Treatment of Landfill Leachate by Fenton Process with Nano sized Zero Valent Iron particles

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ABSTRACT: Leachate treatment from municipal landfills has been always a major anxiety in waste management due to its high level of various contaminations. In this paper the effect of Nanosized Zero Valent Iron particles (NZVI) in Fenton process for the treatment of high COD strength landfill leachate was scrutinized. The results corroborated this procedure was fast and efficient. In fact, about 87% of initial COD (38 g/L) was reduced in an hour. The various operation conditions such as pH, initial H_2O_2 concentration, H_2O_2/Fe molar ratio and temperature in a batch reactor were investigated. The optimum condition was obtained at pH value of 2, temperature of 40°C and H_2O_2 to Fe molar ratio equal to 39 by using only 0.07 M of NZVI. In such conditions, 0.08 M H_2O_2 for the removal of 1 g/L of COD was needed. Furthermore, hydrogen peroxide consumption after Fenton process was evaluated and it was found that it had a direct relationship with COD removal efficiency.

Key words: Fenton process, Nanosized zero valent iron (NZVI), Landfill leachate, COD removal

INTRODUCTION

Sanitary landfills are the primary method currently used for municipal solid waste disposal in many countries, and leachate generated from landfills is a high-strength wastewater exhibiting acute and chronic toxicity. Untreated leachates can permeate ground water or mix with surface waters and contribute to the pollution of soil, ground water, and surface water (Deng & Englehardt, 2006). In Iran due to high fraction of organics in municipal solid waste (about 80%), Chemical Oxygen Demand (COD) of leachate is high and varies between 30 and 100 g/L. On the other hand due to existence of dry climate and lack of water resources, leachate treatment and management are known as one of the greatest environmental concerns. However, with the continuous hardening of the discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachates, conventional treatments (biological or physico-chemical) are not sufficient anymore to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment. It implies that new treatment alternatives species must be proposed (Renou

et al, 2008; Nwabanne *et al.,* 2009; Dabhade *et al.,* 2009; Hassani *et al.,* 2009; Uemura, 2010; AbdulAziz *et al.,* 2010).

The Fenton reaction as one of the Advanced Oxidation Processes (AOPs) is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalyst. These radicals are a very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions (Barbusiński & Majewski, 2003; Lucking *et al.,* 1998). Fenton process was more readily employed to treat landfill leachate, as it is much cheaper and easier to operate compared with other AOPs. (Zhang *et al.,* 2006). Recently there have been numeral reports about landfill leachate treatment by classical Fenton process (H_2O_2/ ferrous salt) (Zhang *et al.,* 2006; Zhang *et al.,* 2005a; Zhang *et al.,* 2009; Lopez *et al.,* 2004; Trujillo *et al.,* 2006; Deng, 2007; Rivas *et al.,* 2004; Hermosilla *et al.,* 2009; Wang *et al.,* 2009). Beside the classical Fenton's reaction, recent studies have focused especially on

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investigation of the Fenton process with alternative iron sources (Barbusiński & Majewski, 2003) such as elemental iron (Fe⁰) that is one of the most widely used zero-valent metal (such as Fe^0, Zn^0, Sn^0, and Al^0) because it is readily available, inexpensive, and nontoxic (Joo & cheng, 2006). Zero-valent iron (Fe⁰) is a mild reducing agent with an $EH^0 = -0.440$ V (Zhang *et al.*, 2005b). In this process NZVI in the presence of H_2O_2 is transformed into Fe^{2+} (Bergendahla & Thies, 2004; Pourbaix, 1966):

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \qquad (1)$$
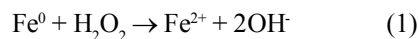
Fe^{2+} can then react with H_2O_2 in traditional Fenton's oxidation reactions (Bergendahla & Thies, 2004; Pignatello, 1992):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \qquad (2)$$
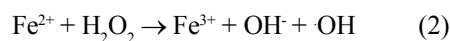
The formed radicals react with organic materials breaking them down gradually in a stepwise process (Martýnez, 2003).

Barbusinski and Majewski (2003) demonstrated that H_2O_2/Fe^0 process was very efficient for discoloration of simulated wastewater containing commercial Azo dye Acid Red 18. Bergendah and Thies (Bergendahla & Thies, 2004) illustrated the effectiveness of using Fe⁰ as the iron source in Fenton's oxidation for treating MTBE-contaminated water. Boussahel et al. (2007) reported that degradation tests of obsolete DDT by Fenton oxidation with zero-valent iron provides a promising alternative to the traditional techniques of elimination also from the economic point of view.

For COD reduction a few research results reported using ZVI and Fenton process. Rodrigues et al. (2008) indicated that combined ZVI and Fenton process was significantly efficient for the COD reduction of an explosive industry effluent. Kallel et al. (2009a, 2009b) presented that zero-valent Fe/H_2O_2 could be considered as an effective alternative solution for the COD and phenolic compounds removal of olive mill wastewater. Furthermore, the innovative nano-technology applied in the environmental remediation by NZVI has erupted promptly and dynamically (Masciangioli & Zhang, 2003; Shu *et al.*, 2009). Lin et al. (2008) compared the effect of particles size on the degradation of AB24 and determined that for the NZVI, the dyes were completely removed in 20 min, whereas 70% of the initial dye remained in the case of micro-size ZVI under otherwise the identical conditions. Zhang (2003) reviewed that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common

environmental contaminants and modified iron nanoparticles enhance the speed and efficiency of remediation. Shu et al. (2009) proved that the integration technique of NZVI particles addition with UV/H_2O_2 process saving time and energy thus it could be innovative and advanced application.

As mentioned, even though there are a few researches on application of microsized zero valent iron by the Fenton process, using nanosized particles in this respect is quite new. So this study investigates Fenton process efficiency for organic load reduction of landfill leachate by NZVI particles and the influence of the initial pH, reaction time, H_2O_2/Fe^0 mol ratio, hydrogen peroxide and NZVI dosage and temperature has been explored.

MATERIALS & METHODS

Leachate samples were taken by polyethylene bottles from the municipal sanitary landfill which was located in Tehran, Iran in March of 2010. Table 1 shows the main characteristics of the leachate used in experiments. The NZVI (Particle size: 8-18 nm, purity: 85%, SSA: 59-79 m²/g, black, spherical) was obtained from Research Institute of Petroleum Industry (Tehran, Iran). A photomicrographic image of the iron nanoparticles was recorded with a Transmission Electron Microscopy (TEM) as shown in Fig. 1. From this figure, we know that the diameter of Zero Valent Iron is smaller than 20 nm. All chemicals used were of analytical grade and were purchased from Merk Co. COD was measured by Hach vials (range 20-1500 mg/L) with HACH spectrophotometer (HACH, DR4000, USA) according to standard method (APHA, 1992). BOD_5 was measured according to the Standard Methods 5210B (APHA, 1992). Concentration of residual H_2O_2 was analyzed by iodometric method (Kang *et al.*, 1999). All chemicals used were of analytical grade and were purchased from Merk Co. COD was measured by Hach vials (range 20-1500 mg/L) with HACH spectrophotometer (HACH, DR4000, USA) according to standard method (APHA, 1992). BOD_5 was measured according to the Standard Methods 5210B (APHA, 1992). Concentration of residual H_2O_2 was analyzed by iodometric method (Kang *et al.*, 1999).

Prior to do the experiments the leachate containing bottle was sufficiently mixed in order to make a homogenous condition for all samples. Then leachate samples (100 ml) were placed in Erlenmeyer flasks. In nitrogen atmosphere a selected amount of NZVI was added to the samples. Then pH was adjusted to the desired value with a pH meter (340i, WTW, Germany) by adding 5 M sulfuric acid and 4 M sodium hydroxide. Leachate samples were subjected to ultrasound sonicating for 10 min with a bath type sonicator
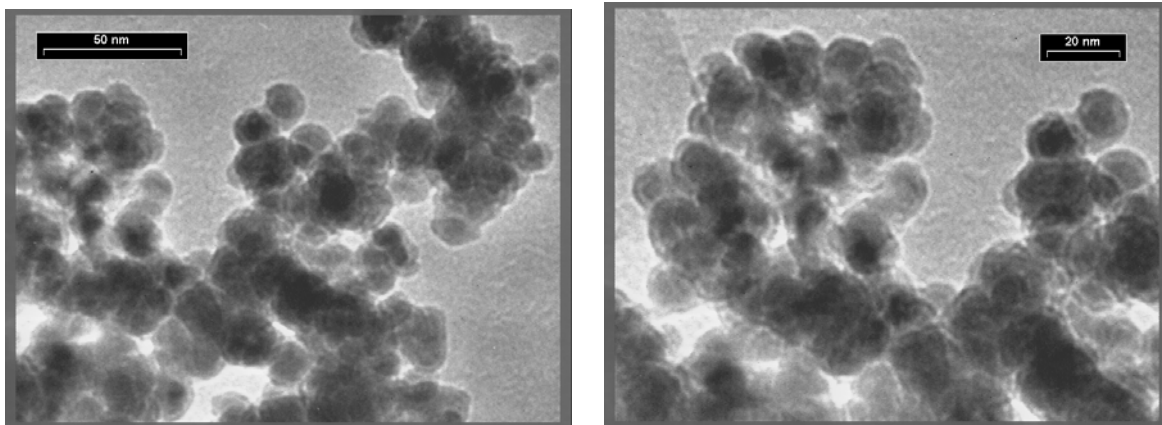
Fig. 1. TEM photomicrograph of a nanoparticle cluster. Size bar is 50 and 20 nm

Table 1. Properties of the leachate used in different experiments

Parameter	Value	Parameter	Value
pH	6.5	Hg (ppm)	< 0.5
COD(mg/L)	38000	Cr (ppm)	0.7
BOD_5(mg/L)	15000	Cu (ppm)	0.075
EC(ms/cm)	60	Fe (ppm)	35
Alkalinity(mg/L as $CaCO_3$)	10000	K (ppm)	1650
Pb (ppm)	<0.1	Mg (ppm)	500
Ca (ppm)	1250	Mn (ppm)	3.2
Cd (ppm)	<0.02	Na (ppm)	5500
Al (ppm)	1.6	Sr (ppm)	9
Ni (ppm)	0.47	Zn (ppm)	1

(Sonoswiss, SW3H). After that, samples were shaken for 15 min at 100 rpm with an orbit type shaker. This procedure increased pH of the samples according to reaction (3) (Zhang, 2003):

$$Fe^0_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \tag{3}$$
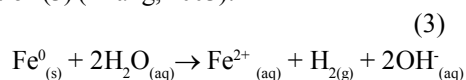
So it was necessary to adjust pH to the desired value again. Then 30% (w/w) H_2O_2 solution was added to the samples in a single step. Finally a continuous shaking at 225 rpm was applied for 3 hours. During the reaction period, samples (20 ml) were taken at pre-selected time intervals and immediately analyzed. At the end of the experiment, the residual amount of H_2O_2 in leachate samples was determined by iodometric method. This method has the advantage that it is hardly affected by organic substances and the stabilizers which are sometimes added to the commercial hydrogen peroxide solutions (kang, 1999). Lopez et al. (2004) previously have used this method for determining the residual amounts of H_2O_2 in the leachate.

For COD analysis, all tests were made after the total removal of residual H_2O_2 from all samples, because the residual H_2O_2 increases the COD value since it acts as a reductant, especially in chromate-based analysis of COD (Barbusinski & Filipek, 2001). To eliminate the remaining H_2O_2 and stop the oxidation reaction, the following procedure according to Deng's method (Deng, 2007) was used: NaOH pellets were added to 20 ml withdrawn samples to increase pH to about 8. Then pH of the samples was adjusted to 9 using sufficient amounts of 4 M NaOH solution and after that, samples were brought to the room temperature for 3 hours sedimentation period. It was checked that this procedure significantly eliminated all the residual H_2O_2 and had no effect on the COD value. Finally, the supernatant was centrifuged for 10 min at 5000 rpm (Hettich, EBA21-Centrifuge) and then COD in the supernatant was measured.

RESSULTS & DISCUSSION

pH and H_2O_2/Fe molar ratio are the most important variables in Fenton process. Several authors have demonstrated that optimal H_2O_2/Fe molar ratio was independent of initial COD and ferrous iron dosage (Zhang *et al.,* 2009; Deng, 2007). Furthermore, Zhang et al. (2009) reported that optimal value of H_2O_2/Fe molar ratio was related to initial pH. Therefore, to determine the optimal ratio of Fenton reagents, in different pH values between 1 to 4 and at a fixed amount of NZVI, H_2O_2 with initial concentration ranging from 0.8 to 4 M was added to the leachate. Results of these experiments are reported in figure 2 a-d. Regarding these figures it can be concluded that COD removal efficiencies increased with the increase of H_2O_2 concentration and maximum COD reduction occurred in the first one hour of the reaction, and after one hour there was hardly any reduction of COD values, even after prolonging the reaction up to 3 hours. Fig. 3 summarizes the effect of pH and H_2O_2/Fe molar ratio on the COD removal. As seen in figure 3, it seems that the variation of COD removal versus initial H_2O_2 concentration is to some extent different for different pH values. This trend shows that the optimal value of H_2O-$_2$/Fe molar ratio is influenced by initial pH which is in agreement with previous study of Zhang et al. (2009). At pH 1 and 3, COD removal increased with increase of initial H_2O_2 concentration, while COD removal changed insignificantly at higher initial H_2O_2 concentrations when pH was 2 or 4. It should be noted that at pH 1 and 3 like pH 2 and 4, the increase of COD removal efficiency declined for higher H_2O_2 concentrations, although this happened earlier at pH 2 and 4 than it did at pH 1 and 3. Overall, what matters more is that the general trend as proposed by such figures indicates that increase of H_2O_2 concentration can help raise COD removal until a certain value. As the concentration goes beyond this, it grows less effective on increasing COD removal.
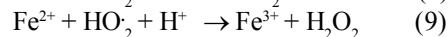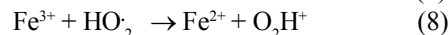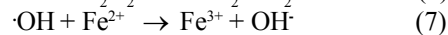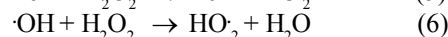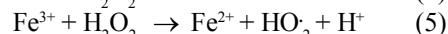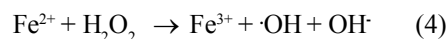
Regarding these results, the optimum condition occurred at pH value between 2 and 3. This agrees with previous studies on the oxidation of organic compounds in leachate treatment (Zhang *et al.,* 2005a; Kang & Hwang, 2000; Lau *et al.,* 2001). pH values below the optimum condition slowed down the reaction due to the formation of complex iron species and formation of oxonium ion $[H_3O_2]^+$ (Kallel, 2009a). On the other hand, as mentioned by Deng & Englehardt (2006), at pH values above optimum range, Fenton oxidation was hindered since the absence of H^+ can inhibit the decomposition of H_2O_2 and therefore reduce the production of ·OH, so the oxidation potential of ·OH decreased with the increase of pH.

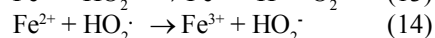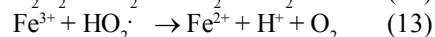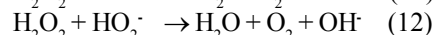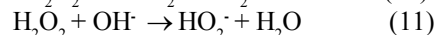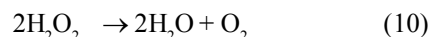As seen in fig. 3, COD removal at pH 2 increases rapidly to about 80% and remains relatively constant upon further increase of H_2O_2 which is in agreement with previous studies (Zhang, 2005a; Deng, 2007). Harber & Weiss (1934) reported that the reaction was second order at low H_2O_2 to Fe^{2+} ratio, but became zero order at high H_2O_2/Fe^{2+}. Zhang et al. (2005a) explained that at high H_2O_2/Fe molar ratio, one or more side reactions occur. So the mechanism changes and the reaction become independent of hydrogen peroxide, therefore less efficient improvement in removals is obtained.

As a result H_2O_2/Fe molar ratio of 39 (2.7:0.07) at pH 2 was selected for further experiments. In comparison with previous studies, this optimum ratio was high which was probably due to the effect of nano particles. For example Kim and Huh (1997) reported an optimal molar ratio of 12.5:1, Zhang et al. (2005a) and Hermosilla et al. (2009) reported a molar ratio of 1.5:1 and Lopez et al. (2004) reported an optimal molar ratio of 18:1. In fact small particle size and high specific surface of nano particles lead to high efficiency and low utilization of NZVI.

Based on reactions 1 and 2, 0.5 M NZVI is needed to decompose 1 M hydrogen peroxide to generate hydroxyl radicals. Therefore, it can be concluded that H_2O_2 to Fe molar ratio must be 2, while according to the obtained results (fig. 3) the optimum ratio is 39. Three possible arguments may be proposed herein. First, there are many other reactions and side reactions in Fenton mechanism, all of which consume Fe and hydrogen peroxide. The classical Fenton free radical mechanism in the absence of organic compounds after reactions 1 and 2 mainly involves the sequence of reactions below (Deng & Englehardt, 2006).

$$Fe^{2+} + H_2O_2 \; \rightarrow Fe^{3+} + ·OH + OH^- \qquad (4)$$
$$Fe^{3+} + H_2O_2 \; \rightarrow Fe^{2+} + HO·_2 + H^+ \qquad (5)$$
$$·OH + H_2O_2 \; \rightarrow HO·_2 + H_2O \qquad (6)$$
$$·OH + Fe^{2+} \; \rightarrow Fe^{3+} + OH^- \qquad (7)$$
$$Fe^{3+} + HO·_2 \; \rightarrow Fe^{2+} + O_2H^+ \qquad (8)$$
$$Fe^{2+} + HO·_2 + H^+ \; \rightarrow Fe^{3+} + H_2O_2 \qquad (9)$$

In addition, some examples of side reactions are as follows (Zhang *et al.,* 2005a):

$$2H_2O_2 \; \rightarrow 2H_2O + O_2 \qquad (10)$$
$$H_2O_2 + OH^- \rightarrow HO_2· + H_2O \qquad (11)$$
$$H_2O_2 + HO_2· \; \rightarrow H_2O + O_2 + OH^- \qquad (12)$$
$$Fe^{3+} + HO_2· \; \rightarrow Fe^{2+} + H^+ + O_2 \qquad (13)$$
$$Fe^{2+} + HO_2· \; \rightarrow Fe^{3+} + HO_2^- \qquad (14)$$

Second, landfill leachate has a lot of various components (Table 1) which may influence on / interfere with Fe and H_2O_2 reaction. Finally, Fenton reagents are not thoroughly exhausted in the reaction. This may
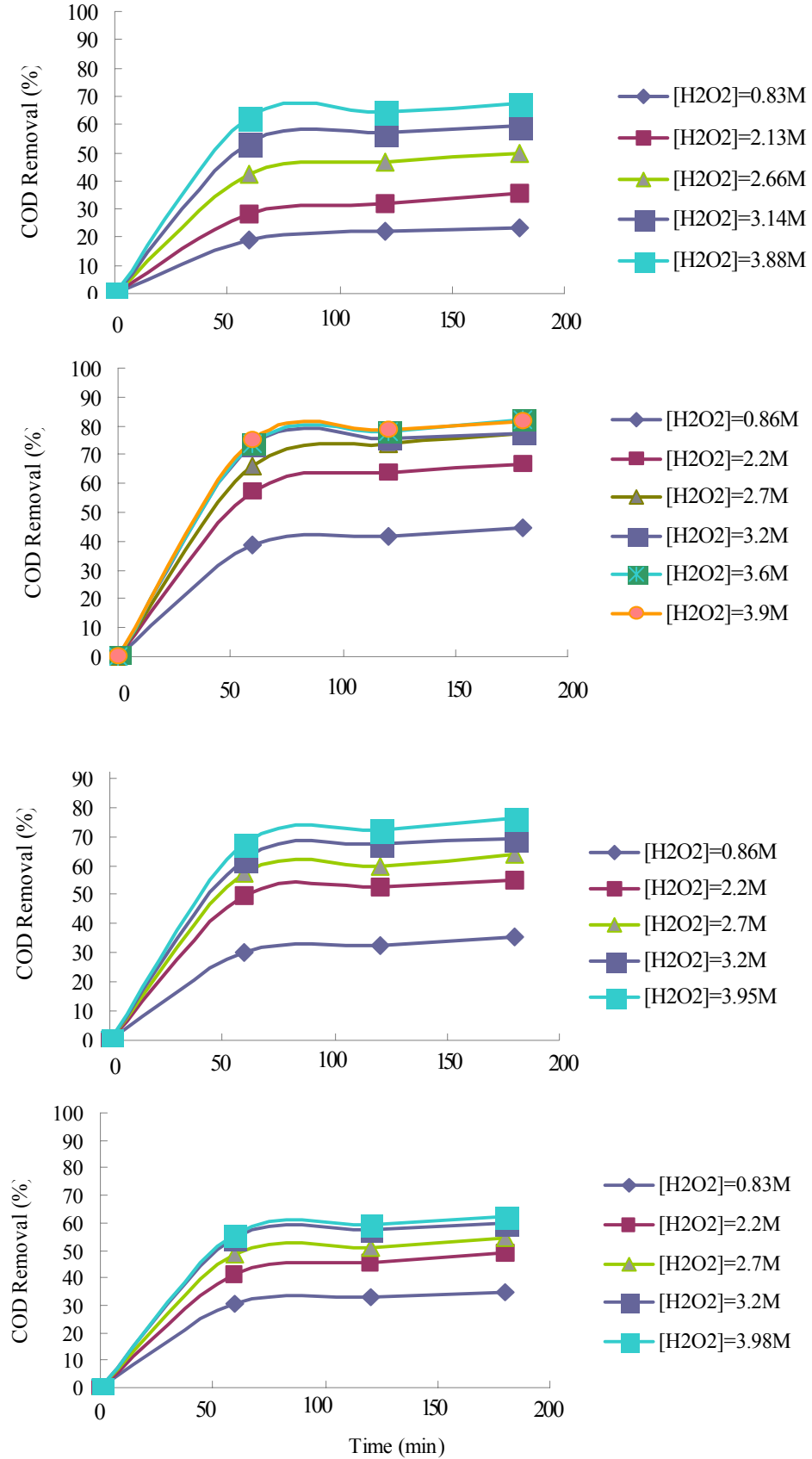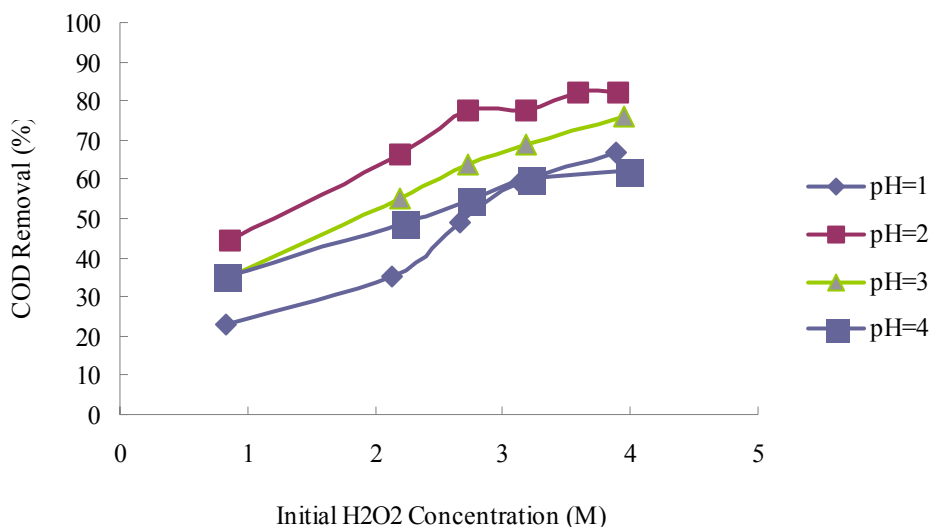
Fig. 2. COD removal efficiency at different H_2O_2 concentration during the Fenton oxidation. a)pH=1, b)pH=2, c)pH=3, d)pH=4 ([NZVI]=0.07 M, Initial COD=38 g/L)

Fig. 3. Effect of initial pH on the COD removal efficiency at different H_2O_2 Concentration ([NZVI]=0.07 M, Initial COD=38 g/L, t=3 hr)

be justified in light of the fact that Fe and H_2O_2 do not completely dissolve and also have unpurified components. According to the previous arguments, NZVI and H_2O_2 are needed more than theoretical values. It is also worth mentioning that as mentioned above, previous authors have also reported different optimum H_2O_2 to Fe molar ratios.

In general, the final pH of the treated solution after Fenton reaction is independent from the initial acidity of solution (Kallel *et al.*, 2009b). Regarding fig. 4, we can observe that with initial pH 3 and 4, the final pH decreases to 2.3 and 2.7 respectively, but at initial pH 1 and 2, it increases to 1.1 and 2.1 respectively. In fact, Fenton oxidation by initial pH between 1 and 4 tends to reach pH value between 2.3 and 2.0 (fig. 4). This is in agreement with the previous study of Kallel et al. (2009b) according to which, pH value reached close to 3.5 after 24 hr by olive mill wastewater. They explained this feature by the fact of transforming wastewater into organic acids with a short chain when it subjected to the Fenton process. The presence of ionized form of these acids is responsible for this buffering effect in the treated solution. On the other hand, we can realize that at higher H_2O_2 concentration, the final pH is lower. This is probably due to more efficient oxidation of Fenton process that leads to more production of short chain organic acids. Fig. 5 shows the consumption of hydrogen peroxide in Fenton oxidation at initial pH between 1 and 4. It is interesting that in higher COD removal efficiency, the higher H_2O_2 consumption was observed which denotes a direct relationship between COD and H_2O_2 consumption. At optimum initial pH 2, higher decomposition of H_2O_2 was observed in

comparison with other pH values. Also at optimum molar ratio, higher consumption of H_2O_2 was occurred. Moreover, when the H_2O_2 consumption was low, sludge settled difficultly due to oxygen bubbles produced from the decomposition of excess hydrogen peroxide.

The rate of COD removal in fenton process is mainly ascertained by availability of fenton reagents, which have major role in formation of hydroxyl radicals. Therefore, after determination of optimum pH and H_2O_2 to Fe molar ratio, it is important to determine the amount of Fenton reagents to reach higher efficiency. Therefore the H_2O_2/Fe molar ratio was fixed at 39 and with initial pH 2, the efficiency of six different amount of Fenton reagent was tested. The results are shown in fig. 6. It was observed that with concentration more than 2.7 M of hydrogen peroxide, COD removal efficiency remains relatively constant. This result is confirmed by the consumption of hydrogen peroxide shown in fig. 7. As seen, when the concentration of H_2O_2 was more than 2.7, percentage consumption of hydrogen peroxide remained relatively constant. This concentration was selected for further experiments. In this ratio, removal of 1 g/L of COD needed 0.08 M hydrogen peroxide.

In order to determine the effect of temperature, leachate samples were prepared according to the experimental procedure and before adding H_2O_2 their temperatures were raised to the desired values (25, 40, 50° C). Subsequently pH value was adjusted on 2 and H_2O_2 was added and they were shaken in the oven to maintain a steady temperature. It was observed that the Fenton reaction was so intense at 40 and 50°C and
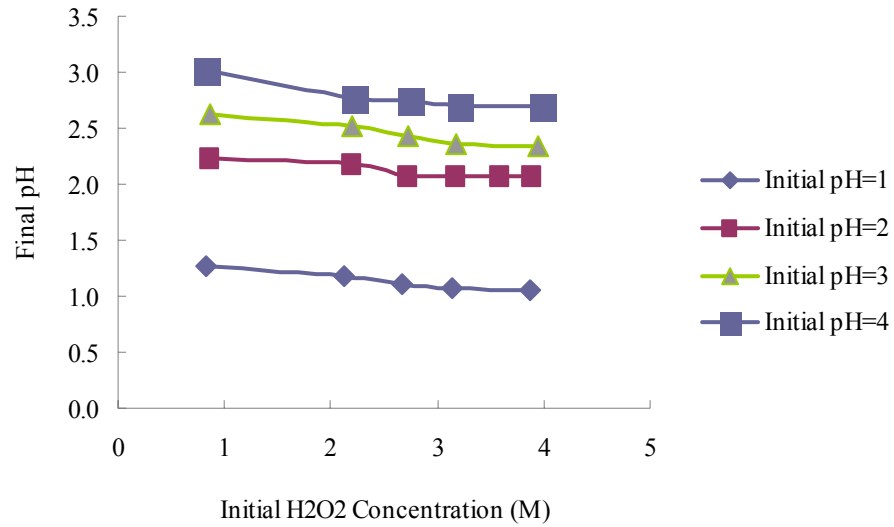
Fig. 4. Final pH of Fenton oxidation at various initial pH and H_2O_2 concentration (initial COD=38 g/L, time=3hr)
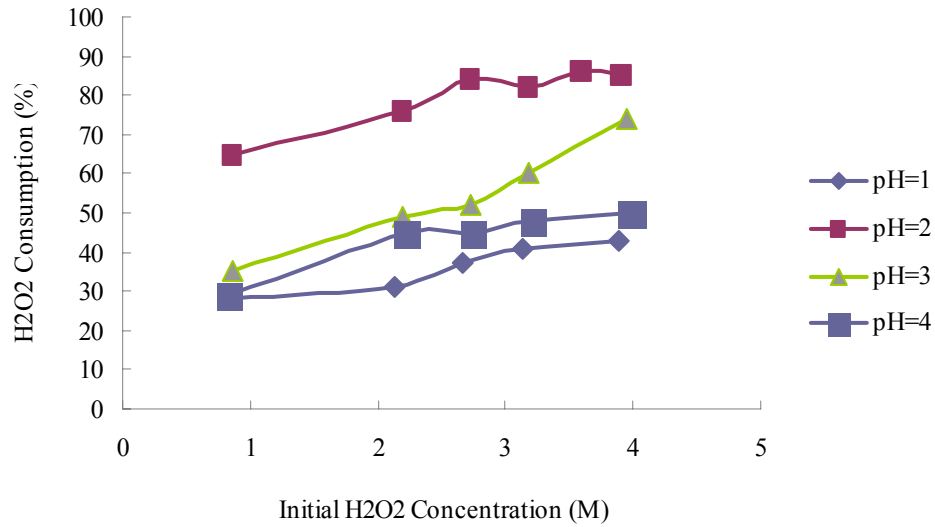
Fig. 5. H_2O_2 consumption at various initial pH and H_2O_2 concentration (initial COD=38 g/L, time=3hr)
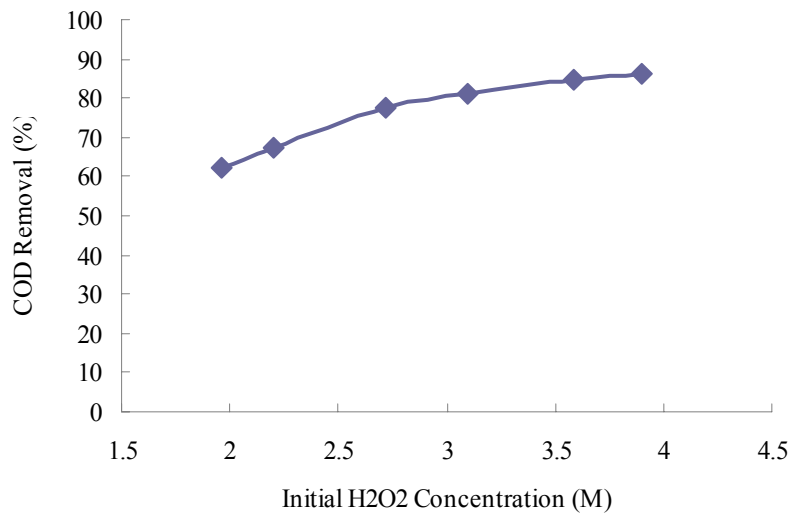
Fig. 6. COD removal efficiency at different dosage (pH=2, $[H_2O_2]/[Fe]$=39, time=3 hr, initial COD=38 g/L)

large amounts of gas were produced. As seen in fig. 8, increasing the temperature has a significant positive effect on COD removal efficiency and about 87% of initial COD was removed within only an hour such that approximately 90% of this amount was achieved in the first 15 min of the reaction. But in ambient temperature (25° C) just about 70% of COD was reduced after an

hour. Therefore, temperature is one of the important factors influencing Fenton oxidation rate as a catalytic reaction. On the other hand, as fig. 8 depicts, increasing the temperature from 40 to 50° C has an insubstantial effect. This is possibly due to inefficient H_2O_2 decomposition that offsets increase of COD removal (Deng & Englehardt, 2006).
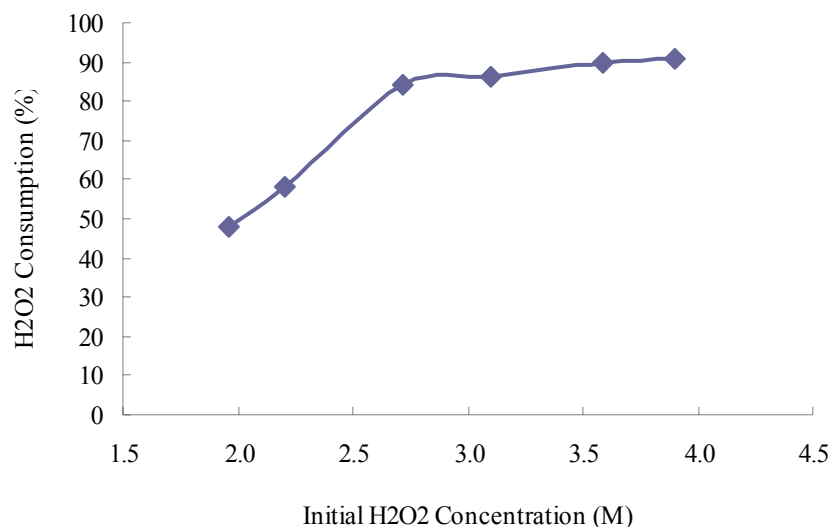

Fig. 7. H_2O_2 consumption at different dosage (pH=2, [H_2O_2] / [Fe]=39, time=3 hr, initial COD=38 g/L)
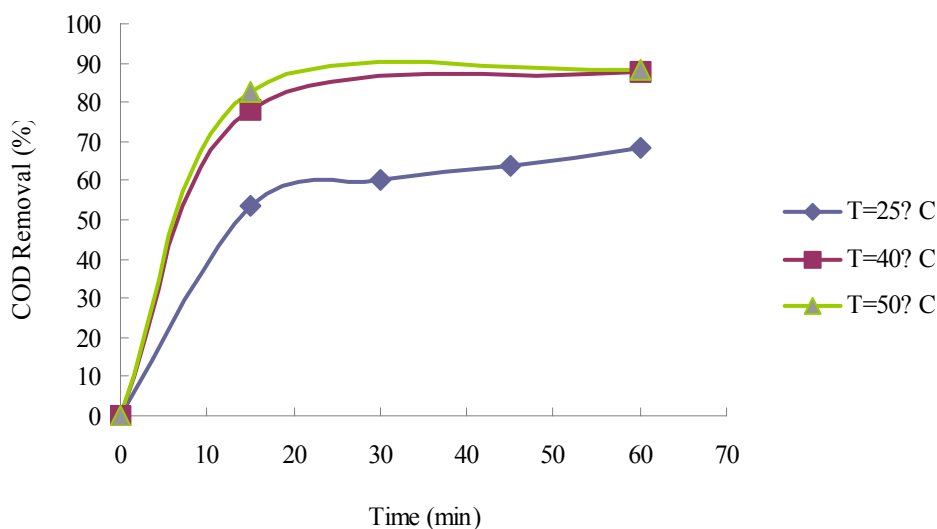

Fig. 8. COD removal efficiency at different temperatures during the Fenton oxidation (pH=2, [H_2O_2]/[Fe]=39, [H2O2]=2.7 M)

CONCLUSION

In this paper effect of Nanosized Zero Valent Iron (NZVI) for enhancement of Fenton reaction in organic load reduction of landfill leachate (initial COD=38 g/L) was investigated. It was observed this technique was a fast and efficient procedure and 87% removal efficiency was obtained in 1 hr while about 90% of this

amount was achieved in the first 15 min of the reaction. The optimal condition was at pH value about 2, temperature of 40° C and H_2O_2 to Fe molar ratio of 39. This molar ratio was much high in compare with the results of previous studies on treatment of landfill leachate by Fenton reaction. This feature was much probably due to using of Nano sized Zero Valnt Iron.

In fact, small particle size and high specific surface of NZVI resulted in high efficiency and low utilization of this matter. The experimental results showed that removal of 1 g/L of COD needed 0.08 M hydrogen peroxide. It was detected that at optimum H_2O_2/Fe molar ratio, increasing of reagents' dosage and temperature leading to increasing of removal efficiency. In temperatures more than $40°C$ there was a mild positive effect on COD removal that maybe it was due to inefficient H_2O_2 decomposition. Furthermore, it was proved that H_2O_2 consumption have direct relationship by COD removal efficiency.

ACKNOWLEDGEMENT

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