purpose, the general effects of pH and initial reagents on the Fenton reaction are reviewed in the beginning.

*Keywords: Fenton reaction, Hydrogen peroxide, pH, Soil organic matter (SOM), The removal efficiency*

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## 1. Introduction

Soil and water contamination by organic pollutants such as hydrophobic organic carbon (HOC) is a major environmental concern. Contaminated soil is not only a contaminated medium, by itself, but also can be the source of pollution for water medium by leaching to the groundwater [1]. One of the main methods for the destruction of biorefractory organic compounds is the advanced oxidation technique which includes oxidants such as ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ), persulfate ( $S_2O_8^{2-}$ ), potassium permanganate ( $KMnO_4$ ) [2-4]. Based on the requirements of each site, one of these oxidants can be more applicable than the others. For example, the higher stability of sulphate free radical, ( $SO_4^{\cdot-}$ ) which is the intermediate radicals of the persulfate activation, makes its higher ability for penetration [5-6]. Fenton reaction is a known treatment option for remediation of contaminated soil, sludge, and wastewater. The most known radical of the Fenton reaction, hydroxyl radical ( $HO^\cdot$ ), is one of the most studied radicals frequently used for soil and water remediation [2,4]. The studies on the Fenton reaction all indicate that  $H_2O_2$  and a ferrous salt (the reagents of the conventional Fenton reaction, catalytic hydrogen peroxide (CHP) reaction) make a strong and effective combination for degradation of organic substances [7].

CHP remediation has been implemented in hundreds field applications over the past two decades. Fenton reaction is frequently used because of its low cost, simplicity, and environment-friendly properties [8]. Fenton reaction, due to its moderate cost, availability of reagents, simplicity in operation (with some considerations), ability to control its environmental side-effects, and its high efficiency, is an attractive and somehow the main choice for treatment of contaminated soil, sludge, and wastewater [9-10]. Even considering all its beneficial effects, the Fenton reaction raises some concerns, such as its contribution to soil sterilization and elimination of a considerable part of soil native microorganisms [11-12]. Despite the long history and wide applications of CHP remediation at hundreds of sites throughout the world over the past decades, the reported results in its efficiency have been highly varied from undetectable remaining concentration to minimal cleanup [13-14]. For example, Ferguson and coworkers studied the application of several oxidative treatments (Fenton's

reagent, hydrogen peroxide, and sodium hypochlorite) to remediate petroleum-contaminated soil at Old Casey Station, East Antarctica [11]. Their results showed that the applied methods at this site, with contamination of over a decade ago, did not significantly reduce petroleum hydrocarbon concentrations, and this process hindered biodegradation through the destruction of subsurface microbial communities. The reasons for these results can be divided into categories like effectivity of contact between reagents and contaminants, the role of factors like SOM, the ratio of initial concentrations of reagents and contaminants, and soil organic matter (SOM) [9,13,15-17].

The conventional Fenton reaction is adding dilute hydrogen peroxide ( $H_2O_2$ ) slowly to a rapidly stirred, degassed iron II-substrate solution [18], which is presented in a general way by Eq.1, in table 1, the very first reaction. This reaction is accompanied by many other parallel and series reactions represented in table 1.  $H_2O_2$  is a strong oxidizing agent with standard potential of 1.80 at pH 0 and 0.87 V at pH 14 with the application for the treatment of many inorganic and organic pollutants [4,18-19]. Based on the definition of the conventional Fenton reaction,  $Fe^{+2}$  is known as the responsible iron species with the highest removal efficiency (RE). Different kinds of iron catalysts have been applied instead of iron II-substrate, such as goethite, hematite, magnetite, ferrihydrite, iron (III) nitrate, iron (II) perchlorate, and waste basic oxygen furnace slag, to treat contaminated soil [18,20-21]. Varied applicability for each of them has been reported based on the applied pH and by considering the state and amount of SOM. The abundant and frequent existence of iron in soil and water media makes Fenton reaction even a more attractive option. Fenton reaction results in different radicals, but the most studied one is  $HO^\cdot$  which is produced by electron transfer of iron II-substrate to hydrogen peroxide and hydroxyl anion [4,22]. The importance of  $HO^\cdot$  stems from its oxidative potential for many chemicals, from biological constituents such as protein, lipids, and carbohydrates [23], to petroleum hydrocarbons [24].

Hydroxyl radical has a high reactivity which leads to this phenomenon that the only barrier in front of its reaction with pollutants would be on the way of its diffusion in the aqueous phase, as a result, it has a short life time of nanoseconds, which means its generation rate cannot compensate for its decomposition rate [17-18, 25]. The rate constants for the reaction of hydroxyl radical with over 600

organic compounds indicate that the vast majority of reactions have second-order constants of  $10^7$ - $10^9 \text{ M}^{-1}\text{s}^{-1}$ . It is reported that in the presence of enough Fenton reactants and continuation of the reaction, mineralization of the organic matters could be happened which is defined as their conversion into inorganic matters,  $\text{CO}_2$ , water, inorganic salts [4]. In Usman and coworkers' study, the complete mineralization of n-alkanes in a Fenton-like process with the catalyst of magnetite, at  $\text{pH}=6.7\pm 0.3$  was reported with a reduction from the initial concentration of  $3200 \mu\text{g}\cdot\text{g}^{-1}$  n-alkanes to  $200 \mu\text{g}\cdot\text{g}^{-1}$  of n-alkanes [5].

Table 1. Reactions of Fenton catalytic reaction. [9]

$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{HO}^-$	$k = 63 \text{ M}^{-1}\text{s}^{-1}$	Eq.1
$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + {}^\bullet\text{HO}_2 + \text{H}^+$	$k = 0.01 \text{ M}^{-1}\text{s}^{-1}$	Eq.2
$\text{HO}^\bullet + \text{H}_2\text{O}_2 \rightarrow {}^\bullet\text{HO}_2 + \text{H}_2\text{O}$	$k = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Eq.3
$\text{HO}^\bullet + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^-$	$k = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Eq.4
${}^\bullet\text{HO}_2 \rightarrow \text{H}^+ + {}^\bullet\text{O}_2^-$	$k = 1.58 \times 10^{-5} \text{ s}^{-1}$	Eq.5
$\text{Fe}^{2+} + {}^\bullet\text{HO}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2$	$k = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Eq.6
$\text{Fe}^{3+} + {}^\bullet\text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2$	$k = 3.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Eq.7
${}^\bullet\text{O}_2^- + \text{H}^+ \rightarrow {}^\bullet\text{HO}_2$	$k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Eq.8
${}^\bullet\text{O}_2^- + \text{Fe}^{2+} + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{Fe}^{3+}$	$k = 1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Eq.9
${}^\bullet\text{O}_2^- + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{O}_2$	$k = 5.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Eq.10
$\text{HO}^\bullet + \text{HO}^\bullet \rightarrow \text{H}_2\text{O}_2$	$k = 4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Eq.11
${}^\bullet\text{HO}_2 + {}^\bullet\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Eq.12
$\text{HO}^\bullet + {}^\bullet\text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Eq.13
$\text{HO}^\bullet + {}^\bullet\text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-$	$k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Eq.14
${}^\bullet\text{HO}_2 + {}^\bullet\text{O}_2^- (+\text{H}^+) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Eq.15

The parameters, which affect the RE of the Fenton reaction, include all site-specific and contaminant-specific parameters [26]. The RE can be affected by some limitations such as  $\text{H}_2\text{O}_2$  and radical scavenging via non-productive reactions, pH change, delivery of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{+2}$ , acid, and stabilizers due to reactive transport, sorption of the contaminants and other organic, mineral reactants, and safety issues regarding the release of volatile and strong oxidant solutions [27]. Two main scavengers of hydroxyl radicals are inorganic matters and SOM, and the effect of SOM is more complex [18]. SOM consists of main functional groups such as aliphatic dicarboxylic acids, phenols, amines, amides, alkoxy, hydroxyl, quinones, ethers and esters [28]. Fulvic acid (FA), humic acid (HA), and humin are the main fractions of SOM. HA can be considered as a natural polymer that is found with differences in soil, sediment, and water, and consists of main covalent linkages of esters, ether and alkyl bonds found in Fourier transform infrared (FTIR) studies [9,29]. Humin and HA show similar analytical characteristics [30]. SOM especially HA and FA are the influential factors affecting Fenton reaction by participating in this reaction by consumption and/or production of hydroxyl radicals and iron ions [31]. Based on Pateiro-Moure and coworkers' study, by Fenton reaction, both the content and the composition of SOM changed; HA content decreased, FA content increased, and humin content did not change [32]. Based on this background, this study aims to review the effect of SOM on Fenton-aided remediation of the organic compounds-contaminated soil and the effective variables and factors and their roles. For evaluating the effects of SOM on Fenton reaction some aspects of the reaction and reagents are determining. Therefore, for assessing the effect of SOM, the explanations for the influence of initial reagents and pH have been reported.

## 2. General basics of Fenton and Fenton-like Reaction

There are different views in evaluating RE of Fenton reaction. To get the highest effectivity of Fenton reaction, having a better understanding of the effects of pH, the impact of  $\text{H}_2\text{O}_2$  concentration, different iron species, and cycles between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  states are essential [24]. Some improvements focused on enhancing RE by increasing the speed of Fenton reaction. Applying initial reagents at high concentrations is usually the proposed solution. It is reported that applying the reaction in the condition that  $\text{HO}^\bullet$  would participate in the higher reactivity

would be beneficial for the destruction of organic compounds, which are considered as contaminants [24]. Some other improvements have been focused on changing the conventional catalyst of this reaction. The applied methods for achieving these purposes by focusing on changing and improving the Fenton reaction reagents are called Fenton-like or modified Fenton reaction. It is supposed that the base of the Fenton reaction happens in the solution. As it is reported by Villa and coworkers, the lower decomposition of  $H_2O_2$  by mineral ion than the soluble iron is attributed to the lower availability of the metal ion in the solution when the reaction happens in one heterogeneous system [12]. This conclusion is based on the assumption that the reaction is happening in the solution, while it is reported that reaction with  $H_2O_2$  can happen on the solid surface as well [18]. In Fenton-like reactions for keeping iron in the soluble form, application of chelators including aminopolycarboxylates, polyhydroxy aromatics, and N-heterocyclic carboxylates has been considered [33]. One view for examining the effects of parameters on Fenton reaction is evaluating the factors which lead to consumption of  $HO^\circ$  by chemicals other than contaminants. SOM and mineral species such as carbonates, which are the most likely ones, are named as the scavengers of the hydroxyl radicals [18]. The produced intermediates are also considered hydroxyl scavengers. The hydrocarbon intermediates from the Fenton's reaction are produced due to the lack of reactants, for example, polycyclic aromatic hydrocarbon (PAH) can produce oxy-PAHs during the oxidation process [34].

### 2.1 Effects of initial reagents of Fenton reaction

Fenton reaction is providing  $HO^\circ$  and Fenton reaction is considered as the source of  $HO^\circ$ . As can be seen from reactions in table 1, reactions related to the Fenton reaction have some sub-cycles. For the Fenton reaction, existing two main reagents,  $H_2O_2$  and  $Fe^{+2}$ , for all other sub-cycles is important. Because of the consumption of  $H_2O_2$  in parallel and series reactions and production of  $Fe^{+2}$  by catalytic reactions, the initial value of  $H_2O_2$  is usually higher than  $Fe^{+2}$  [10]. The products of this reaction are  $HO^\circ$ ,  $HO^\cdot$ , and  $Fe^{+3}$ .  $HO^\circ$  is produced only by the reaction between  $Fe^{+2}$  and  $H_2O_2$ .  $HO^\circ$  has the highest reaction constant with most contaminants. Reactivity of  $HO^\circ$  with alkanes has kinetic constant rate of  $k = 10^7 - 10^9 \text{ M}^{-1}\text{s}^{-1}$  and its kinetic constants with for alkenes and aromatics are around  $k = 10^9 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$ . Greater oxidation of aromatic organic contaminants than

aliphatic organic contaminants in soil is also reported. In addition, it is represented that the reduction of aromatic total petroleum hydrocarbon (TPH) by oxidation is greater than the aliphatic fraction [35-38]. For example, as it is reported by Mater and coworkers, during the oxidation process of the aromatic compounds, the consumption of iron and  $H_2O_2$  was less in comparison with the oxidation of the aliphatic compounds [37].  $HO^\circ$  is the prerequisite of other reactions and, more importantly,  $Fe^{+3} - Fe^{+2}$  cycle, the reactions are represented in table 1 [25].  $Fe^{+3}$  by completing  $Fe^{+3} - Fe^{+2}$  cycle is indirectly affecting  $HO^\circ$  production. It can be one reason why  $HO^\circ$  conventionally is considered as the main responsible radical for the destruction of pollutants. Both studying other radicals produced through other reactions in overall Fenton reactions and determining which of the suspected radicals are responsible for the destruction of contaminants in each step have always been a source of conflict and subsequent researches [18]. These different radicals and anions cause reactions other than the conventional Fenton reaction, Eq.1. Perhydroxyl radical ( $^\circ HO_2$ ), superoxide anion ( $^\circ O_2^-$ ) and hydroperoxide anion

( $HO_2^-$ ) are among the produced species in the presence of high concentrations of hydrogen peroxide [15,18,22,25,39]. The presence of different pollutants and different intermediates produced through contaminant destruction makes the study more complex.

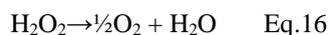
The reaction of hydrogen peroxide with  $HO^\circ$  leads to the production of perhydroxyl radicals ( $^\circ HO_2$ ) which is known as a weaker radical in oxidation capabilities [17]. The reported results of the responsible reactive oxygen species are different. Traditionally superoxide radical and perhydroxyl radical are considered as the reactive radicals, but superoxide radical has been shown to participate in the destruction process with significant effects [40]. From this perspective, it can be concluded that the matrix of the mixture of the reactive oxygen species is participating in the removal or destruction process, altogether with different degrees [13]. The most-reported results for the required value of  $H_2O_2$  concentration in the destruction process have an optimum value. The reason is attributed to the scavenging effect of  $HO^\circ$  in the solution. As it is reported in Kanel and coworkers' study, the phenanthrene oxidation rate was enhanced by an increase in  $H_2O_2$  concentration values from 1M to 5M, while  $H_2O_2$  concentration more than 5M led to a decrease in the reaction rate [41]. Availability of  $H_2O_2$  is a key matter in having a consistent catalytic

Fenton reaction, as  $\text{H}_2\text{O}_2$  is the key component in producing all three involved reactants ( $\text{HO}^\circ$ ,  $^\circ\text{HO}_2/^\circ\text{O}_2^-$ ) and any reaction or condition, which leads to dissociation or decomposition of  $\text{H}_2\text{O}_2$  through any reaction, will result in less  $\text{H}_2\text{O}_2$  available for  $\text{HO}^\circ$  production [42]. When  $\text{HO}^\circ$  is consumed by  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$  will be produced by other sub-cycles, but in longer time and in the case of the existence of sufficient  $\text{Fe}^{+2}$ . There are results related to decrease in RE due to increase in hydrogen peroxide concentration [18,20,22,39]. Ferrarese and coworkers reported a decrease in RE of Fenton reaction-aided destruction of PAH and TPH (aliphatic hydrocarbons) by increasing the hydrogen peroxide dosage above 100 mmol/sample for samples at an initial contamination level of 2800 mg/kg PAH [22]. Watts and coworkers believed that in the modified Fenton reaction, which is catalyzed by a high concentration of  $\text{H}_2\text{O}_2$  (with different reported values:  $\geq 2\%$ ,  $>0.3 \text{ M}$ , or  $>1000 \text{ mg/L}$ ), the other reactive oxygen species and radicals, non-hydroxyl radicals, are responsible for higher RE [18]. On the other hand, Yeh and coworkers showed that change in hydrogen peroxide concentration from 0.01% to 0.5% was not a determining parameter in reaction degradation of octachlorodibenzo-p-dioxin [39]. They reported the strong sorption of the contaminants as the reason for this observation. They showed that at high  $\text{H}_2\text{O}_2$  concentration, scavenging effect of  $\text{H}_2\text{O}_2$  for  $\text{HO}^\circ$  increased, and this effect decreased the available values of  $\text{H}_2\text{O}_2$  for pollutant degradation. On the other hand, high initial concentrations of  $\text{H}_2\text{O}_2$  can enhance RE by increasing desorption [43].

### 2.2 Effects of pH on Fenton reaction

Fenton/Fenton-like processes are affected by pH that is mostly attributed to the pH effect on iron ions ( $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ ) and  $\text{H}_2\text{O}_2$ . One of the major problems of the Fenton reaction is its optimal pH, which is at acidic range [44]. At basic condition, which results in precipitation of  $\text{Fe}^{+2}$ , iron turns to an ineffective catalyst in these situations [18]. Adding one acid (usually acid sulphuric) for achieving the acidic range is required, which causes dramatic ecological impacts to many soils with near neutral or slightly alkaline effects [45]. The pH drops in the beginning of the Fenton reaction [46] due to the production of  $\text{H}^+$ . For the basic Fenton reaction, owning soluble  $\text{Fe}^{+2}$  with the aim of keeping  $\text{Fe}^{+2}$  in the liquid phase to be able to proceed with the reaction in that phase, the optimal pH is reported to be around 3. Therefore, in conventional Fenton reaction, acidic range of pH 3-4 is more suggested; increase in pH leads to

precipitation of  $\text{Fe}^{+2}$ , and at  $\text{pH} < 3$  proton solvation of  $\text{H}_2\text{O}_2$  and formation of oxonium ions ( $\text{H}_3\text{O}^{+2}$ ) reduces the reactivity of  $\text{H}_2\text{O}_2$  with ferrous ions [18]. For  $\text{pH} > 7$ , RE reduces as  $\text{H}_2\text{O}_2$  decomposes into  $\text{H}_2\text{O}$  and  $\text{O}_2$ , as it is reported by Eq.16 [41]:



There are considerable documented results of the effectivity of the contaminant destruction in acidic range. The higher reductive condition in the low pH is another reason why low pH is more favorable for Fenton reaction [18]. This optimum value was chosen based on the results for the highest RE of the target contaminants in the shortest time in the liquid phase. Whereas there are other reported results indicating higher achieved RE at pH close to the neutral condition (pH 7). For adjusting the soil pH to the acidic region for the large volume, the effectivity of the Fenton reaction will be reduced, for resolving this problem, using naturally occurring iron minerals helps in applying Fenton reaction at near-neutral pH [47], as the optimal pH depends on the Fe catalyst type and external additives. The presence of  $\text{Fe}^{+2}$  or  $\text{Fe}^{+3}$  is one of the main parameters affecting the optimum pH of Fenton and Fenton-like efficiency [18,39]. At different pH ranges, participating iron will be different. Except the initial form of added catalyst, one of the iron forms would participate, depending on the solution pH in the aqueous phase. Using iron minerals, magnetite and goethite, as catalysts for contaminant degradation shows that the Fenton reaction has occurred on the surface of iron minerals by electron transfer, and as a result, the degradation accelerates by increasing the mineral contents [20]. Among these iron minerals, those with both  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ , like magnetite, are named as more effective reagents than minerals with just  $\text{Fe}^{+3}$  like goethite [20]. Understanding how to control the applicability of pH range helps to increase RE of Fenton reaction for the field usage. For example, phosphates can be used as a stabilizer that leads to higher effectivity of Fenton-like reaction at near-neutral pH [47]. At neutral pH conditions, ferric ( $\text{Fe}^{+3}$ ) ions can be found as hydroxy complexes or even as oxide-hydroxide phases [10]. Yu and coworkers reported that by increasing the initial pH from 3.5 to 7.5, removal of bisphenol A (BPA) decreased, while by increasing the initial pH from 7.5 to the higher values, the degradation rate increased [44]. In the Kanel and coworkers' study, using goethite as the catalyst in Fenton reaction at neutral pH 7 showed higher efficiency in comparison with the acidic pH [41]. Kanel and coworkers evaluated

the phenanthrene degradation by Fenton-like oxidation by using goethite, at different initial pH from 3 to 10 [41]. By increasing the pH from 3 to 7, degradation rate increased in natural pH (pH 7) by reaching 80% decomposition of spiked sand sample, at 16.8 mg/kg goethite and H<sub>2</sub>O<sub>2</sub> at 5M, after 30 min [41]. The high degradation at pH 7 had been attributed to hydroxylated form of iron Fe(OH)<sup>+</sup>, which reacted faster with hydrogen peroxide [41]. There are some results indicating that Fe(OH)<sup>+</sup> is a more powerful species in comparison with Fe<sup>+2</sup> at acidic range, pH 2-4 [37-38]. Another explanation for the reduction of RE at acidic pH can be the reaction of the excess hydrogen ion (H<sup>+</sup>) in the solution at pH<3 with HO<sup>°</sup> [42].

### 3.Effects of SOM on Fenton reaction

#### 3.1 Dual effects of SOM on Fenton reaction

SOM has effects on Fenton reaction in the treatment of contaminated soil, however certain doubts about their roles exist [48]. The interaction of Fenton reaction with SOM is not completely understood, and different researches reported its dual capabilities [9,13]. SOM can affect Fenton reaction by competing with target contaminants for hydrogen peroxide and/or hydroxyl radicals, while it can promote the production of hydroxyl radicals [13]. The interaction of SOM and Fenton reaction is also a function of the adsorption state of SOM and contaminants, the reactivity of the contaminants, and the type of the catalyst [18].

The effects of SOM, including HA and FA, on the efficiency of Fenton reaction have been reported in many studies. Different passages for reaction between SOM and Fenton reaction-related reagents and chemicals have been reported. Two possible ways for the participation of SOM in Fenton reaction have been suggested. Some studies report an increase in RE of Fenton reaction by an increase in HA concentration, while in some others, higher HA concentration is considered as the main reason for a decrease in treatment efficiency [18]. In one way, SOM [16] and HA [9,49-50] can enhance the Fenton reaction efficiency by reducing Fe<sup>+3</sup> to Fe<sup>+2</sup> and performing the role of metal chelates [48]. In this way, it can increase the production rate of hydroxyl radicals. Huling and coworkers reported that in the peat-amended reactor, HO<sup>°</sup> production rate was 2.3 times greater than the reactor without peat [48]. While in their study, the effect of peat, as a source of SOM, for increasing consumption of HO<sup>°</sup> in

comparison with H<sub>2</sub>O<sub>2</sub> is insignificant. Xu and coworkers reported that Fe-SOM could lead to oxidizing TPH in solid phase of soil by producing HO<sup>°</sup> on the surface [51]. In the mentioned study, RE of TPH was 67% in types of soil with Fe-SOM in comparison with control soil samples with 6% RE. Alternatively, SOM can decrease RE of Fenton reaction by consumption of HO<sup>°</sup> [9,15-16,49,52]. SOM, like contaminants, is the consumers of HO<sup>°</sup>, so SOM is reported as the scavengers of hydroxyl radicals, and leads to a decrease in RE [15-16]. Lower decomposition kinetic rate of phenol in soil with higher SOM was reported by Romero and coworkers [53]. Goi and coworkers reported an optimum ratio for H<sub>2</sub>O<sub>2</sub> to transformer oil weight at 4:1 in peat on determining the effect of peat on the destruction of transformer oil by hydrogen peroxide [15]. In this study, increasing the ratio from 1.6:1 to 4:1 increased RE from 22% to 47%, and increasing from 4:1 to 8:1 decreased RE for soil with high SOM. In their study, for the sample with high SOM at the optimum condition of transformer oil weight at 4:1, RE reached 47%, while in the sand sample, the ratio of 0.04:1 had above 80% RE. Competition between hydrogen peroxide and SOM for HO<sup>°</sup> and the less contact between the oxidant and contaminants because of rapid reactions in high reactant dosage were mentioned as the reasons for this observation [15]. Depending on the magnitude of the effect of each of them, one of these two effects or both of them can be observed. Factors such as organic material and contaminant states (e.g., soluble or sorbed), the hydrophobicity and the reactivity of the probe contaminants, the nature of the used catalyst can be determining in the final and the net effect of these two different influential ways [18]. Participation of HA in any reaction leading to increasing HO<sup>°</sup> scavengers can be offset by its effects in enhancing the production of free radicals [12, 54]. In the Lindsey and coworkers' study, FA was reported as the responsible fraction for both the production and consumption of HO<sup>°</sup>, but the net production rate was higher, which led to the destruction of contaminants [49]. Higher compatibility of FA in a reduction of Fe<sup>+3</sup> to Fe<sup>+2</sup> than HA in the destruction of TNT was reported by Li and coworkers [55]. As they reported, FA could increase kinetics of destruction of TNT from 0.037 to 0.067 min<sup>-1</sup> while it had minimal effects on the total destroyed mass. The HA ability in donating or accepting electron is related to its functional groups such as aromatic moieties and its origin, as aromatic functional groups such as hydroxyl or phenolic HO<sup>°</sup> in HA causes appropriate local environments for

reduction of  $\text{Fe}^{+3}$  [9]. The higher destruction value of aromatic moieties of SOM than its aliphatic functional groups by reaction with Fenton is also reported. For example, Leifeld and coworkers showed a higher decomposition of aromatic carbons than aliphatic carbon of soil [36]. The destruction of the fraction of SOM located into the interlayers is greater than the fraction located on the surface. Treating the soil with  $\text{H}_2\text{O}_2$  and analyzing the soil with nuclear magnetic resonance (NMR) show the increase in alkyl C and decrease of O-alkyl C and aromatic C, which indicates the resistance of SOM located into the interlayer of clay mineral is higher toward destruction by hydrogen peroxide [13].

### *3.2 Effects of pH on SOM in relation with Fenton reaction*

The pH affects the reaction between Fenton reagents and SOM. At neutral pH, a decrease in  $\text{H}_2\text{O}_2$  decomposition rate and an increase in  $\text{HO}^\circ$  generation rate was reported by increasing SOM [13]. They explained that covering iron from participating in reaction at neutral pH can be the reason for the low destruction of  $\text{H}_2\text{O}_2$ . While, the higher decomposition of hydrogen peroxide in the soil with higher SOM percentage in natural pH was reported by Romero and coworkers [52]. At neutral pH, RE of organic pollutants in the presence of SOM is higher than in its absence, while at pH 3.5 addition of humic substance leads to a decrease in RE [56]. However, Bissey and coworkers reported an insignificant effect of SOM on  $\text{H}_2\text{O}_2$  decomposition rate at pH 3 and the activity of  $\text{HO}^\circ$ , which was attributed to the minimal influence of SOM in comparison with the iron catalyst [13]. For showing the chelation power of SOM, stability constant of  $\text{HA-Fe}^{+3}$  2.8, at circum-neutral pH can be compared with the significantly higher stability constants of  $\text{EDTA-Fe}^{+3}$ , 27.7 [16,49]. By adsorption of  $\text{Fe}^{+2}$  on HA, HA and  $\text{Fe}^{+2}$  form complexes, which are reduced to  $\text{HA-Fe}^{+3}$  complexes by the electrons from HA macromolecules, and resulting in the  $\text{HA-Fe}^{+2}/\text{Fe}^{+3}$  complexes which can possibly act as an organic acid with the potential of breaking covalent/hydrophobic linkages of HA [9,51]. On the other hand, it is shown that hydrolysed  $\text{Fe}^{+2}$  leads to a drop in pH that is a favourable environment for decomposing HA [9]. Therefore, based on the Fan and coworkers' study, HA was decomposed into smaller fractions with the increased decomposition of methomyl in the presence of  $\text{OH}^\circ$  [9]. Moreover, Bissey and coworkers' results showed that CHP-related radicals at neutral pH did not affect SOM, while these radicals could destroy

SOM at acidic pH [13]. Moreover, Voelker and coworkers showed the effect of FA on Fenton reaction and they reported that the carboxylate ligands, in FA, by making complexes with  $\text{Fe}^{+2}$  could promote oxidation in Fenton reaction at pH 5, and without considerable change in RE at pH 3 [50]. Based on their study, at pH 3, FA had insignificant effect on  $\text{H}_2\text{O}_2$  degradation, while at pH 5 this effect was considerable, and they concluded that the effect of FA on Fenton reaction was like small carboxylic acid such as oxalate. It was reported by Georgi and coworkers that the addition of HA increased the oxidation of organic compounds at pH 5-7, but its effects had not lasted for a long time due to the oxidation of HA [33]. It is showed by Georgi and coworkers that HA could extend the applicability of Fenton reaction to higher pH ranges near to 7 [33]. However, Bissey and coworkers reported that SOM loss was greater at acidic pH than at neutral pH [13]. Based on their results, SOM had not been affected by  $\text{HO}^\circ$  activity at pH 3, while at neutral pH the soil with higher SOM showed higher  $\text{HO}^\circ$  activity. In addition, enhancement in the effectivity of CHP reaction by a decrease in  $\text{H}_2\text{O}_2$  decomposition rate and generation of  $\text{HO}^\circ$  by SOM at neutral pH is reported by Bissey and coworkers, but not any other differences in RE at pH 3 were observed by an increase in SOM content [13]. They reported that the destruction of SOM was related to  $\text{H}_2\text{O}_2$  amount.

### *3.3 Effects of SOM on Fenton reaction through its microenvironments*

Another way that SOM can play roles in RE of organic contaminants destruction is taking part in adsorption-desorption processes [49]. SOM is considered a determinative factor in sorption processes. Sorption of contaminants onto SOM reduces the destruction of contaminants by Fenton reaction in two ways, one by consumption of  $\text{HO}^\circ$  and the other by retarding its oxidation [13]. Entrapment in pores and voids of SOM can hinder the Fenton reaction, but it is reported that Fenton reaction can improve the remediation process by enhancing desorption directly [45]. In Bogan and coworkers' study, sorption of PAH by SOM was reported as the reason for inverse correlation between SOM content and RE of PAH [57]. Organic pollutants can be entrapped into the holes of SOM, and over time, they will be indistinguishable from SOM [28]. The percentage of total organic carbon (TOC) in total soil and percentage of each fraction of SOM are important factors in analyzing the effect of SOM on RE of Fenton reaction. A threshold for

organic carbon is 5%, above which its efficiency reduces because of the adsorption of PAH onto SOM and the consumption of  $\text{HO}^\circ$  [48]. Furthermore, it is explained that according to the threshold of 5% of TOC, the higher content of humin leads to entrapment of contaminants into humin fraction, and the soil with higher TOC but lower humin has higher RE. Pateiro-Moure and coworkers by studying pyrene sorption parameters found that the humin percentage was the key factor in desorption hysteresis, and as the oxidation enhanced the humin percentage, desorption after oxidation became more hysteric [32]. Therefore, except from the above-mentioned threshold, the percentage of each fraction is determining in the sorption and consequently in RE of the adsorbed contaminants. In Pateiro-Moure and coworkers' study, an increase in  $\text{H}_2\text{O}_2$  up to reaching the humin fraction could lead to increase in the decomposition of SOM [32]. Hydroxyl radicals can participate in the reaction with the dissolved form more effectively than the contaminants attached to the particulate form [58]. Sedlak and coworkers argued that for reacting the particulate form, hydroxyl radicals needed to diffuse across the interface, so it made an extra resistance for the reaction [58]. When contaminants are partitioning on the surface or adsorbed by physical attraction, they can be considered as more accessible pollutants than the adsorbed by chemical forces or into micropores. HA causes enhancement in contact between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{+2}$ , the two major initial reagents of the Fenton reaction [49]. Sequestration of iron as one of the main initial reagents and pollutants into spatially separated microenvironmental sites will lead to a decrease in effectivity of Fenton reaction due to the presence of SOM and consequently due to the isolation of the pollutants from the  $\text{HO}^\circ$  formation site [24,49]. RE of PAH can be decreased by participating of HA in chelation of iron and binding of PAH to hydrophobic HA sites [24,49]. An increase in Fe-SOM with an increase in SOM was reported in Xu and coworkers' study, and they argued that transfer of  $\text{Fe}^{+2}$  from the liquid phase to the solid phase in higher SOM concentration is easier [51]. They explained that due to the reaction of  $\text{H}_2\text{O}_2$  with SOM,  $\text{Fe}^{+2}$  could be transferred from the liquid phase to the solid phase, and iron ions from soil would be transformed to the solid iron by SOM, and HA with its functional moieties such as alcohol, ether, and CO could make adsorption or complexation form with iron. In Georgi and coworkers' study, an increase in optimum pH of Fenton reaction to 5 and more by adding HA to the soil could be due to the above-mentioned complexes of iron with SOM which brings

the iron ions into microenvironmental sites on SOM [57]. The presence of HA leads to an increase in parathion decomposition rate due to the acidic microenvironment in HA [42]. Functional groups in HA are capable of protonation, which leads to produce a locally environment with acidic properties [42]. As a result, when  $\text{HO}^\circ$  is produced on the surface of solid matrix with iron oxide, destruction of contaminants on the surface can happen directly by  $\text{HO}^\circ$  [51]. The effects of intermediates need to be considered as well. The oxidation intermediates in the presence of HA can complex with  $\text{Fe}^{+2}/\text{Fe}^{+3}$ . The results of this complexation are faster reduction of  $\text{Fe}^{+3}$  and increase in degradation of PAH such as parathion [42].

#### 4. Conclusion

By increasing our knowledge about the Fenton reaction, this important reaction can have wider applications from scientific and engineering points of view, especially for environmental applications. The complexity of the Fenton reaction can be due to the effect of a wide range of variables and factors. Besides the considerable amounts of involved chemicals in this reaction, the catalytic nature of this reaction adds to the complexity of the analysis. One of the major influential factors is the effects of SOM on reaction from the content, physical and chemical aspects. This study tries to provide a review of many of the important studies in this area. Parameters such as initial reagents and pH are affecting the way that SOM interacts with contaminants, soil particles, and Fenton reagents. By considering the chemical aspects of functional moieties of SOM and their physical structures, almost all required aspects in the analysis of SOM effects on Fenton reaction can be included.

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