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Comparison The Efficacy Of Fenton And "nZVI + H_2O_2" Processes In Municipal Solid Waste Landfill Leachate Treatment (Case Study: Hamadan Landfill Leachate)

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ABSTRACT: Leachate contains large amounts of pollutants, including organic and inorganic materials as well as the types of pathogens. This study was performed with the aim of determining the efficiency of Fenton and" nZVI(nanoparticles of zero valent iron) + H_2O_2" processes for reducing chemical oxygen demand (COD), 5-day biological oxygen demand (BOD_5), total solids (TS)and color of Hamadan city landfill leachate. Experiments were performed in batch reactor and main affected factors; pH, reaction time, concentration of iron and H_2O_2 were investigated. Also the efficiency of processes was analyzed using One-Way ANOVA statistical test and SPSS-13 software. The highest removal efficiencies obtained with "nZVI + H_2O_2" process (48.67%, 52%, 10.44% and 53% for COD, BOD_5, TS and color, respectively in 2.5 g/L iron nanoparticles concentration,29137 mg/L H_2O_2, pH = 2.5 and 60 min reaction time). Based on the results, the nZVI + H_2O_2 process can be applied as Hamadan city landfill leachate treatment to correct the BOD_5/COD ratio to increase the biodegrability of this type of wastewater.

Key words: Leachate, Treatment, Environment, Fenton process

INTRODUCTION

slimy liquid that contains many dangerous chemicals and is called "leachate", leak from the wet solid wastes accumulated and buried in landfills, after being out of the time(Lopez *et al.*, 2004; Zhang et al. 2007).This fluid contains significant quantities of pollutants including organic matter (such as fatty acids and alcohols) and inorganic materials (like heavy metals) and is also a variety of pathogens.100 ml leachate contain more than 10^8 coliforms. This Leachate can move to the underlying soil layers under the effect of different mechanisms, and may be entered into the underground water table. Increased concentrations of these substances in water may be somewhat higher than existing standards and underground water actually be considered as contaminated water(Petruzzelli *et al.*, 2007; Sarvako 2007; Yang and D Engelhard 2006). Unfortunately, engineering design and construction of sanitary landfill sites in Iran still has not found its legal status and in some regions, wastes are landfilling unsanitary or are left uncovered on the ground. The leachate characteristic depends on composition of solid wastes and biological-chemical processes that occurs on the landfill. Other factors such as climate conditions, the final cover of soil, rainfall, soil type and topography will impact on leachate quality and will vary considerably landfill leachate quality (Kashitarash Esfahani *et al.*, 2012; Lopez *et al.*, 2004).Ability of a method for treating leachate is dependent on leachate characteristics and flexibility of method against the leachate quality changes. Different methods of leachate treatment, including biological and physical-chemical can be used to the variety characteristics of leachate(Kashitarash Esfahani 2011; Sarvako 2007). Biological treatment technologies (including aerobic and anaerobic processes) are used to effectively treating for leachate with high BOD_5/COD relation (1-2 years old

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leachate).this kind of leachate is in the early stages of production(Bergendahl and TP 2004; Lopez *et al.,* 2004; Petruzzelli *et al.*, 2007; Sarvako 2007; Yang and D Engelhard 2006). biological treatment cannot eliminate non-biodegradable organic materials due to the existence of non-biodegradable and toxic substances within the older leachate (leachate with 50-10 years of age) ,so the use of physical- chemical processes are required as pre- treatment, post- treatment, and sometimes the full treatment to achieve the desired standards((Petruzzelli *et al.*, 2007; Sarvako 2007; Tengrui *et al.*, 2007; Yang and D Engelhard 2006). Among the used physicochemical processes, the Fenton process in recent years has been much studied and found to be one of the most effective and economical methods for landfill leachate treatment. In this process, hydrogen peroxide in the presence of ferrous salts is added to leachate and produced very strong hydroxyl radical in combination with organic materials that are strong oxidant for resistant organic compounds .So iron and hydrogen peroxide are the two main factors of treatment efficiency and costs. Today, Fenton's reagent is used for the treatment of various industrial wastewater containing toxic organic compounds (like phenol and formaldehyde) such as complex dyeing wastewaters, chemicals, plastics and rubber industrial wastewaters and even landfill leachates. Also, there is many reports on the use of nanotechnology as a process of treatment and removal of pollutants from the environment(Kashitarash Esfahani December 2010; Sarvako 2007; Tengrui et al. 2007). Iron nanoparticles technology as a new generation of environmental monitoring is a convenient and effective solution that can solve many environmental problems.Nanoparticles are able to use for treatment pollutants into less harmful substances due to small size, high surface area, the crystalline order and a network of unique and highly reactive(Masciangioli and Zhang 2003; Sung and Francis 2006; Tanapon *et al.*, 2007). nanoparticles of zero valent Iron (nZVI) are effective for a wide variety of transport and detoxification of environmental pollutants such as chlorinated solvents, organo Chlorinated pesticides, PCBs, heavy metals, etc (Boussahel *et al.*, 2007; Zhong *et al.*, 2007).We think that Nanoparticles of iron and hydrogen peroxide can be used in the process of "nZVI + H_2O_2"for landfill leachate treatments.

Hamadan city landfill leachate percolate slowly through the soil into a pond with very slow flow. Age of this landfill leachate can be estimated at about 5-10 years (BOD_5/COD = 0.23). The aim of this study was to determine the efficiency of Fenton and" nZVI + H_2O_2" processes to reducing COD, BOD_5, TS and color of Hamadan city landfill leachate.

MATERIALS & METHODS

This study is a fundamental study to compare the efficiency of Fenton and" nZVI + H_2O_2" processes to reducing COD, BOD_5, TS and color of Hamadan city landfill leachate. About 750 tons per day of domestic waste and 5 tones of hospital wastes are entered into the Hamadan city landfill located 23 km of Hamadan-Tehran Road in west of Iran. There isn't any treatment facility in this place and raw leachate is discharge to the environment without any treatment.

Leachate samples were collected in polyethylene bottles from landfill in Hamadan city, and were maintained at 4 ° C temperature in accordance with standard procedures (APHA and WPCF 2005). The site of sampling was selected in a way that samples represented whole landfill leachate conditions. Raw leachate was then transferred to the laboratory for analysis; the results are presented in Table 1.

Table 1. Properties of Hamadan landfill raw leachate

Parameter	Range
BOD_5 (mg/L)	20000
COD(mg/L)	85000
TS(mg/L)	200000
Color(Pt.Co)	15000
pH	6.5
BOD_5/COD	0.34

Chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), total solids (TS) were determined according to standard methods(APHA and WPCF 2005). Color was determined by 8025 HACH DR. 2500. Iron nanoparticles used in this study were prepared from Plasmachem. GmbH Berlin, Germany and other chemicals purchased from Merck Company. Properties of iron nanoparticles and H_2O_2 used in this study are presented in Tables 2 and 3.

Iron sulfate (II) and H_2O_2 were used in the Fenton process experiments. Batch experiments were covered by aluminum foil to prevent evaporation and water shed after a desired time. pH=8.5 was adjusted. Coagulants were not adding for proper comparison between the performances of oxidation step in two studied processes so efficient removal process is lower than usual. And finally settling took for 45 minutes. contact time (in the amount of 60, 90 and 120 min), pH values (2/5, 4/5, 6/5) concentrations of iron sulfate (in amounts of 1/25, 2/5 and 5 g/L) and the concentrations of H_2O_2 (in the amount of 14.5, 29.1, 58.2 g/L) were investigated on removal efficiency.

Iron nanoparticles were used instead of Iron sulfate in removal experiments using "nZVI + H_2O_2" process. In these experiments the amount of contact time (10,20,30,40,60,80,90 min), pH values (2/5,4/5,6/5), iron nanoparticles concentration values(1/25,2/5 and 5 g /

Table 2. Physico-chemical properties of used iron nanoparticles in this study

Properties	Average value
Specific surface area (BET), m^2/g	>12
Average primary particle size, nm	30-60
Particle full range, nm	5-200
Particles' shape	Spherical
Fe-state	Ferromagnetic
Bulk density/cm^3	0>0.5
Carbon content, wt%	11-14
-cu	<0.4
-w	<0.2

Table 3. Properties of used H_2O_2 in this study

H_2O_2	Commercial name
liquid	Shape
1.11	(kg/L) density
Merck Company	Company
30	%w/v

L) and H_2O_2 concentration values (14.5, 29.1, 43.7 and 58.2 g/L) were investigated. To increase the reliability and accuracy and precision testing, sampling and analysis of samples in each stage of the operation was repeated three times.

Removal efficiency at different stages was calculated by using the results and the initial concentrations with the equation (1):

$$E = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

That C_i and C_f are the initial concentration and final concentration of studied parameters, respectively. Finally the optimum values of each variable were selected and performance of iron nanoparticles was evaluated by using One-Way ANOVA test statistic and SPSS-13 software.

RESULTS & DISCUSSION

The results of the performance of nZVI + H_2O_2 and Fenton processes in reducing Hamadan city landfill leachate COD, BOD_5, TS, and color are given in Figs (1 - 4). It should be noted that the low removal efficiencies of Fenton in compared with other Fenton studies is due to elimination of coagulation and flocculation step for appropriate and perfect compared between removals of just the oxidation step with nZVI+ H_2O_2 process that is oxidation process too. According to the pilot projects that we did, The removal efficiency of Fenton and nZVI+ H_2O_2 processes will increase to approximate 30 to 50% respectively, depending on the coagulant material and settling time used for each of these two processes that can be considered in next researches.

Various in reaction times were investigated in the first step of experiments. One-Way ANOVA test was statistically significant (p-value 0.05) for different values of reaction time in both processes. As shown in fig.1 increasing reaction time to 90 minutes in Fenton process increased the removal efficiency of all four factors and the rate of elimination was not significantly changed in more than 90 minutes. This means that the reaction between ferrous ion and H_2O_2 can be completed in 90 minutes. Range of contact time of Fenton process has been reported between 30 minutes to 3 hours in various studies(Farrokhi et al. 2009; jashni and Omranimanesh 2008).Highest COD removal in Farokhi M. et al, entitled " The Study on Biodegradability Enhancement of Landfill Leachate by Fenton Oxidation " gain in 90 minutes retention time. The removal efficiency in less than 90 minutes has reduction and in more than 90 minutes has not changed appreciably. He also has stated that the reaction between H_2O_2 and ferrous ion end and will be completed in 90 minutes(Farrokhi *et al.*, 2009). The result of our study was consistent with the Farokhi results. In the "nZVI + H_2O_2" process, Increasing contact time up to 60 min increased removal efficiency of BOD_5, COD and color and reduce the TS removal efficiency. Also in this process increasing the number of collisions with time increases absorption opportunities and so efficient removal of BOD_5, COD and color increased with contact time. But increasing contact time reduces the removal efficiency of TS so in this regard, more research is needed. The highest removal efficiency of the TS was observed in the retention time 20 minutes. Hundal and colleagues in 1997 showed that zero valent iron (ZVI), in combination with H_2O_2 can be break down TNT and RDX compounds in soil contaminated with more efficiency than ZVI alone. The amount of iron required to achieve the same level of treatment was also lower (Hundal *et al.*, 1997).

The results of this study indicate that the removal efficiency of the main factors (BOD5 and COD) is reduced with increasing pH from 2.5 to 6.5 in Fenton and nZVI+H_2O_2 processes. Also One-Way ANOVA test confirmed these results for the pH study (p-value< 0 /

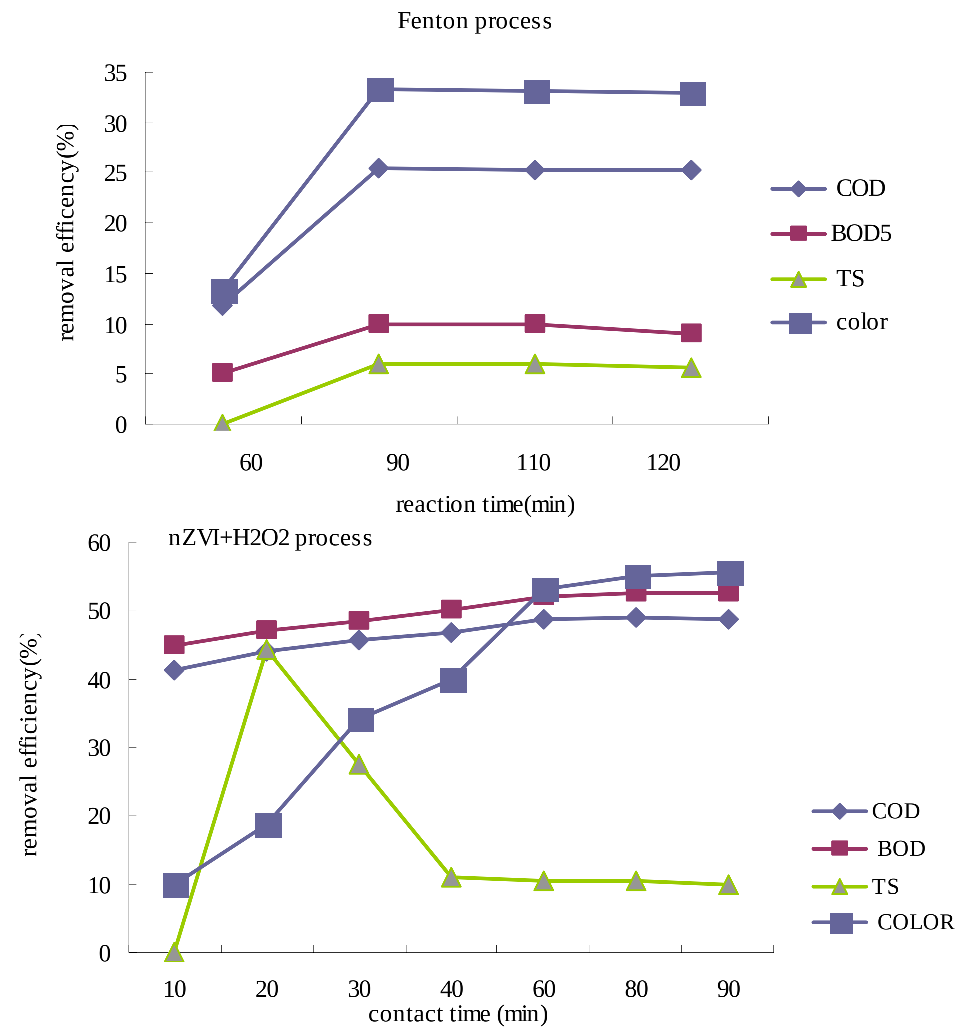

Fig. 1. Effect of contact time variation on the removal efficiency of COD, BOD_5, TS and color of Hamadan landfill leachate by the Fenton and nZVI+ H_2O_2 processes (T=18±1 ^{oC}, pH = 2.5, the concentration of the iron (ferrous sulfate / nZVI) = 2.5 g/L and H_2O_2=29.137 g/L)

05 for BOD_5, COD, TS and color). In other words, reducing in BOD_5 and COD removal efficiency and increasing in TS and the color removal efficiency can be seen with increasing pH from 2.5 to 6.5 by the Fenton process and nZVI + H_2O_2 process. Increasing pH from 2.5 to 6.5 reduce removal efficiency of the main factors (BOD_5 and COD) in nZVI + H_2O_2 process because reducing the pH can increase the corrosion of iron nanoparticles and also iron hydroxide produced more in low pH. In the other hand oxidation and reduction reactions at low pH are done better. High pH Reduce the oxidation - Reduction potential so amount of ZVI added to the reaction will not work as well and will be ineffective. Increasing in color removal efficiency and TS can be that the color removal is not done by Fenton process and is done by adsorbing and because the more adsorption occurs in high pH, the efficiency of color removal increases with increasing pH while the Fenton process that is a major factor in COD and BOD5 removal will be less efficient in the high pH thus high pH have been less the eliminate of these factors. The optimum pH for the Fenton process based on various studies has been reported between 2- 4.5(Farrokhi et al. 2009; jashni and Omranimanesh 2008; Sedlak and Andren 1991).The reason stated with Sedlak and his colleague was that hydroxyl radicals are more produced through reaction with organometalic complexes in the range of pH =2-4.Also the reaction rate or the reduction of hydrogen peroxide in this range of pH is increased (Tang and Chen 1996).Zhang and colleagues showed that the higher COD removal efficiencies is obtained at pH less than 3.5 in Fenton process and the optimum pH range for COD with higher concentrations is between 2-2.5 (Zhang *et al.*, 2007).

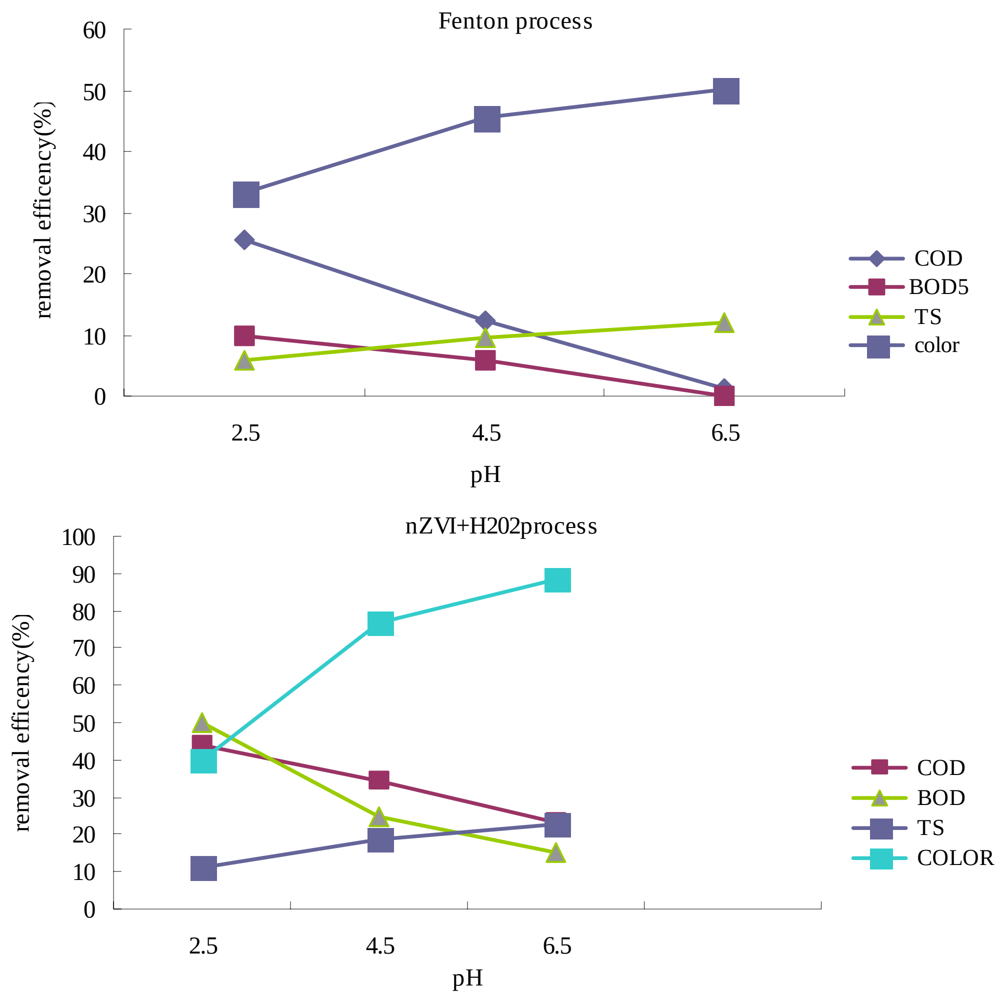

Fig. 2. Effect of pH variation on the removal efficiency of COD, BOD_5, TS and color of Hamadan landfill leachate by the Fenton and nZVI+ H_2O_2 processes (T=18±1 ^{oC}, the concentration of the iron = 2.5 g/L, H_2O_2=29.137 g/L and contact time =90 min in Fenton process and 60 min in nZVI+ H_2O_2 process)

One-Way ANOVA test showed significant differences for different levels of H_2O_2 concentration (p-value<0.05 for BOD_5, COD, TS and color). It means that the concentration of H_2O_2 is effective on the removal efficiency. In both Fenton process and nZVI + H_2O_2 process, removal efficiency of BOD_5, COD, TS and color increased with H_2O_2 concentrations up to 29.137 g/L and at higher and lower than this value did not get good results. Farrokhi in his study has stated that presence of excess or less amounts of hydrogen peroxide can change the production quantity of hydroxyl radicals so the COD will increase(Farrokhi *et al.*, 2009).The results of our study was consistent with the Farokhi results so that the amounts more than 29.137 g/L of H_2O_2 decreased removal efficiency in Fenton process.

Furthermore, excess amount of H_2O_2 float iron sludge due to H_2O_2 spontaneous decomposition and production of hydrogen gas and also cause problems in downstream processes and even will prevent biological treatment (Farrokhi *et al.*, 2009; jashni and Omranimanesh 2008).numerous differences in the optimal ratio of iron to hydrogen peroxide have been observed in various studies. Antonio Lopez and colleagues in their study as “Fenton’s pre-treatment of mature landfill leachate “, reached the acceptable removal efficiency in leachate with COD = 10540 mg/L by using 10,000 mg/L H_2O_2 (w/w35%) and 830 mg/L Fe^{2+} (1/12 ratio)(Lopez *et al.*, 2004) that was approximately similar to our study.

One-Way ANOVA test showed significant differences for different levels of iron concentration on the removal efficiency of COD, BOD_5, color and TS in both processes with the p-value <0.05.Increasing the active surface area and more possibility for contact

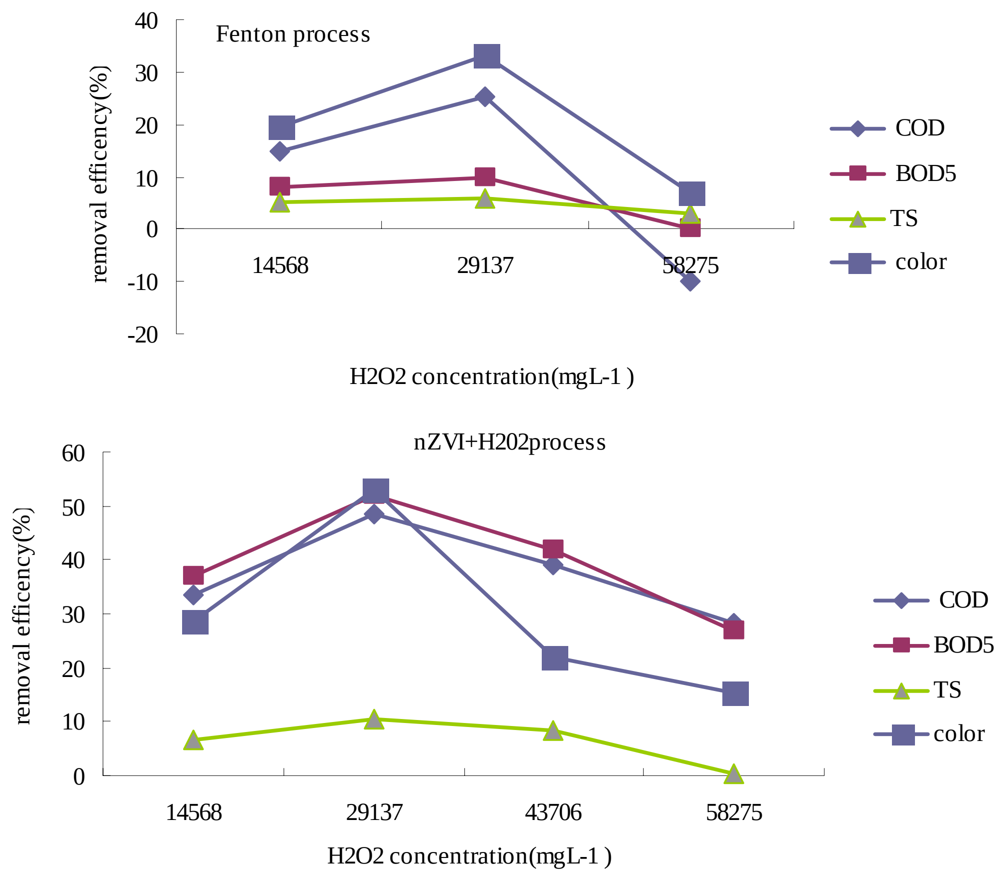

Fig. 3. Effect of H_2O_2 concentration variation on the removal efficiency of COD, BOD_5, TS and color of Hamadan landfill leachate by the Fenton and nZVI+ H_2O_2 processes (T=18±1 ^{oC}, the concentration of the iron = 2.5 g/L ,pH=2.5 and contact time =90 min in Fenton process and 60 min in nZVI+ H_2O_2 process)

within the organic and inorganic substances present in the leachate with iron nanoparticles and increasing the oxidation-reduction reactions are the reasons for increasing the removal efficiency in the nZVI + H_2O_2 process by nanoparticles concentration increasing .but It is important to note that increasing concentrations of iron nanoparticles from 2500 to 4,000 and 5000 mg/L in the conditions listed, decreased COD, BOD_5, color and TS removal efficiency is the nZVI + H2O2 process. These results indicate that the excess ions from the iron nanoparticles can cause turbidity in the treated leachate and interference in treatment, so reduce the effectiveness of treatment. Tang and colleagues showed that the degradation of the azu dye using iron powder and H_2O_2 is rather than Fenton systems such as iron sulfate and H_2O_2 because iron powder has smaller particles and so dye adsorption on the iron powder with smaller size is more(Tang and Chen 1996).additionally removal of BOD_5, COD, TS and color by Fenton process increased with ferrous sulfate concentration up to 2500 mg/L. the excess amount of this material can also attack to hydroxyl radicals and interference in treatment.

CONCLUSION

As in Fig. 5 can be seen, the efficiency of nZVI+H_2O_2 process is higher than the Fenton process in BOD_5, COD, TS and color removal. In Fenton process, even with a reaction time of 120 minutes the highest removal was less than 50% (without coagulation and flocculation step) but the optimal time for approximately 50% BOD_5 and COD removal was 60 minutes in nZVI+H_2O_2 process (without coagulation and flocculation step) and so it is preferred due to the smaller dimensions of the reactor in this process and less used materials.

Also The amount of removed BOD_5, COD, TS and color from leachate with concern to the consumed amount of iron nanoparticles by the nZVI + H_2O_2process and the amount of iron sulfate in the Fenton process is calculated and graphs are shown in

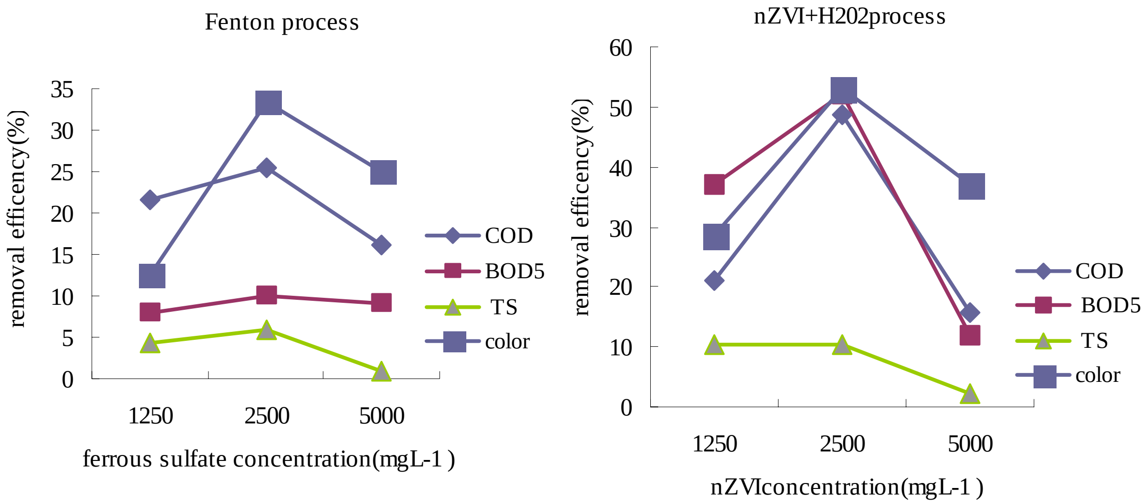

Fig. 4. Effect of iron concentration variation on the removal efficiency of COD, BOD_5, TS and color of Hamadan landfill leachate by the Fenton and nZVI+ H_2O_2 processes (T=18±1 ^{OC}, the concentration of the H_2O_2 = 29.137 g/L ,pH=2.5 and contact time =90 min in Fenton pro

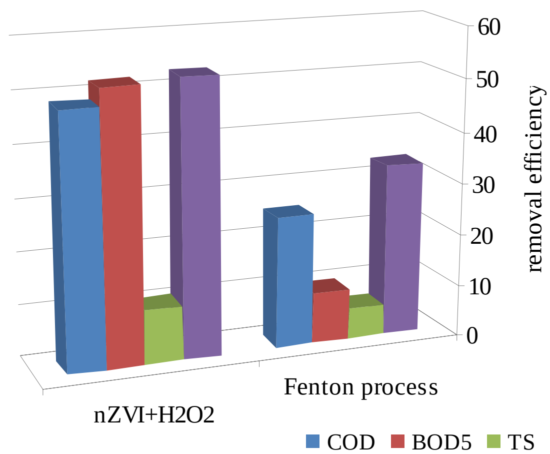

Fig. 5. Comparing the efficiency of the used treatment processes in this study in the removal of BOD_5, COD, TS and color Hamadan city landfill leachate ((pH =2.5, concentration of the iron (ferrous sulfate / iron nanoparticles) = 2.5, H_2O_2 concentration in g/L = 29.137, temperature = 18 ° c ±1, reaction time in Fenton process and nZVI+H_2O_2 process was 90 min and 60 minutes, respectively)

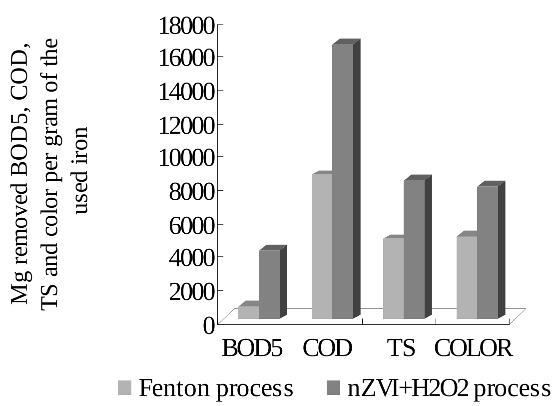

Fig. 6. Removal of BOD_5, COD, TS and color per gram of the used iron (Nanoparticle iron or ferrous sulfate) at optimum conditions for each reaction (Fenton and nZVI+H_2O_2)

Fig. 6. This data is related to the optimal reaction conditions. Fenton process as compared to nZVI + H_2O_2 process need the long time, In addition to this ,BOD_5, COD, TS and color removed per gram of nanoparticles in compared with iron sulfate (II), is much more. Iron nanoparticles in compared with iron sulfate (II) have smaller size, larger specific surface and thus more reactive, which eliminates high in low time in small amounts of nanoparticles.

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