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Monitoring of pH, Oxidation-Reduction Potential and Dissolved Oxygen to Improve the Performance of Dimethyl Phthalate Removal From Aqueous Solutions

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Abstract

Since the process of heterogeneous Fenton is more complex and dynamic than the common Fenton process, control and online monitoring is entirely vital for optimum operation of this system. This study was aimed to investigate the effects of pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) variations on dimethyl phthalate (DMP) removal from aqueous solutions using the heterogeneous Fenton process with nano zero-valent iron (nZVI). Parameters affecting the process like contact time (5 - 120 minutes), pH (2 - 10), H_2O_2 concentration (0.01 - 1 mmol/L) nZVI content (0.01 - 0.5 g/L) and initial DMP concentration (2 - 50 mg/L) were also studied. It was found that, at optimum amounts (pH = 4, H_2O_2 concentration = 0.1 mmol/L, nZVI = 0.05 g/L, initial DMP concentration = 2 mg/L, and contact time = 60 minutes), approximately 98% of the pollutant was removed. This process could treat DMP well from aqueous environments and can be introduced as a cheap and effective method.

Keywords: Dimethyl Phthalate, Heterogeneous Fenton, Nano Scale Zero-Valent Iron, Monitoring

1. Introduction

Phthalic acid esters (PAEs) are an important group of persistent pollutants, widely employed for increasing flexibility, transparency, durability, and longevity of hard polyvinyl chloride (PVC) resins, and they are spread in the environment because of their week physical bonding in plastic structures, as they have been identified in soil, air, food, sewage sludge, landfill leachate, and even rain (1-3). PAEs are regarded as priority pollutants on account of having mutagenic and carcinogenic effects (2, 4).Dimethyl phthalate (DMP) is the most simple and common compound of PAEs which has low molecular weight and is considered as a good solvent. It is also applied in various industries like cosmetics, insect repellent, insecticide carries, and propellants (2, 5). This compound can disturb endocrine glands performance, natural growth, leukocyte chromosomes and so forth (2, 5-8). Since phthalates are hydrophobic, current conventional methods are not able to remove these compounds from water environments (1).

New and modern ways are required for the treatment of these compounds from the industrial effluents. Recently, coagulation, sedimentation, adsorption with chitosan and activated carbon, aerobic and anaerobic biological processes and advanced oxidation processes (AOPs) for removal of phthalates from aqueous solutions have been studied. However, lack of adequate removal, preparation, regeneration of absorbents cost, and sensitive microorganisms to condition changes such as methane production as a result of phthalate degradation are some disadvantages of these methods (9). Among these, advanced oxidation processes are highly effective in removal of water and wastewater because of the following advantages: high efficiency, easy operation, and high ability in removing unbiodegradable pollutants (3, 4).

One of the main mechanisms of AOPs is on the basis of active hydroxyl radical formation, able to treat target pollutants. Fenton process is an AOP capable of oxidizing well in the presence of iron ions (10, 11). Nonetheless, high volume of sludge production, lack of a reaction between ferric ions and H_2O_2, consumption of the generated $OH^\bullet$ and need for a permanent source of ferric ions are the major downsides of this process (12, 13). The heterogeneous Fenton process is a suitable alternative to the common method, which is aimed to use reversibly iron catalysts. Heterogeneous Fenton by means of catalysts of zero-valent iron (ZVI), Fe_3O_4 and Fe_3O_4/ Fe^0 has been studied for treatment of various pollutants (14-16).

Nano zero-valent iron (nZVI) has a higher reaction power and specific surface area than ZVI. nZVI causes the reduction of intermediates and, in turn, these products are easily and quickly degraded over the Fenton process (17). It should be noted that online monitoring of the heterogeneous Fenton process with nZVI in order to control optimally the process nearly has not been investigated in previous studies; monitoring of economic parameters: oxidation-reduction potential (ORP), dissolved oxygen (DO), and pH can enhance the feasibility of using this process (18). When nZVI is added to wastewater to remove DMP, ORP can change rapidly and nZVI can consume DO. Moreover, reduction of DMP by nZVI results in H^+ consumption or OH^- production. Therefore, online monitoring of the method is essential (18, 19).

The main objective of the study was to investigate DMP removal by means of the heterogeneous Fenton process. Furthermore, parameters of ORP, DO and pH were monitored during the process.

2. Materials and Methods

In this study, all the samples were prepared synthetically and all the chemicals (analytical grade) were purchased from Merck Co. (Germany). The standard stock solution was prepared by dissolving 0.832 mL of DMP solution (purity 99%) in 1000 mL dilution water and then the concentrations were prepared by serial dilutions of this stock. To adjust the pH, H_2SO_4 (0.1 N) and NaOH (0.1 N) were used, using a pH meter (HACH sension1 model). A mechanical mixer was used to provide enough mixing and the catalyst was separated from the samples by centrifugation as well as cellulose acetate filter. The samples taken out were analyzed by an HPLC device (Smart line auto sampler 3950 HPLC, A5005-1, KNAUER Company, Berlin, Germany) equipped with a UV detector (K2600-KNAUER, Germany) with C18 column (4.6 mm × 250 mm). The mobile phase was an acetonitrile and distilled water (0.01 M, pH = 6) in the ratio of 50:50 v/v. The volume of all injections was 40 μL (1). Moreover, the retention time was 5.1 ± 0.01. Figure 1 shows the HPLC chromatograph and the molecular structure of DMP. All the experiments were performed by changing pH values (2-10), H_2O_2 concentration (0.01 - 1 mmol/L), nZVI content (0.01 - 0.5 g/L) and initial DMP concentration (2 - 50 mg/L) and optimum amounts were attained by the one-at-a-time method. To increase the precision and confidence coefficient of the findings obtained, all the experiments were repeated three times and the averages were reported. The amount of DMP removal in this process was calculated through Equation 1:

$$R = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

Where C_i and C_e are, respectively, initial and equilibrium concentrations of DMP.

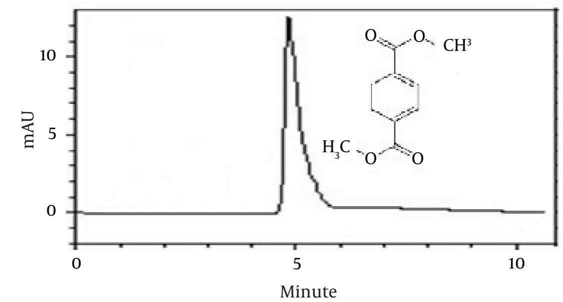

Figure 1. Chromatograph and Molecular Structure of Dimethyl Phthalate

3. Results and Discussion

3.1. pH Effect

Figure 2 presents the effect of pH solution on DMP removal by the process. As can be seen, with increasing the pH value from 2 to 4, the efficiency reached 85.7% in 60 minutes. The highest efficiency (88.5%) was attained in 120 minutes. However, the efficiency decreased with increasing the pH value. Since the highest efficiency was observed at pH of 4, it was chosen as the optimum pH. Since the pH of solution has a control effect on the activity of the catalysts and oxidant and predominant species of iron ion as well as H_2O_2 stability in the media, it is one of the most important factors in removing the pollutant in the Fenton process (20).

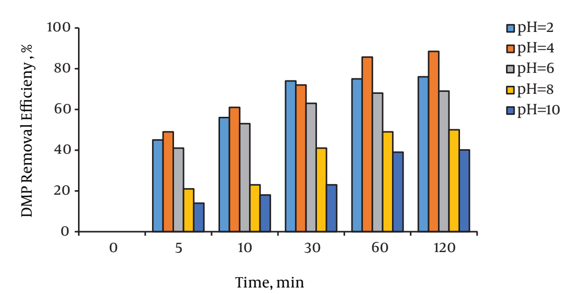

Figure 2. Effect of pH on Dimethyl Phthalate Removal, DMP concentration = 10 mg/L; H_2O_2 concentration = 0.1 mmol/L; nZVI dosage = 0.05 g/L.

The mechanism of oxidant production includes Fe^0 oxidation and then the Fenton reaction. At first, Fe^0 is oxidized by H_2O_2 (reaction 1) (21, 22). Next, the oxidants responsible for organic matters oxidation (mainly $OH^\bullet$) are formed by the Fenton reaction (reaction 2). At pH values above 5, a weaker oxidant like ferric ion (for example FeO^{+2}), which acts more selective than $OH^\bullet$, can be created over reaction 3 (23):

(1) $Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O$

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

(3) $F^{2+} + H_2O_2 \rightarrow Fe\,(IV)\,(e.g., FeO^{2+}) + H_2O$

A decrease in efficiency at high pH values can be attributed to H_2O_2 degradation; in addition to this, the oxidation potential of $OH^{\bullet}$ declines and ferric hydroxide complexes are formed resulting in a decrease in $OH^{\bullet}$ production (22). The degradation of DMP is very little at the pH value of 2, because at low pHs the stability of H_2O_2 is high and also H_3O^{+} is created which prevents H_2O_2 from reacting with Fe^{+2}. Therefore, an amount of $OH^{\bullet}$ is produced and, in turn, the efficiency decreases (24). According to the obtained results, the pH range between 4 and 6 had a desirable performance.

The results of similar studies accord with those of the current study. A study by Moon et al. in which the heterogeneous Fenton with nZVI was used to remove azo dye (Orange II), reported that at pH = 3, the highest efficiency occurred (17). Kallel et al. showed that the highest chemical oxygen demand (COD) removal happened at pH values from 2 to 4 when this method was utilized to treat olive mill wastewater (25). Xu et al. investigated 4-chloro-3-methyl phenol removal by means of heterogeneous Fenton with nZVI (23).

3.2. H2O2 Effect

With increasing the H_2O_2 concentration from 0.01 - 1 mmol/L, DMP removal increased from 47.8 to 88.5% (Figure 3). A 35% drop was seen in efficiency when the concentration of H_2O_2 was raised to 1 mmol/L. Therefore, the content of 0.1 mmol/L was selected as the optimum amount.

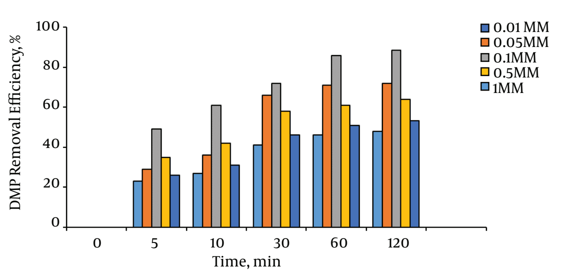

Figure 3. Effect of H_2O_2 Concentration on Dimethyl Phthalate Removal, pH = 4; DMP concentration = 10 mg/L; nZVI dosage = 0.05 g/L.

It should be noted that this variable is very important in Fenton process and is a key control parameter in wastewater treatment plants. The oxidation power of the process increases when there is an increase in $OH^{\bullet}$ from H_2O_2 degradation in the solution. At the beginning of the reaction, increasing H_2O_2 concentration had a positive effect on the efficiency, but a decline was observed in efficiency over time. Although in oxidation Fenton process hydroxyl radicals are mainly responsible for pollutant degradation, at high contents of H_2O_2 competitive reactions happen as follows (24):

(4) $OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$

(5) $HO_2^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + H_2O + O_2$

(6) $2HO_2^{\bullet} \rightarrow 2H_2O_2 + O_2$

(7) $HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2$

(8) $2OH^{\bullet} \rightarrow H_2O_2$

It can be found from reactions 4 - 8 that some of hydroxyl radicals are consumed before DMP oxidation and it creates an inhibitory effect. The efficiency went down when the concentration of H_2O_2 exceeded 0.1 mmol/L. The bottom line is that for noticeable formation of hydroxyl radicals H_2O_2 should be at its optimized amount (24). The results of a study by Kallel et al. are in agreement with our findings (25). The concentration of 0.3 mmol/L of H_2O_2 was reported as the optimum amount in a study by Xu et al. who investigated 4-chloro-3-methyl phenol removal (23). In addition, Hou et al. found the economical and optimum amount of H_2O_2 for Rhodamine B treatment (26).

3.3. nZVI Effect

Scanning electron microscopy (SEM) images of nZVI before and after heterogeneous Fenton oxidation are shown in Figure 4. Based on the illustration, the structure of nZVI is compact, which is because of the magnetic force among fine particles. As can be seen, all the particles have spherical shapes. After the heterogeneous Fenton reaction, density decreased and iron oxide is formed as a result of nZVI corrosion in aqueous solutions. This leads to leakage of Fe^{+2} and Fe^{+3} from the surface of nZVI and iron oxide (9). According to Figure 5, determined sites in Fourier transform infrared spectroscopy (FTIR) spectrum before and after heterogeneous Fenton oxidation include 3415 cm^{-1} (stretching vibration of OH) and 1633, 1504, 1235, and 987 cm^{-1} are for FeO bonds in Fe_2O_3 and Fe_3O_4 (9).

The findings from the effect of nZVI concentrations on the efficiency are shown in Figure 6. With increasing the concentration of DMP to 0.05 g/L, the highest removal efficiency (51.7%) was seen and then it decreased. Therefore, 0.05 g/L of DMP was selected as the optimum amount.

Increasing nZVI and active sites results in more H_2O_2 degadation and consequently more hydroxyl radicals are produced, which enhances the DMP removal. Of course, at concentrations higher than the optimum amount, nZVI, which is added to the solution, is accumulated and it makes hydroxyl radicals to be scavanged and it finally decreases the efficiency (9).

Besides, when there is more nZVI in the solution, most of Fe^{+3} ions change to $Fe\,(OH)^{+2}$, which in acidic conditions are left out and the performance decreases (22). The study by Moon et al. showed that the efficiency reached from

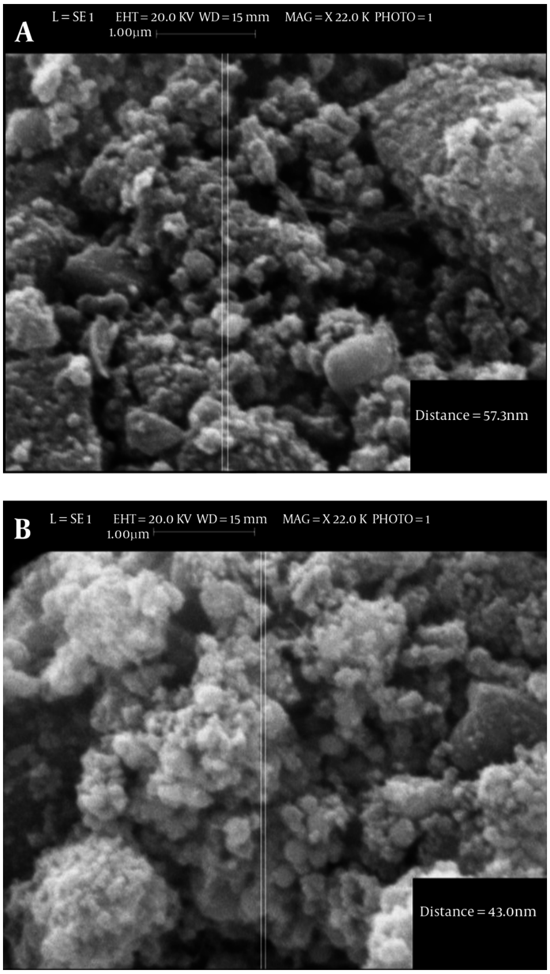

Figure 4. Scanning Electron Microscopy Images of nZVI, A, before and B, after the heterogeneous Fenton oxidation.

30% to 95% with increasing the nZVI amount from 5 to 20 mg/L, but an increase in concentration to 100 mg/L did not change the results (17). Gulkaya et al. found that in Fenton process, up to 95% of COD was removed at the optimum amount of $FeSO_4$ (5.5 g/L) (27).

3.4. Effect of Initial Dimethyl Phthalate Concentration

As can be seen in Figure 7, with increasing the initial DMP concentration from 2 to 50 mg/L the efficiency decreased from 98.6% to 35.4% in 120 minutes.

The increase of pollutant molecules in the solution can make them to be absorbed on the nZVI surface and more active sites to be occupied. This causes the sites to be unavailable for H_2O_2 molecules and results in a decrease in hydroxyl radical formation on the surface of nZVI. Like our study, Xu et al. claimed that the increase of 4-chloro-3-methyl phenol caused a decrease in efficiency (23). Further, Babuponnusami et al. found that phenol removal by means of heterogeneous photo electro Fenton-like process decreased with increasing the initial phenol content (20).

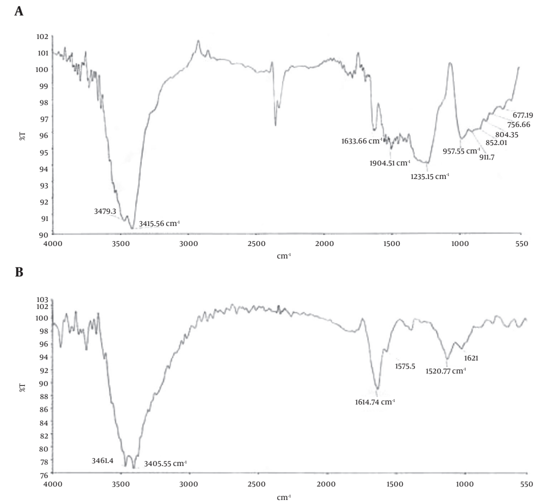

Figure 5. Fourier Transformed Infrared Spectra of nZVI, A, before and B, after the Fenton process.

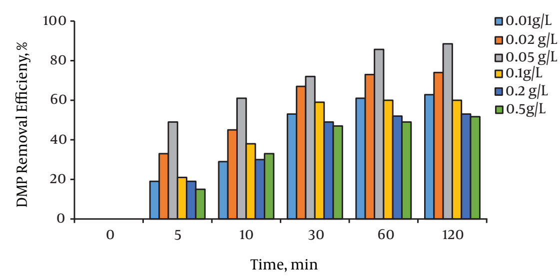

Figure 6. Effect of nZVI on Dimethyl Phthalate Removal, pH = 4; DMP concentration = 10 mg/L; H_2O_2 concentration = 0.1 mmol/L.

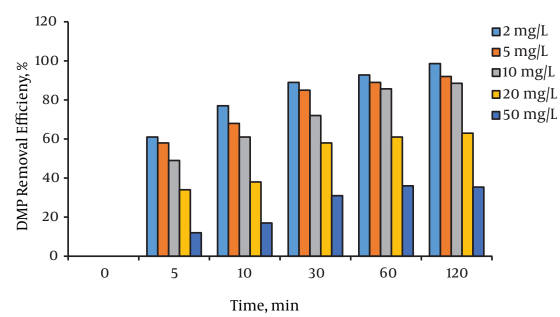

Figure 7. The Effect of Initial Dimethyl Phthalate Concentration on Dimethyl Phthalate Removal, pH = 4; H_2O_2 concentration = 0.1 mmol/L; nZVI dose = 0.05 g/L.

3.5. Effects of H2O2, nZVI, and nZVI/H2O2

To evaluate the effect of each contributing parameter in the Fenton-nZVI process for removal of DMP, the effects of individual parameters were investigated and shown in Figure 8. DMP degradation in the presence of H_2O_2, nZVI, and nZVI/H_2O_2 was determined 10.1%, 53.5%, and 88.5%, respectively, indicating that the most degradation of DMP was achieved through the nZVI/H_2O_2 process due to the release of Fe^{2+}/Fe^{3+} from nZVI followed by reaction of the spices with H_2O_2 and then the production of highly reactive hydroxyl radicals, which were able to degrade DMP (10).

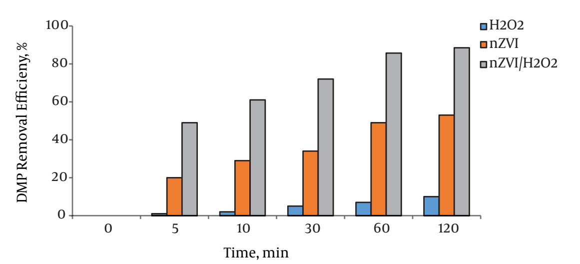

Figure 8. Effects of H_2O_2, nZVI and nZVI/H_2O_2 on Dimethyl Phthalate Removal, DMP concentration = 2 mg/L; pH = 4, H_2O_2 concentration = 0.1 mmol/L; nZVI.

3.6. Oxidation-Reduction Potential Variations in Heterogamous Fenton Process With nZVI

There are two oxidation and reduction reactions. Therefore, the changes of ORP are not unusual and it is very necessary that this parameter is monitored. In addition, the changes of H^+/OH^- and DO take place with reactions related to nZVI reduction or Fenton oxidation (18).

As can be clearly seen in Figures 9 and 10, after adding nZVI, ORP decreased. nZVI lowers ORP because it has strong oxidation power (E° = -0.4 V). There was no significant relationship between ORP and contact time, while the parameters of ORP and nZVI were entirely related together. At low and high contents of H_2O_2, the decrease of ORP is more noticeable (19).

With increasing the nZVI, the pH of the solution went up. Based on reactions 9 -11, nZVI consumes H^+ ions and reacts with dissolved oxygen and releases OH^- ions. Fe^{+2} ions from nZVI enter the next oxidation reactions and Fe^{+3} ions are generated.

(10) $2Fe^0 + O_2 + H^+ \rightarrow 2Fe^{2+} + 4OH^-$

(11) $2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-$

In aqueous solutions, DO is an ordinary oxidant and electron receiver. It is used on account of its reaction with electrons generated from nZVI corrosion in water (reaction 10). Figure 6 illustrates that by adding H_2O_2, DO increases.

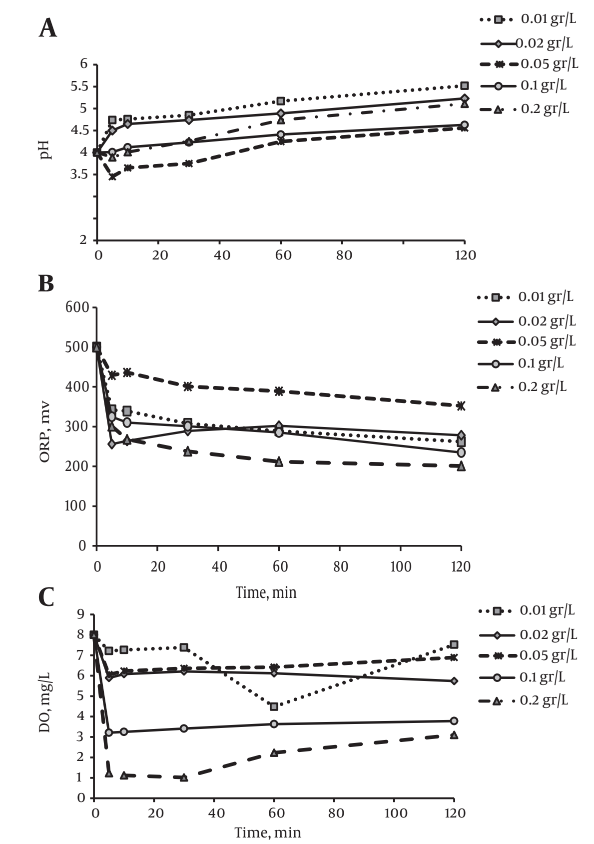

Figure 9. The Variations of pH, Oxidation-Reduction Potential and Dissolved Oxygen on the Heterogeneous Fenton Process With nZVI at Different Amounts of nZVI, pH = 4; DMP concentration = 10 mg/L; H_2O_2 dose=0.1 mmol/L.

A very important point to make here is that at low concentrations of H_2O_2 the recompense of the reduced DO of the system is harder (18).

4. Conclusions

The results showed that the maximum efficiency of heterogeneous Fenton process in DMP removal was at pH = 4. In addition, the removal efficiency under optimal condition of reaction parameters is 92.8%. Variation monitoring of ORP, pH and DO of samples showed that increasing the time and nZVI led to decrease of ORP. Furthermore, there was no significant relationship between ORP and reaction time; however, the relationship between ORP and nZVI was significant. On the other hand, the addition of H_2O_2 to the system stabilized the decline ORP. Addition of nZVI to the system increased pH and decreased DO. However, reduction of DO over time slowly adjusted and even in some doses increased DO again. Addition of H_2O_2 resulted in the

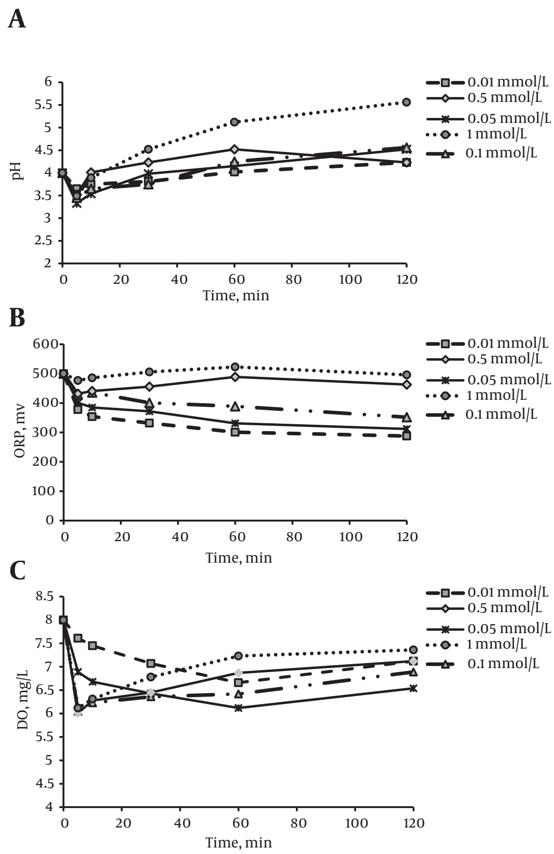

Figure 10. A, The effect of pH; B, ORP; C, DO, on heterogeneous Fenton process with nZVI at different contents of H_2O_2. pH = 4; DMP concentration = 10 mg/L; nZVI dose = 0.05 g/L.

increase of DO. The results showed that there was a high correlation between nZVI dose, H_2O_2 concentration and removal efficiency.

Overall, the heterogeneous Fenton process with nZVI can degrade DMP in a low contact time, of course, at optimized amounts. More importantly, monitoring of the process parameters, pH, DO and ORP, can enhance the efficiency of the system and lead to a dramatic increase in costs.

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