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A comparative study of removal of methyl tertiary-butyl ether (MTBE) from aquatic environments through advanced oxidation methods of H_2O_2/nZVI, H_2O_2/nZVI/ultrasound, and H_2O_2/nZVI/UV

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ABSTRACT

This study compares the efficiency of oxidation with H_2O_2 and nanoscale zero-valent iron (nZVI)in the presence of ultrasound and that of oxidation with ultraviolet radiation and H_2O_2/nZVI in the removal of MTBE from aqueous solutions. The effects of some parameters, such as ultrasound, contact time (2–60 min), concentration of hydrogen peroxide (5–20 ml/L), concentrations of nZVI (0.15–0.45 g/L), pH (2–9), and concentration of MTBE (50–750 mg/L) were investigated. In this study, the best MTBE removal efficiency was obtained at a rate of 89.56% in a concentration of 50 mg/Lat pH 3.5 with optimal H_2O_2 concentration of 10 ml/L, nZVI concentration of 0.25 g/L, and oxidation time of 15 min. Comparison of the effects of ultrasound with those of ultraviolet radiation, in similar conditions, showed no significant difference in efficiency between the ultrasound and UV ($p > 0.05$). However, comparing the efficiency of oxidation in the presence of ultrasound and without ultrasound in similar oxidation conditions showed significant differences ($p < 0.05$). In optimum conditions for oxidation, H_2O_2/nZVI/ultrasonic can be used as a convenient and efficient method to reduce concentration of MTBE in contaminated waters.

Keywords: MTBE; nZVI; H_2O_2; UV; Ultrasound

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1. Introduction

Nowadays, methyl tertiary-butyl ether (MTBE) is widely used as an oxygenated compound to raise the octane number and quality of fuels [1]. Therefore, MTBE is now a common contaminant in groundwater [2]. Given the potential health effects of high concentrations of MTBE on humans and its aesthetic consequences at low concentrations in terms of water taste and odor, during the last decade many studies have been carried out to find an appropriate method to eliminate MTBE from contaminated water sources [3–5]. Advanced oxidation processes (AOP_S), which are used for oxidation of resistant organic compounds and synthetic organic compounds, have been focused upon for this purpose [6]. Studies show that the use of advanced oxidation methods in conjunction with each other not only reduces the use of chemicals, but also improves the process efficiency in oxidizing the organic compounds [7,8]. These processes typically involve the production and use of hydroxyl radicals ($OH^·$) as a strong antioxidant for destruction of

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compounds that cannot be oxidized by common oxidants such as oxygen, ozone, and chlorine. During this process and under appropriate conditions, organic compounds ultimately change into water and carbon dioxide [9]. One of the recent methods presented for advanced oxidation of contaminants is the use of nanoscale heterogeneous catalysts in order to create sustainable and appropriate conditions for the formation of hydroxyl radical in the oxidation environment [10]. The most commonly used heterogeneous catalyst for the oxidation of contaminants is nanoscale zero-valente iron (nZVI). Studies show that nZVI is efficient in the removal of hazardous organic compounds such as chlorinated organic compounds and in the dechlorination of such compounds [11]. The mechanism of contaminant removal through ZVI includes the direct transfer of electrons from ZVI to the contaminant, which changes the contaminant into non-toxic or less-toxic compounds. On the other hand, ZVI in the presence of dissolved oxygen can oxide and decompose contaminant compounds as a result of transferring two electrons to the O_2 molecule producing H_2O_2 [12]. Hydrogen peroxide formed in this process can be reduced by transfer of two electrons from the ZVI to water molecules. In addition, the combination of H_2O_2 and Fe^{2+} (Fenton process), as shown in the chemical Eqs. (1)–(3), can lead to the formation of hydroxyl radical ($OH^{\cdot}$) as the most important factor in the oxidation of organic compounds [13]:

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{1}$$

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{3}$$

One of the innovations in the area of oxidation with active radicals is that of combining ultrasound with Fenton process (Sono-Fenton), which improves the efficiency of the Fenton process. This method has been used for removing phenolic compounds from aquatic environments and for wastewater treatment in the industries [14,15]. Bergendahl and Thies investigated Fenton's oxidation of MTBE with zero-valent iron. They used ZVI as Fenton oxidation source and the oxidation reactions were able to degrade over 99% of the MTBE within 10 min at pH 4 and 7 using an optimal ratio of H_2O_2:MTBE ratio of 220:1 [16].

Selli et al. studied the kinetic parameters of MTBE degradation using photocatalytic and ultrasound oxidation. They found that MTBE concentration decreased according to a first-order rate law. The study also evaluated the time profile of the reaction intermediates indicating that these pollutants degrade under different oxidation processes in experimental conditions [17]. Hong et al. have investigated the degradation of MTBE by anodic Fenton treatment (AFT). The results showed that MTBE and its degradation products were fully degraded in 32 min via AFT (Fe^{2+}:H_2O = 1:5) [18]. Ahmd Khodaday Darban et al. studied the reduction of MTBE concentration in water using Fenton method and determined the changes resulting from reaction conditions in producing byproducts. The results showed that the MTBE removal efficiency was about 99.99% at pH 3 [6]. Mohammad Rezaei studied the efficiency of the ultrasonic process in dispersive liquid–liquid microextraction technique for MTBE compounds at 200–400 kHz. The results showed that the technique is 70 percent efficient for the removal and reduction of MTBE in groundwater contaminated with gasoil and MTBE products [19].

On the other hand, over the past decade, due to the increase in applied research on the oxidation of contaminants with ultrasound, this technology has also been proposed as an improved method for the oxidation of contaminants. Under vibrations induced by ultrasound, water molecules are hemolyzed and form hydroxyl radicals and hydrogen atoms. These radicals in ultrasound systems of aqueous solutions directly affect the efficiency of oxidation [20]. On the other hand, according to some studies in the area of oxidation of contaminants by photo-Fenton (H_2O_2/Fe^{2+}/UV) and the high efficiency of this method in degrading contaminants, in this study, the efficiency of MTBE oxidation via three processes of H_2O_2, H_2O_2/nZVI/UV, and H_2O_2/Fe^{2+}/UV was investigated and the results were compared to delineate the effectiveness of ultrasound in the H_2O_2/nZVI oxidation process under optimal oxidation conditions.

2. Materials and methods

2.1. Laboratory materials and instruments

In this study, MTBE ($(CH_3)_3COCH_3$) with a purity of 99.9% and hydrogen peroxide (H_2O_2) with a purity of 30% were used. Other chemicals used included *n*-pentane, toluene, hydrochloric acid (HCl), and sodium hydroxide (NaOH). All these chemicals were purchased from Merk Company with laboratory purity. All experiments used co-distilled water produced by distilled water machine with rotary vacuum pump (PECOL Laboratory EquipmentLAN SHAN). nZVI was also synthesized.

The Elmasonic-S60h ultrasonic device with a constant frequency of 60 Hz and power of 500 kW for producing ultrasonic waves was used. A medium pressure mercury vapor lamp was used as a UV generator. This system had a 125-watt bulb with a maximum 1,020 μW/cm^2 at 247 nm wavelength purchased from ARDA company in Holland.

2.2. Oxidation reactor

This is a descriptive cross-sectional study carried out in laboratory scale in a double-walled plexiglass batch reactor (Figs. 1 and 2). First, one liter co-distilled water was added to the reactor. Then, based on the variables and research objectives, a factor was considered as variable, and the others were kept constant. In various stages of testing, various amounts of MTBE, nZVI, and hydrogen peroxide were added to the reactor. To adjust the temperature, cool water was used in the reactor chamber. The samples were put in a centrifuge device for 5 min at 4,000 rpm. *n*-pentane was used as an extractor and toluene as internal standard.

In the MTBE removal via H_2O_2/nZVI/ultrasonic process, the effects of some parameters such as contact time (2–60 min), concentration of hydrogen peroxide (5–20 ml/L), concentrations of nZVI (0.15–0.45 g/L), MTBE concentrations (50–750 mg/L), and pH (2–9) were investigated. Samples were taken from the reactor before and after the test conditions and were injected into the GC system after the MTBE extraction. The remaining MTBE was measured. Immediately before use, samples were prepared from the appropriate stock solution. Along with all the experiments, blank samples were used to assess the environmental changes but no change was observed in them. In total, 120 samples were injected into the GC system. In order to avoid the volatility of each compound through the surface, creation of empty space at the top of the sample was prevented. All samples were collected in glass containers with Teflon lids, stored at 4℃ and analyzed in shortest time. Each experiment was repeated twice and sometimes more on a factor at a time basis in two laboratories approved by the Environment Protection Organization.

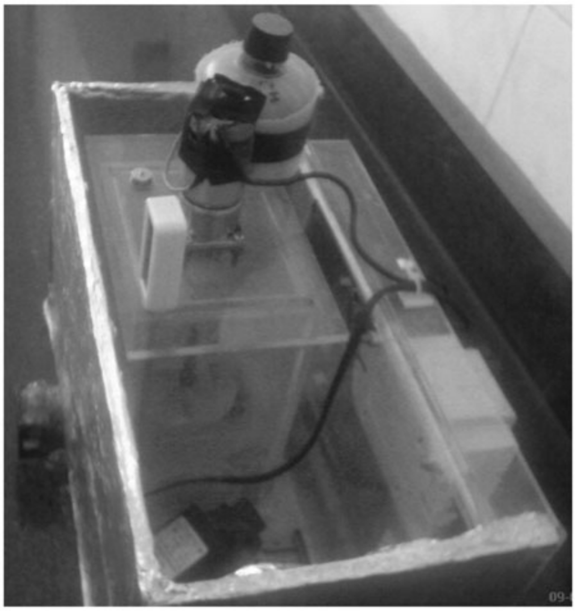

Fig. 1. The reactor used in this study (H_2O_2/nZVI/UV).

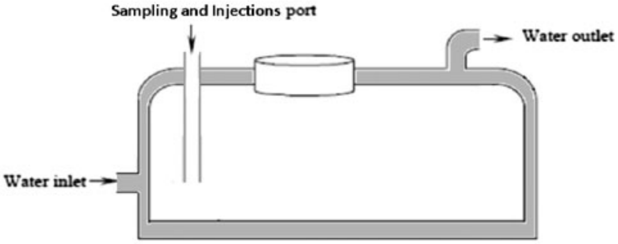

Fig. 2. Schematic diagram of oxidation H_2O_2/nZVI, H_2O_2/nZVI/ultrasound.

The data collected for the study were analyzed using SPSS via independent sample *t*-test. Excel software was used to draw the graphs and tables.

2.3. Synthesis of nanoparticles

According to the literature, there are different methods for the synthesis of iron nanoparticles. Nanoscale zero-valent iron (nZVI) can be produced through recovery of ferric iron (Fe(III)) or ferrous iron (Fe(II)) in aquatic environments with sodium borohydride ($NaBH_4$) [21] or through decomposition of pentacarbonyliron (Fe)CO)$_5$) in argon or in an organic solvent [22]. It can also be produced through the recovery of hydrogen from iron oxide [23].

Iron nanoparticles used in this study were synthesized using sodium borohydride. During the synthesis process, nZVI were synthesized by adding a solution of 1.0 M sodium borohydride to a solution of ferric chloride ($FeCl_3{\cdot}6H_2O$) at room temperature. The ferric chloride solution was produced via dissolving 0.5406 g of $FeCl_3{\cdot}6H_2O$ solids in water–ethanol solution with a volume ratio of 4/1 (4 volumes water to one volume ethanol). Borohydride solution was created using sodium hydroxide 0.1. Different test conditions, such as pH, concentration of reactants, stirring speed, titration speed, reaction time, and the temperature can significantly affect the structure and properties of iron particles. Therefore, in order to achieve consistent and uniform structure of nanoparticles, it is necessary to maintain test conditions constant. After the preparation of the solutions, sodium borohydride solution was added drop by drop (a drop per 2 s) to ferric chloride solution at intense mixing and vacuum conditions. With the addition of the first drops of sodium borohydride solution, solid black particles which were iron particles appeared immediately. This phase lasted about 30 min. During this time, the lid was fully closed so that nanoparticles were synthesized in a vacuum. Suction filtration method was used for separating the black nZVI from the liquid phase. Isolated nanoparticles were washed three times with 25 ml ethanol so that all water therein was extracted. This can be considered as the most important phase of nZVI synthesis, because it prevents rapid oxidation of nZVI. The washed particles were put in the oven and dried at a temperature of 50˚C for a night. In order to prevent oxidation in the air, nZVI was stored in ethanol solution (5%) [24,25]. TEM electron microscope was used to determine the characteristics of the produced nZVI (Fig. 3).

An example of the XRD spectrum of nZVI is shown in Fig. 4. Apparent peaks at the 2θ of 46.5˚ and 38˚ indicate the presence of both Fe^0 and Fe_3O_4.

2.4. GC analysis

Achieving final concentrations of MTBE after oxidation process requires drawing calibration curve and obtaining the related line equation using solutions with standard concentrations of MTBE. To this end, different concentrations of MTBE were prepared and injected into the gas chromatograph. Next, the related area under the curve for each concentration was determined, and the corresponding calibration curve was plotted.

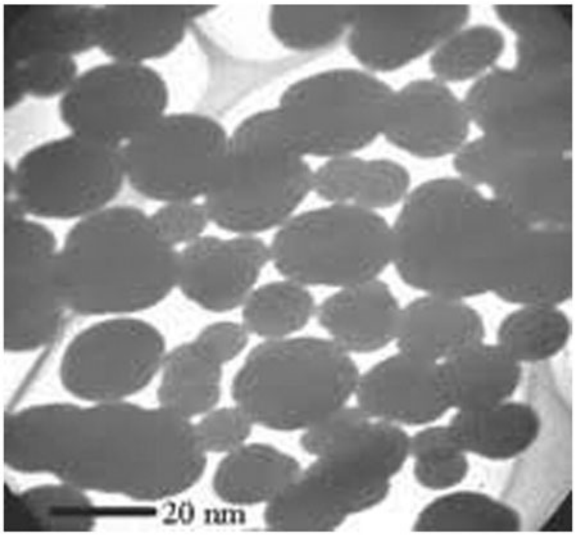

Fig. 3. TEM image of synthesized nZVI.

MTBE concentrations were measured by gas chromatograph Shimadzu GC-17A equipped with a FID detector. BPX5 capillary column (30 m × 0.25 mm i.d., 0.5 μm film thickness) was used. The direct injection volume was two microliters. The nitrogen carrier gas had a 99.9995% purity with a flow rate of 10 ml/min and the temperature conditions were as follows: detector temperature: 250˚C; temperature of injection site: 180˚C; column temperature 32˚C; column temperature gradient 6˚C/min; upper column temperature: 115˚C; and initial time: 2 min.

Shimadzu gas chromatography/mass spectrometry (GC/MS) 17A was used to determine the byproducts. BPX5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used. The direct injection volume was two microliters. The helium carrier gas had a 99.9995% purity with a flow rate of 36.7 ml/min and the temperature conditions were as follows: detector temperature: 300˚C; temperature of injection site: 230˚C; column temperature 32˚C; column temperature gradient 10˚C/min; upper column temperature: 115˚C; and initial time: 0.5 min.

3. Results

3.1. The effect of pH

The effects of MTBE oxidation via H_2O_2/nZVI process in the presence of ultrasound were measured at different pH ranges. Given that different oxidation conditions can affect the efficiency of the process, in order to achieve the optimum pH for MTBE oxidation, pH was changed while other conditions including initial H_2O_2 concentration, initial nZVI concentration, and contact time were kept constant. In oxidation conditions with 5 ml/LH_2O_2, 0.15 g/LnZVI, and 50 mg/LMTBE, at pH 2, 3.5, 5, 7, and 9, the MTBE removal efficiency decreased to 69.98, 81.46, 72.87, 51.05, and 40.15%, respectively, so that the efficiency at pH 2 was less than that at pH 3.5. That is why the pH range of 3.5 was chosen as the optimal pH level (Fig. 5).

3.2. The effect of oxidation time

Investigating the effect of oxidation by H_2O_2/nZVI in the presence of ultrasound indicated significant changes in the MTBE concentration in the early minutes of oxidation. The extent of MTBE reaction by time can be divided into two different phases in terms of speed. The oxidation rate in the initial minutes of

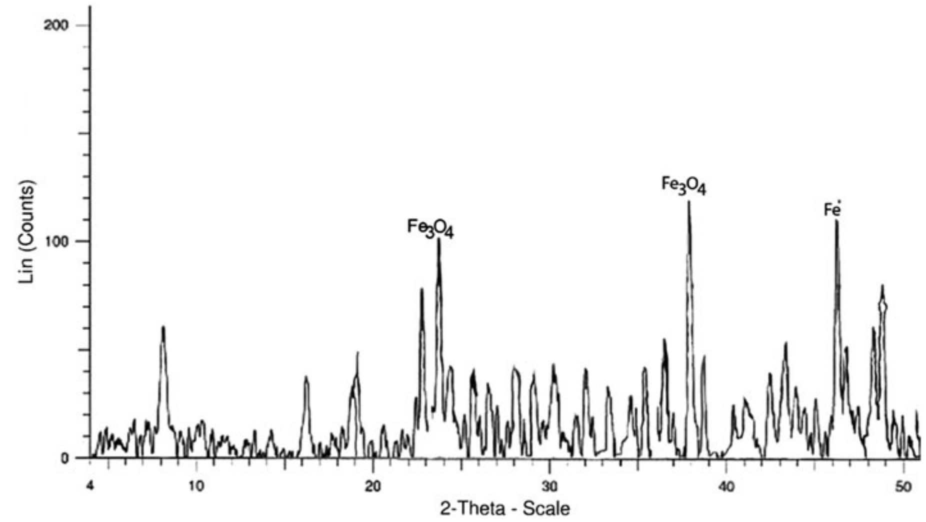

Fig. 4. XRD pattern of synthesized nZVI.

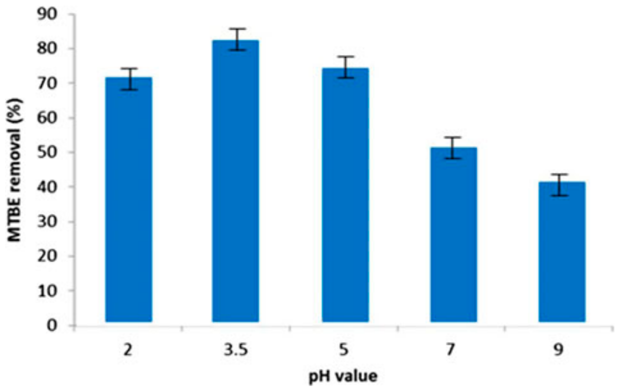

Fig. 5. Changes in the MTBE removal efficiency under conditions with 5 ml/LH_2O_2, 0.15 g/LnZVI, and 50 mg/LMTBE at different levels of pH.

the process (especially in the first ten minutes) was very high. In conditions with 5 ml/LH_2O_2, 0.15 g/LnZVI, and 50 mg/LMTBE at optimal pH, the initial MTBE concentration decreased by 64.46 and 81.46%, respectively, within 2 and 15 min after the start of the experiment. After the 15th minute to the 60th minute, oxidation continued but the rate was much lower than in the early minutes. After 60 min of oxidation in these conditions, the concentrations of MTBE decreased to 84.99%. Given the optimum time of 60 min in experiments, the one-way ANOVA results showed that the effect of time on the MTBE removal efficiency was not significant from the 15th minute to the 60th minute (p-value > 0.05). Therefore, 15 min was chosen as the optimum time (Figs. 6 and 7).

3.3. The effect of initial concentration of H_2O_2

In this study, the results of the effect of initial oxidizer concentrations on the MTBE removal efficiency showed that at initial concentration of 5 mg/L, as the lowest concentration, the optimal pH level, and nZVI concentration of 0.15 mg/L, after 15 min, the MTBE removal efficiency reached 84.99%. In the same situation, the removal efficiency for 10 ml/LH_2O_2 was equal to 88.71%. H_2O_2 concentrations of 15 and 20 ml/L were also studied. It was observed that the MTBE removal efficiency decreased by increasing H_2O_2 concentrations, so that it was 31.62 and 51.24% for H_2O_2 concentrations of 15 and 20 ml/L, respectively (Fig. 8).

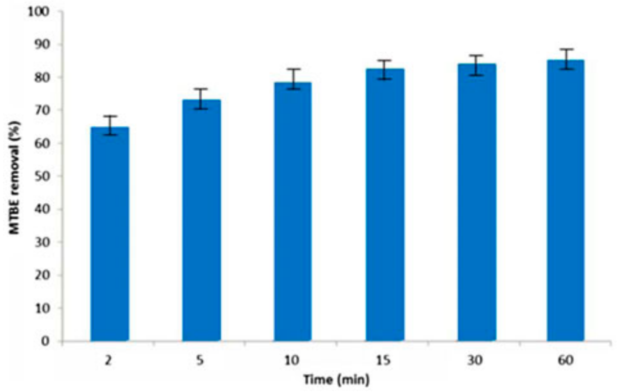

Fig. 6. Changes in the MTBE removal efficiency in conditions with 5 ml/LH_2O_2, 0.15 g/LnZVI, and 50 mg/LMTBE at pH 3.5 at various intervals during the 60-min oxidation.

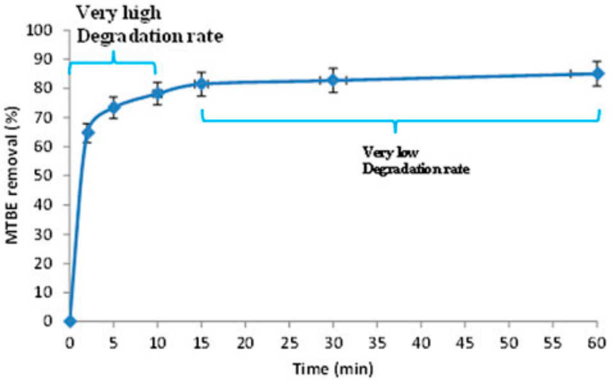

Fig. 7. Changes in the MTBE removal efficiency in conditions with 5 ml/LH_2O_2, 0.15 g/LnZVI, and 50 mg/LMTBE at pH 3.5 at various intervals during the oxidation process.

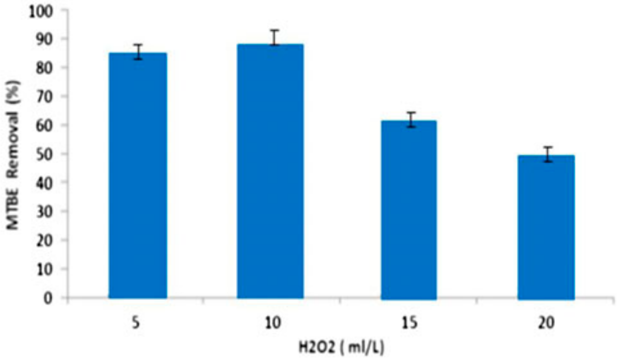

Fig. 8. The effect of initial H_2O_2 concentration changes (5, 10, 15, and 20 ml/L) on the MTBE removal efficiency in conditions with 0.15 g/LnZVI and 50 mg/LMTBE at pH 3.5.

3.4. The effect of nZVI

In H_2O_2/nZVI oxidation in the presence of ultrasound, the results of changes in initial concentration of nZVI injected into the reactor showed that the efficiency of the oxidation process is significantly influenced by this factor. At optimum pH conditions, H_2O_2 initial concentration of 10 mg/L, and MTBE concentration of 50 mg/L, after 15 min of oxidation, the MTBE removal efficiency for nZVI 0.15 g/L was about 88.71%. In the same conditions, with increasing nZVI concentrations to 0.25 mg/L, the MTBE removal efficiency decreased to 89.56%. The results for nZVI concentrations of 0.35 and 0.45 g/L showed that in these oxidation conditions, the removal efficiency reduced to 62.71 and 43.48%, respectively (Fig. 9).

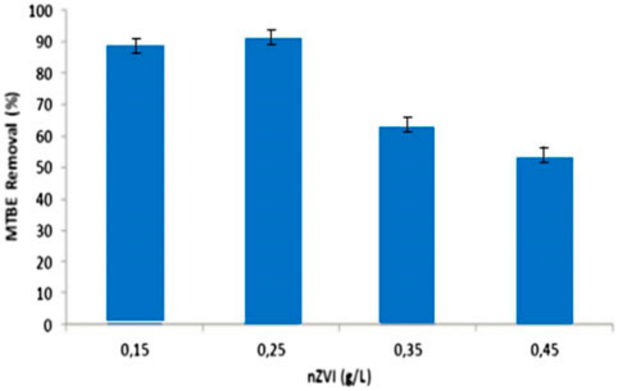

Fig. 9. The effect of changes in initial nZVI concentration on the MTBE removal efficiency in conditions with 10 ml/LH_2O_2 and 50 mg/LMTBE at pH 3.5.

3.5. The effect of initial MTBE concentration

The effect of H_2O_2/nZVI oxidation in the presence of ultrasound on different MTBE concentrations was studied. Given the optimum conditions obtained from tests for pH, H_2O_2 concentration, and nZVI concentration, the removal efficiency values at various MTBE concentrations indicated that with increasing initial MTBE concentrations, the removal efficiency decreased. In pH 3.5, initial H_2O_2 concentration of 10 ml/L and initial nZVI concentration of 0.25 g/L, the MTBE removal efficiency decreased to 89.56, 80.30, 72.24, 50.14, and 39.16% for MTBE concentrations of 50, 100, 250, 500, and 750 mg/L, respectively.

3.6. H_2O_2/nZVI oxidation reaction in the presence of ultraviolet radiation

The oxidation reaction of MTBE was investigated in optimal pH, H_2O_2, and nZVI conditions in the presence of UV without ultrasound. The results of oxidation with UV radiation showed that oxidation efficiency varied at different initial MTBE concentrations. At pH 3.5, initial H_2O_2 concentration of 10 ml/L and initial nZVI concentration of 0.25 g/L, the removal efficiency for MTBE concentrations of 50, 100, 250, 500, and 750 mg/L decreased to 81.12, 72.25, 60.20, 48.25, and 30.26%, respectively.

3.7. H_2O_2/nZVI oxidation reaction without UV and ultrasound

To evaluate the effects of UV radiation and ultrasound on the efficiency of the oxidation process, oxidation of various MTBE concentrations with the H_2O_2/nZVI without UV and ultrasound was

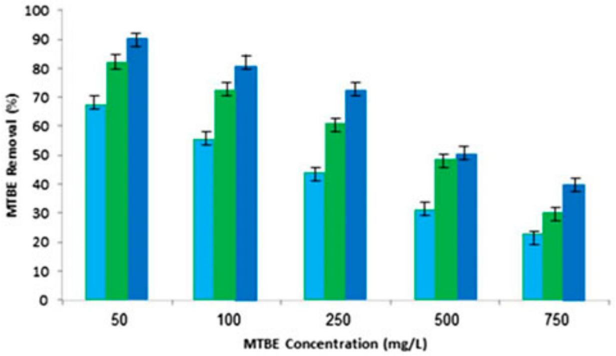

Fig. 10. Comparison of the efficiency of the MTBE oxidation with three methods of H_2O_2/nZVI (🟦), H_2O_2/nZVI/UV (🟩), and H_2O_2/nZVI/ultrasound (🟦).

investigated. Similar to oxidation in the presence of UV or ultrasound, in this situation, increasing the initial MTBE concentration reduced the oxidation efficiency. The efficiency at the initial MTBE concentrations of 50, 100, 250, 500, and 750 mg/L, the removal efficiency decreased to 67.60, 55.23, 42.32, 30.63, and 21.77%, respectively. Fig. 10 shows the comparison of the efficiency of the MTBE oxidation with three methods of H_2O_2/nZVI, H_2O_2/nZVI/UV, and H_2O_2/nZVI/ultrasound.

3.8. Intermediate compounds of MTBE oxidation process

In this study, intermediate compounds produced as a result of the MTBE oxidation under optimal test conditions were investigated. According to previous studies, oxidation of MTBE in aqueous solutions leads to the formation of intermediate compounds such as tertiary butyl formate(TBF), tertiary butyl alcohol (TBA), acetone, methyl acetate, isobutylene, formaldehyde, acetic acid, formic acid, and hydrogen peroxide [17,26,27].

TBF is an intermediate material formed early in the MTBE oxidation process and its concentration increased with time. TBA and acetone are two other compounds simultaneously formed during MTBE oxidation shortly after TBF concentration increased. Depending on the oxidation process, after a specified duration, the concentration of these compounds reduces [28]. Other intermediate compounds such as methyl acetate, formic acid, and acetic acid form at very low concentrations from the initial moments of the process. The concentration of these compounds increases with time. The concentration of hydrogen peroxide increases constantly during the oxidation process [28,29].

One of the most common mechanisms of the formation of TBF, TBA, and acetone is a process in which radical hydroxyl attacks the methoxy group of MTBE resulting in the formation of TBF as a result of the following reactions (Eqs. (4)–(6)) [30]:

$$[CH_3]_3C\text{–}O\text{–}CH_3 + OH^{\cdot} \rightarrow [CH_3]_3C\text{–}O\text{–}CH_2^{\cdot} + H_2O \quad (4)$$

$$[CH_3]_3C\text{–}O\text{–}CH_2^{\cdot} + O_2 \rightarrow [CH_3]_3C\text{–}O\text{–}CH_2O_2 \quad (5)$$

$$2[CH_3]_3C\text{–}O\text{–}CH_2O_2^{\cdot} \rightarrow 2[CH_3]_3C\text{–}O\text{–}CHO + H_2O \quad (6)$$

The TBF compound formed in this process can convert into TBA as a result of hydrolysis and the hydroxyl radical attack. It can also be formed as the second major intermediate compound as a result of the attack by hydroxyl radicals on tertiary butyl in the MTBE. During the oxidation process, the produced intermediate compounds convert into acetone as a relatively stable intermediate compound. The results of this study showed that in the early minutes of the process, TBF and TBA compounds were formed simultaneously, but the concentration decreased gradually. However, acetone concentrations increased rather slowly and reached its maximum amount at the end of the oxidation process. Therefore, to ensure the complete analysis of MTBE and its dangerous intermediate compounds, the oxidation process should be completed so that the process of stabilization and mineralization of the compounds is completed.

Study of the effects of time on H_2O_2/nZVI/US oxidation method showed that MTBE concentration undergoes significant changes quickly and in the early minutes of oxidation. According to the results, oxidation rate was very high in the first minutes after the

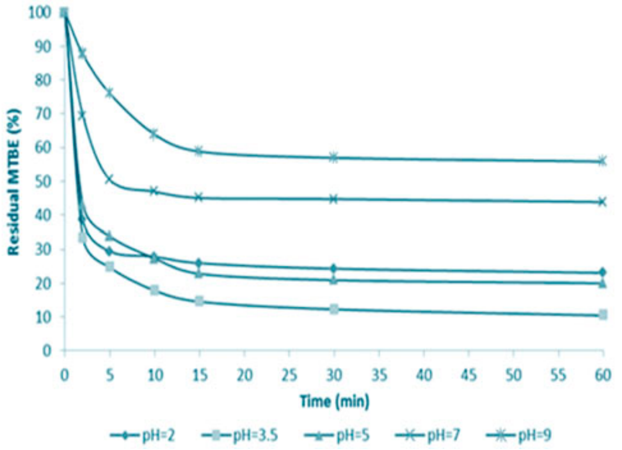

Fig. 11. Remaining MTBE percent 60 min after the oxidation at 10 ml/LH_2O_2, 0.25 g/L nZVI, and 500 mg/L MTBE.

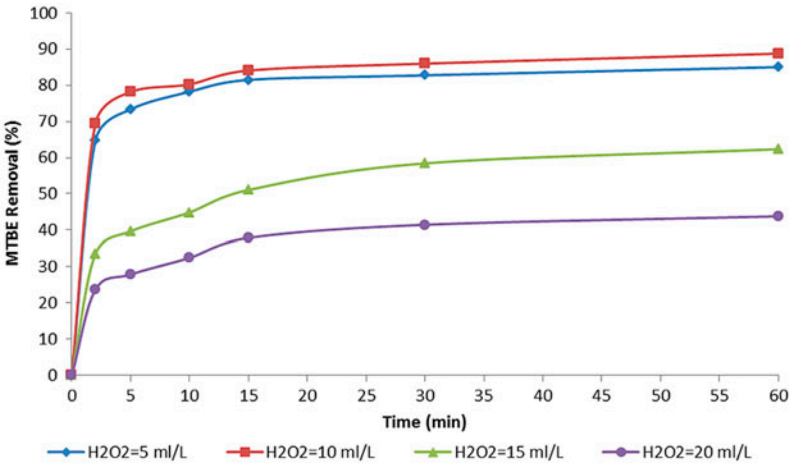

Fig. 12. Changes in the MTBE removal efficiency by time, under optimal conditions (pH 3.5, nZVI = 0.25 g/L) at various concentrations of H_2O_2.

start of the process (especially the first ten minutes). The results of oxidation in H_2O_2 concentration equal to 10 ml/L, nZVI = 0.25 g/L, and MTBE = 500 mg/L and in pH values of 2, 3.5, 5, 7, and 9 are shown in Fig. 11. The results show that the percentage of remaining MTBE 60 min after the beginning of oxidation, in pH values of 2, 3.5, 5, 7, and 9, the MTBE removal efficiency decreased to 23.07, 10.44, 19.99, 43.88, and 56.86%, respectively.

Fig. 12 shows changes in the MTBE removal efficiency in optimum oxidation conditions at different concentrations

4. Discussion

In this study, conditions affecting oxidation and the removal of MTBE using H_2O_2/nZVI/ultrasonic oxidation process were investigated. The results indicated that operating factors and conditions can have a significant impact on the MTBE oxidation efficiency. The solution pH is one of these factors. At acidic pH conditions, the removal efficiency was higher than at neutral or alkaline conditions. During the oxidation process, over time, the pH changes and due to production of H^+ ions in the test environment (Eq. (7)), pH descends slowly. These pH changes lead to different MTBE removal efficiency curves at various pH ranges [30]. The results of this study on the effect of pH are consistent with those of Burbano et al. who specifically examined the effect of pH on the degradation of MTBE with Fenton reagent. They studied various pH ranges from neutral to acidic and found that the highest removal of MTBE occurred when the pH was in the range of 3–3.5 [31]. According to Fenton chemistry, with increasing pH, various types of iron are deposited in the form of $Fe[OH]_3$ and cause the decomposition of H_2O_2 to O_2. On the other hand, with decreasing pH under highly acidic conditions, Fe[III] is converted to Fe(II). Both of these conditions can reduce the concentration of oxidants [32]:

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+} \quad (7)$$

The results of this study showed that the highest MTBE concentration removed during the first 15 min and the removal efficiency showed little change thereafter. These results show that due to high speed and capability of hydroxyl radical in the oxidation of MTBE, the time required for optimal oxidation of this compound is relatively low. Zha et al. [33] studied the oxidation of amoxicillin via nZVI/H_2O_2 method and found similar results about the effects of time. In their study, 70 and 9% of AMX was removed after 3 and 9 min, respectively, at conditions of H_2O_2 6.6 mM, nZVI 500 mg/L, AMX 50 mg/L. However, in the study by Hwang et al. [1] on MTBE oxidation via Fenton-like method, at initial concentration of 11 mM MTBE, 6 mM H_2O_2, and 5 mM Fe^{2+}, after 90 min only 45% of the initial MTBE concentration was removed. These differences in the effect of oxidation time can be attributed to the use of nZVI and its role in accelerating the oxidation process. On the other hand, according to the results of investigating the production of intermediate compounds as a result of the MTBE oxidation, in order to ensure the oxidation and removal of most of these compounds, the oxidation should continue for at least 60 min.

It was also observed that determining the appropriate concentration of H_2O_2 significantly affects the removal efficiency. In the oxidation process using H_2O_2, concentrations less than optimum significantly decreased the efficiency. Concentrations less than optimum increased the consumption of chemical materials and the related costs and decreased the oxidation efficiency due to hydrolysis of H_2O_2 molecules. This range of concentration can be called the critical oxidizer concentration. In many studies carried out in this area, the increase in oxidizer concentration to a certain level increases the efficiency [1,6,12] because increased oxidizer concentration increases the $OH^{\cdot}$ production. However, excessive H_2O_2 leads to a reduction in the MTBE removal. In this study, this occurred at H_2O_2 concentration greater than 10 mg/L that can be attributed to consumption of hydroxyl radicals by surplus residual H_2O_2 (Eqs. (8) and (9)):

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \tag{8}$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \tag{9}$$

As the effect of $HO_2^{\cdot}$ produced in this process is lower than that of $OH^{\cdot}$, the MTBE removal efficiency decreases significantly. This is consistent with the results obtained by Li et al. [13] on Fenton-like oxidation of 2,4-DCP in aqueous solution using iron-based nanoparticles as the heterogeneous catalyst. In their study, they used H_2O_2 concentrations of 1–15 mM and found that at H_2O_2 concentrations of 10 mM and over decreased the pollutant removal efficiency so that the removal efficiency reduced from 87% at a concentration of 10 nM to 15% at a concentration of 25 mM.

An increase in nZVI dose from 0.15 to 0.25 g/L increased the MTBE removal efficiency. This can be attributed to the effect of nZVI on potential degradation of H_2O_2. With an increase in concentration of nZVI, the formation of oxidizing radicals increases. However, this increase has limitations, because higher than optimum nZVI concentration leads to turbidity and decreases the optimal effect of oxidizer on MTBE [33]. Another reason for the decline in efficiency can be the removal of hydroxyl radicals by nanoparticles [34]. The results of the study by Zha et al. on nZVI concentration showed that higher than optimum concentration of nZVI reduced the oxidation efficiency [33]. However, the results of the study by Shu et al. showed that with increasing nZVI concentrations, contaminant removal efficiency increased. The reason for this difference could be the concentration levels investigated by Shu et al. that were less than 0.03 g/L [7].

Another factor influencing the MTBE removal efficiency was initial concentration of this compound. By increasing the initial MTBE concentration, removal efficiency decreased. The reason is that despite increased concentrations of MTBE compared to the initial value, the radicals generated in the oxidation process remain unchanged, and this reduces the radicals available for the oxidation of MTBE, which decreases the removal efficiency. Burdano et al. [31] studied the kinetics of MTBE oxidation via Fenton method and found that with increasing initial concentration of pollutants from 1 to 5 mg/L, the efficiency of oxidation process for removing the contaminants decreases. In the study by Sun et al. [8] entitled oxidative decomposition of p-nitroaniline in water by solar photo-Fenton AOP, similar results were obtained with increasing the initial concentration of the pollutant. This study was carried out in these conditions: 10 mM hydrogen peroxide, 0.05 mM/L ferrous ion, and a pH of 3 where increasing initial concentration of p-nitroaniline from 72×10^{-3} mM/L to 217×10^{-3} mM/L decreased the removal efficiency at equal durations.

Efficiency of oxidation via the process of H_2O_2/nZVI in the presence of ultrasound was measured and compared with the efficiency values obtained in the presence of UV instead of ultrasound and in the absence of these two factors in similar oxidation conditions. The results of this comparison which was carried out using one-way ANOVA indicated no significant difference between the effect of ultrasound and that of UV on MTBE oxidation efficiency at different concentrations ($p = 0.560$). However, there was a significant difference between MTBE oxidation efficiency in the presence of either ultrasound or UV and the efficiency in the absence of these two factors. p-values obtained from this analysis were $p = 0.003$ and $p = 0.042$, respectively, which show a high level of significance, especially in the case of ultrasound.

5. Conclusion

The results of the study on MTBE oxidation show that rate and extent of MTBE degradation increases significantly via H_2O_2/nZVI chemical oxidation in combination with ultrasound. The increase depends substantially on the oxidation conditions including pH, oxidizer concentration, nZVI concentration, and the initial MTBE concentration. Under optimal conditions, it is possible to reduce the concentration of this pollutant to a desirable level. Concentration of nZVI and H_2O_2 has a critical range out of which the removal efficiency reduces significantly. PH condition has an important influence on the speed and efficiency of the oxidation reaction. Therefore, maintaining a proper pH range is essential to achieve the highest removal efficiency. Oxidation occurs in two temporal phases with high and low speed, and the optimum speed can be obtained this way. Finally, according to the results, we can conclude that the H_2O_2/nZVI chemical oxidation method in combination with ultrasound can be used to reduce MTBE contamination of water sources. It can also be used as a pretreatment unit or in the process of biological treatment.

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