

## Organic load removal of landfill leachate by fenton process using Nano Sized Zero Valent Iron particles

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**Abstract**—The present study was conducted to elucidate the effect of Nano sized Zero Valent Iron particles (NZVI) as an iron source in fenton process for the organic load reduction of high COD strength landfill leachate (initial COD 38000 mg/l). The influence of operating variables such as reaction time, initial pH, H<sub>2</sub>O<sub>2</sub>/Fe<sup>0</sup> molar ratio, temperature, hydrogen peroxide and NZVI dosage was evaluated and the optimum value of each parameter was ascertained. According to the results, optimum operating condition can be recommended as initial pH 2, temperature of 40° C, H<sub>2</sub>O<sub>2</sub>/Fe molar ratio of 39 by using only 0.07 M of NZVI. It was determined that temperature has intense effect on COD removal efficiency and in the optimum condition fenton reaction was so violent which the rate of COD removal reached to 87% in an hour.

**Keywords**-Fenton Process, Nano Sized Zero Valent Iron (NZVI), Landfill leachate, COD removal

### I. INTRODUCTION

Leachates are defined as the aqueous effluent generated as a consequence of rainwater percolation through wastes, biochemical processes in waste's cells and the inherent water content of wastes themselves [1]. Nowadays, treatment of landfill leachate, which is one of the main pollutants of soil and water resources, is of great importance. In addition, discharge regulations and standards are becoming more and more stringent, world widely. As a result, today there is increasing interest in developing new and more efficient technologies for treatment of landfill leachate.

The catalytic decomposition of hydrogen peroxide by ferrous ion (i.e., Fenton's reagent) was first described by Fenton (1894) and is one of the most commonly used advanced oxidation processes (AOPs) for wastewater treatment [2]. Huang et al. [3] discussed the advantages and disadvantages of AOPs and suggested that methods like the Fenton process are the most promising technologies for the treatment of wastewaters. Recently there have been numeral reports about landfill leachate treatment by classical fenton process (H<sub>2</sub>O<sub>2</sub>/ferrous salt). [4-9]. Beside the classical Fenton's reaction, recent studies have focused especially on investigation of the Fenton process with alternative iron sources [10]. In recent years Zero Valent Iron (ZVI) (or Fe<sup>0</sup>) has been the subject of numerous studies. ZVI is effective for the reduction of a diverse range of contaminants, including dechlorination of chlorinated solvents in contaminated groundwater, reduction of nitrate to atmospheric N<sub>2</sub>, immobilization of numerous inorganic

cations and anions, reduction of metallic elements, and the reduction of aromatic azo dye compounds and other organics such as pentachlorophenol and haloacetic acids [11]. These results open promising perspectives since their conception as a fast and economical alternative iron source for fenton reaction. Some authors narrated information on effectiveness of ZVI in fenton oxidation of variety of contaminant such as treatment of MTBE [12], discoloration of Azo dye compounds [10], DDT degradation [13], phenolic compounds removal [14] and COD reduction [15-16].

However, 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<sub>2</sub>O<sub>2</sub>/Fe<sup>0</sup> molar ratio, hydrogen peroxide and NZVI dosage and temperature has been explored.

### II. MATERIALS AND METHODS

#### A. Materials and analytical methods

The stock leachate sample was taken by polyethylene bottle from the municipal sanitary landfill which is located in Tehran, Iran, in March of 2010 and preserved in refrigerator at 4°C according to the Standard Methods [17]. The main characteristics of the leachate sample were pH 6.5-7, COD 38000 mg/l, BOD<sub>5</sub> 15000 mg/l, Alkalinity as CaCO<sub>3</sub> 10000 mg/l, conductivity 60 mScm<sup>-1</sup>.

All chemicals used were of analytical grade and purchased from Merk Co and ZVI particle size was in the range of 5-7 μm. COD was measured with Hach spectrophotometer (HACH, DR4000, USA) using hach vials (range 20-1500 mg/l), according to Standard Methods [17]. BOD<sub>5</sub> was measured according to the Standard Methods 5210B [17]. Concentration of residual H<sub>2</sub>O<sub>2</sub> was analyzed by iodometric method [18]. pH was adjusted and controlled using a pH meter (340i, WTW, Germany).

#### B. Experimental procedure

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 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 (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 (1), so it was necessary to adjust pH to the desired value again. Then 30% (w/w) H<sub>2</sub>O<sub>2</sub> 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, residual amounts of H<sub>2</sub>O<sub>2</sub> in leachate samples were determined by iodometric method [18].

For COD analysis, all tests were made after the total removal of residual H<sub>2</sub>O<sub>2</sub> from all samples, because the residual H<sub>2</sub>O<sub>2</sub> increases the COD value since it acts as a reductant, especially in chromate-based analysis of COD [19]. To eliminate the remaining H<sub>2</sub>O<sub>2</sub> and stop the oxidation reaction, the following procedure according to Deng's method [8] 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<sub>2</sub>O<sub>2</sub> 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.

### III. RESULTS AND DISCUSSION

#### A. Effect of initial pH and H<sub>2</sub>O<sub>2</sub>/Fe<sup>0</sup> molar ratio

pH and H<sub>2</sub>O<sub>2</sub>/Fe molar ratio are the most important variables in fenton process. Several authors have demonstrated that optimal H<sub>2</sub>O<sub>2</sub>/Fe molar ratio was independent of initial COD and ferrous iron dosage [6,8]. Furthermore, Zhang et al. [6] reported that optimal value of H<sub>2</sub>O<sub>2</sub>/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 (7 g NZVI / lit of leachate), H<sub>2</sub>O<sub>2</sub> with initial concentration ranging from 0.8 to 4 M was added to the leachate. Results of these experiments are reported in Fig. 1. Regarding this figure it can be concluded that COD removal efficiencies increased with the increase of H<sub>2</sub>O<sub>2</sub> concentration. As can be seen in Fig. 1, the optimum molar ratio is different at each pH value which is in agreement with previous study of Zhang et al. [6]. Inferring these results, the optimum condition occurred at pH 2. Lower pH values slowed down the reaction due to the formation of complex iron species and formation of oxonium ion [H<sub>3</sub>O<sub>2</sub>]<sup>+</sup> [15]. However, at pH values

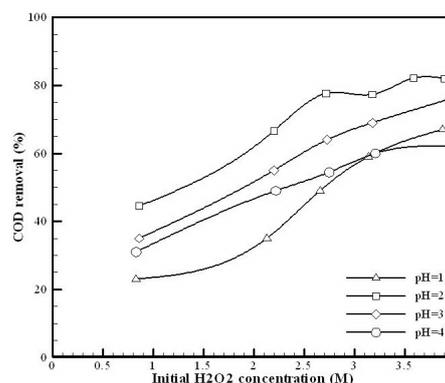


Fig. 1. Effect of initial pH on the COD removal efficiency at different H<sub>2</sub>O<sub>2</sub> Concentration (7 g NZVI/l of leachate, initial COD=38 g/l, time=3hr)

above 2 also fenton oxidation was hindered because the absence of H<sup>+</sup> can inhibit the decomposition of H<sub>2</sub>O<sub>2</sub> and therefore reduce the production of .OH, so the oxidation potential of .OH decreased with increasing of pH [20].

As seen in Fig. 1, COD removal at pH 2 increases rapidly to about 80% and remains relatively constant upon further increase of H<sub>2</sub>O<sub>2</sub>. Harber and Weiss [21] reported that the reaction was second order at low H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> ratio, but became zero order at high H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>. Zhang et al. [4] explained that at high H<sub>2</sub>O<sub>2</sub>/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<sub>2</sub>O<sub>2</sub>/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 [22] reported an optimal molar ratio of 12.5:1, Zhang et al. [4] and Hermosilla et al. [2] reported a molar ratio of 1.5:1 and Lopez et al. [23] reported an optimal molar ratio of 20:1. In fact small particle size and high specific surface of nano particles lead to high efficiency and low utilization of NZVI.

#### B. Effects of dosage

After determination of optimum pH and H<sub>2</sub>O<sub>2</sub> to Fe molar ratio, it is important to determine the amount of fenton reagents to reach higher efficiency. Therefore the H<sub>2</sub>O<sub>2</sub>/Fe molar ratio was fixed at 39 and with initial pH 2, the efficiency of four different amount of fenton reagent was tested. The results are shown in Fig. 2. It was observed that with concentration more than 2.7 M of hydrogen peroxide, COD removal efficiency remains 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.

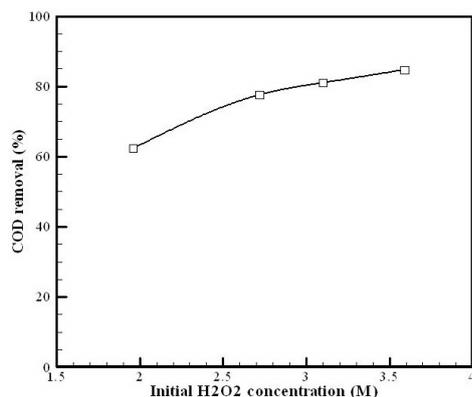


Fig.2. COD removal efficiency at different dosage (pH=2,  $[H_2O_2]/[Fe]=39$ , time=3 hr, initial COD=38 g/l)

### C. Effect of temperature

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 large amounts of gas were produced. As seen in Fig. 3, increasing the temperature has a significant effect on COD removal efficiency and about 87% of initial COD was removed within only an hour. But in ambient temperature (25° C) just about 70% of COD was reduced after an hour. It is interesting that about 90% of total COD removal was achieved in the first 15 min of reaction. As Fig. 3 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 [20].

### IV. 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 about 90 percent removal efficiency was obtained in 1 hr and about 90% of total COD removal was achieved in the first 15 min of 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,

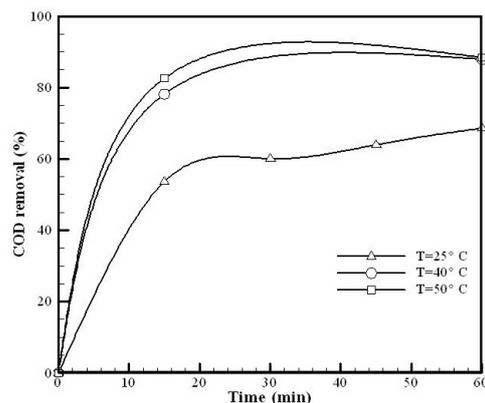


Fig.3. COD removal efficiency at different temperatures during the fenton oxidation (pH=2,  $[H_2O_2]/[Fe]=39$ ,  $[H_2O_2]=2.7$  M)

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.

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### REFERENCES

- [1] Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., Moulin, P., Landfill leachate treatment: Review and opportunity, *Hazard. Mater.* 150 (2008) 468-493.
- [2] Hermosilla, D., Cortijo, M., Huang, C. P., Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes, *Sci. Total Environ.* 407 (2009) 3473-3481.
- [3] Huang, CP., Dong, C., Tang, Z., (1993). Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. *Waste Manage.* 13, 361-377.
- [4] Zhang, H., Choi, H. J., Huang, C., (2005). Optimization of Fenton process for the treatment of landfill leachate. *Hazard. Mater.* 125, 166-174.
- [5] Zhang, H., Choi, H., Huang, C., (2006). Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor. *Hazard. Mater.* 136, 618-623.
- [6] Zhang, H., Choi, H. J., Canazo, P., Huang, C. P., (2009). Multivariate approach to the Fenton process for the treatment of landfill leachate. *Hazard. Mater.* 161, 1306-1312.
- [7] Trujillo, D., Font, X., Sanchez, A., (2006). Use of Fenton reaction for the treatment of leachate from composting of different wastes. *Hazard. Mater.* 138, 201-204.
- [8] Deng Y., (2007). Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *Haz. Mat.* 146, 334-340.
- [9] Rivas, F., Beltran, F., Carvalho, F., Acedo, B., Gimeno, O., (2004). Stabilized leachates: sequential coagulation-flocculation + chemical oxidation process. *Hazard. Mater.* 116, 95-102
- [10] Barbusinski, K., Majewski, J., (2003). Discoloration of Azo Dye Acid Red 18 by Fenton Reagent in the Presence of Iron Powder. *Pol. J. Environ. Stud.* 12, 151-155.
- [11] Joo, S. H., Cheng, I. F., (2006). *Nanotechnology for Environmental Remediation*. Springer Sci.+Business Media, Inc., 233 Spring Street, New York, NY 10013, USA.

- [12] Bergendahl, J. A., Thies, T. P., (2004). Fenton's oxidation of MTBE with zero-valent iron. *Wat. Res.* 38, 327-334.
- [13] Boussahel, R., Harik, D., Mammari, M., Lamara-Mohamed, S., (2007). Degradation of obsolete DDT by Fenton oxidation with zero-valent iron. *Desalination*. 206, 369-372.
- [14] Kallel, M., Belaid, C., Mechichib, T., Ksibia, M., Elleuch, B., (2009). Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron. *Che. Eng. J.*, 150, 391-395.
- [15] Kallel, M., Belaid, C., Boussahel, R., Ksibi, M., Montiel, A., Elleuch, B., (2009). Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide. *Hazard. Mater.* 163, 550-554.
- [16] Barreto-Rodrigues, M., Silva, F. T., Paiva, T. C.B., (2008) Combined zero-valent iron and fenton processes for the treatment of Brazilian TNT industry wastewater. *Hazard. Mater.* 165, 1224-1228
- [17] Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 1992, 18<sup>th</sup> Ed. Washington DC, USA.
- [18] Kang, Y. W., Cho, M.J., Hwang, K.Y., (1999). Correction of hydrogen peroxide interference on standard chemical oxygen demand test. *Wat. Res.* 33, 1247-1251.
- [19] Barbusinski, K., Filipek, K., (2001). Use of Fenton's Reagent for Removal of Pesticides from Industrial Wastewater. *Pol. J. Environ. Stud.* 10, 207-212.
- [20] Deng, Y., Englehardt, J. D., (2006). Treatment of landfill leachate by the Fenton process. *Wat. Res.* 40, 3683 – 3694.
- [21] Harber, F., Weiss, J.J., The catalytic decomposition of hydrogen peroxide by iron salts, *J. Am. Chem. Soc.* 45 (1934) 338-51.
- [22] Kim, Y. K., Huh, I. R., Enhancing biological treatability of landfill leachate by chemical oxidation, *Environ. Eng. Sci.* 14 (1997) 73-79.
- [23] Lopez, A., Pagano, M., Volpe, A., Di Pinto, A., (2004). Fenton's pre-treatment of mature landfill leachate. *Chemosphere.* 54, 1005-1010.