

Sequence-Fenton Reaction for Decreasing Phenol Formation during Benzene Chemical Conversion in Aqueous Solutions

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ABSTRACT

Advanced oxidation processes such as Fenton reagent generates highly reactive hydroxyl free radicals to oxidize various compounds in the water and wastewater. The efficiency of different Fenton-related oxidative processes such as Fenton, solar-Fenton, UV-Fenton and Fenton reactions in different batch reactors was examined using benzene as pollutant in aqueous solutions. A batch study was conducted to optimize parameters like pH, hydrogen peroxide concentration, temperature, reaction time and ferrous ion concentration governing the Fenton process. The concentrations of produced phenol were measured at the end of the reactions. The role of sequence reaction was tested for decreasing phenol formation during benzene conversion. At optimum conditions, different Fenton-related processes were compared for the degradation of benzene. Increased degradation efficiency was observed in photo-Fenton processes as compared to conventional Fenton process. The formation of phenol in Fenton reaction depended on reaction time, sequence in reaction, purity of hydrogen peroxide and other compounds such as alcohols that contributed into the reaction. In the Fenton process, carboxylic acids like acetic acid and oxalic acid were formed as the end products during the complete degradation of benzene. With the increase in mono-valence, two-valence ions and hardness, Fenton's efficiency decreased, respectively. Sequence Fenton reaction produced less phenol and its end products had smaller COD as compared to conventional Fenton process.

Keywords: *Benzene, Phenol, Fenton process, Sequence-Fenton processes, Aqueous solutions*

INTRODUCTION

In addition to many other hydrocarbon constituents, petroleum contains benzene, toluene, ethylbenzene and xylenes (BTEX). These are the most significant components in terms of pollution potential as they are the most soluble pollutants. Leaks of petroleum, leading to contamination of soil and groundwater by BTEX compounds, are widespread. Benzene (C₆H₆) typically makes up less than 2% of petroleum, but is imperative since it is considered the most toxic and persistent of all petroleum components.

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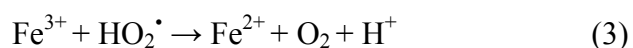
Benzene is a colorless liquid at room temperature (melting point 5.5 °C) with a density of 0.87 g/cm³ at 20 °C. It has a relatively low boiling point (80.1 °C) and a high vapor pressure (9.95 kPa at 20 °C), causing it to evaporate rapidly at room temperature. It is slightly soluble in water (1.8 g/l at 25 °C) and miscible with most organic solvents. One of the most important problems in working with benzene is vaporization from liquid phase to gas phase. There are many methods applied for decreasing benzene in liquid phase such as anaerobic biodegradation, electro-oxidation and Advanced Oxidation Process (AOP_s). Among AOP_s, the Fenton's reagent has been efficiently used as a

chemical process for aromatic compounds removal from aqueous environments. The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions (Groher, 2001).

This reaction allows the generation of hydroxyl radicals as shown in reaction (1):



The Fe^{3+} produced can react with H_2O_2 and hydroperoxyl radical in so-called Fenton-like reaction, which leads to regenerating Fe^{2+} (reaction 2 and 3). Fe^{2+} regeneration is also possible by reacting with organic radical intermediates (reaction 4) (Bishop, 1968):



There are 4 types of the chemical reactions of the hydroxyl radical in water:

(a) hydroxyl radical addition to an unsaturated compound, aliphatic or aromatic, to form a free radical product; (b) hydrogen abstraction, where an organic free radical and water are formed; (c) electron transfer, where ions of a higher valence state are formed reducing hydroxyl radicals to hydroxide ions; and finally (d) radical interaction where the hydroxyl radical reacts with another hydroxyl radical to combine or to disproportionate to form a stable product (Peres et al., 2003).

Here we report the application of the Fenton reagent to the oxidation of benzene to the phenols and another product with less toxicity. Afterwards we compare other related processes, such as photo-Fenton and solar-Fenton for increasing efficiency of benzene removal. Factors to consider when assessing the feasibility of Fenton's reagent include the formation of off-gases (1 liter of 1% hydrogen peroxide produces approximately 3 liters of oxygen gas), the formation of heat, and the need to reduce pH (at

least temporarily) to $\text{pH} < 4$. Fenton's reagent decomposes to oxygen and water. Contaminants can be completely oxidized to carbon dioxide and water (Bishop, 1968). The main advantages of Fenton reaction are as follows (Susan and Masten, 2001):

1. Un-reacted H_2O_2 degrades to oxygen.
2. Reaction times with most organics and OH radicals are fast.

The main limitations of Fenton reaction (for benzene removal) are formation of precipitation, consumption of hydrogen peroxide by side reactions, large amounts of reagents needed and many side reactions due non-specific nature of $\cdot\text{OH}$ (Susan and Masten, 2001).

MATERIALS AND METHODS

Benzene (Merck), H_2O_2 (10% & 35%), NaCl (Merck), CaCl_2 (Merck), CaCO_3 (Merck), ethanol 99.5% (Merck), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck), phenol (>99%), ethanol (98%) were used for Fenton reactions. Benzene concentrations were measured by a PU 4410 Gas Chromatograph equipped with a packed column (length, i.d. mm, and thickness mm) and a FID detector. The temperature of injection was 200 °C. The column temperature was typically 50 °C. Nitrogen was used as the carrier gas. All samples were measured as headspace and directly injected into the GC.

Phenol concentrations were measured by PU 8700 UV/Visible spectrophotometer. 4-aminopyrine forms a colored solution which quantity of its absorption is measured in 500 nm wavelength (Kanzaki et al., 2004). The samples were treated with 1 N NaOH to stop the oxidation process and subjected to analysis (Isoshi et al., 2000). Then, overall efficiency was studied by the reduction in benzene concentration and chemical oxygen demand (COD), was measured by potassium dichromate titrimetric method. For COD measurements, the samples were pretreated with NaOH, heated at 40 °C to remove residual H_2O_2 ; then, with ad-

dition of CaCl_2 , iron was precipitated and separated from solution.

In all experiments the benzene was injected directly into 10 ml of solution containing ferrous salts.

Fenton process was carried out in duplicate and in a batch mode. Benzene solution of $0.112 \mu\text{M}$ concentration (870 mg/l) was used for the experiments. The solutions were adjusted in several pHs using 1 N NaOH or 1 N H_2SO_4 . A known amount of FeSO_4 and H_2O_2 were added to 10 ml solution. A shaker device was used to ensure complete mixing of the reagents. Experiments were carried out with two vials, primarily with sunless then glassy vials.

In conventional Fenton processes, when hydrogen peroxide was added to solution containing benzene and ferrous salts, the color of the solution changed from yellow to brown and the solution became turbid within 2 min.

Changes in GC measurements were used for optimizing the parameters involved in the Fenton reaction.

In the first experiment, 3 samples were prepared with different shaking rates. For the first sample, primarily we shook the vial rapidly for 5 min by hand and then put it in a shaker unit which was set up at a rate of 100 rpm; For the second one, the sample was put in the shaker unit at the same rate. And the third one was tested in a quiescent condition. The reaction conditions for all the samples were similar and the consumed concentration of H_2O_2 was lower than optimum conditions.

In the second experiment, 3 samples were prepared in vials with different volumes and the volume of the solution in the 50, 100 and 300 cm^3 vials was 10 cm^3

Afterwards, ethanol was examined as a solvent for increasing benzene removal efficiency and reducing produced phenol. The concentrations of the reactants were defined as follows: $\text{FeSO}_4 = 1 \text{ g/l}$, benzene = 870 mg/l, H_2O_2 (10%) = 0-1000 ml/l ($\text{ml} = 10^{-3} \text{ l}$), ethanol = 50 and 100 ml/l.

Having evaluated the effects of one and two valance ions and also the hardness agents on the

benzene removal efficiency, some agents such as NaCl (as mono-valanet ion), CaCl_2 (as divalent ion) and CaCO_3 (as hardness agent) would have been added in the vials.

In Solar-Fenton reaction, the solar induced oxidation of benzene was performed at dark state, which lamplight radiate on glassy vials. The solar radiation, luminance and temperature during the experimental time were in the range of $400\text{--}595 \text{ Wm}^{-2}$, 98–100 klx and $32\text{--}35 \text{ }^\circ\text{C}$, respectively. The distance between lamp and vials was 20 cm.

Two UV lamps were used for UV-Fenton experiments. The distance between lamp and vials was 20 cm. The glassy vials (including reacting solution) of 100 ml capacity were placed on shaker. A medium pressure mercury lamp (150W) was used as an UV source of 254 nm. The lamp was located at the center of the vials. Sequence-Fenton reaction was conducted by a sequent H_2O_2 injection in the vials. H_2O_2 oxidant was added to the vial in two steps. Firstly, 200 ml/l of H_2O_2 (10%) was injected to the vial which contained benzene (870 mg/l) and FeSO_4 (1 g/l). After 90 min, different volumes of H_2O_2 were added to vials which contained the reaction products of the first stage. The residual phenol concentration was measured at the end of the stages

RESULTS

The optimum pH, H_2O_2 (10%) and Fe^{2+} concentrations (for 870 mg l^{-1} benzene) were found to be 3-4, 0.11mM (mole) and 0.036mM, respectively. Maximum degradation of 99% was attained at following mass ratios:

$$\text{Fe}^{2+} / \text{H}_2\text{O}_2 = 0.01$$

$$\text{H}_2\text{O}_2 / \text{Substrate} = 20.5$$

$$\text{Fe}^{2+} / \text{Benzene} = 0.23$$

The residual concentration of phenol in the solution was about 257.1 mg/l (which is equivalent to 34% of produced phenol).

The optimum pH and temperature values were in the range of 3-5 and $30\text{--}50 \text{ }^\circ\text{C}$, respectively. In all of the cases, the pH of treated solution

decreased to 2.3–2.5 and the COD of the effluent was about 900 mg/l.

The results have shown that, if the volume of the vial and shaking rate increased, then the efficiency of benzene removal could be increased too. Namely, for the above vials the benzene removal efficiency in 300 and 100 cm³ vials was 30% and 20% higher than the 50 cm³ vial, respectively (Fig.1).

Fig. 2 shows the benzene removal efficiency in the presence of 50 ml/l ethanol.

In Fig. 3 and 4, the effects of mono-valent ions, divalent ions and hardness agents on the benzene removal efficiency have been shown. In conventional Fenton reaction, benzene removal efficiency and phenol formation were compared in two purities of 10% (200 ml/l) and 35 % (180 ml/l) of H₂O₂. The residual phenol concentration was measured at the end of reactions. In the Fig. 5-a and 5-b, the results of the reactions with these two purities have been shown.

Four processes have been tested and compared with each other for benzene removal. These processes consist of H₂O₂/UV, conventional Fenton, Fenton in transparent and opaque vials, UV-Fenton and Solar-Fenton processes.

Fig. 6 shows the degradation of benzene by different Fenton-related processes as a function of time.

In Fig. 7, benzene degradation by Solar-Fenton and conventional Fenton processes have been compared as a function of time.

In Sequence-Fenton reaction the color of solutions changed in both steps. In the first stage, the colour changed from white to dark gray, and then changed to yellow. In sequence-Fenton process, the residual phenol concentration was measured as zero when a 300ml/l H₂O₂ was added to the vial and the time for complete reaction was adjusted to 30 min in the second step (Fig. 8). The COD of end-products was 400 mg/l.

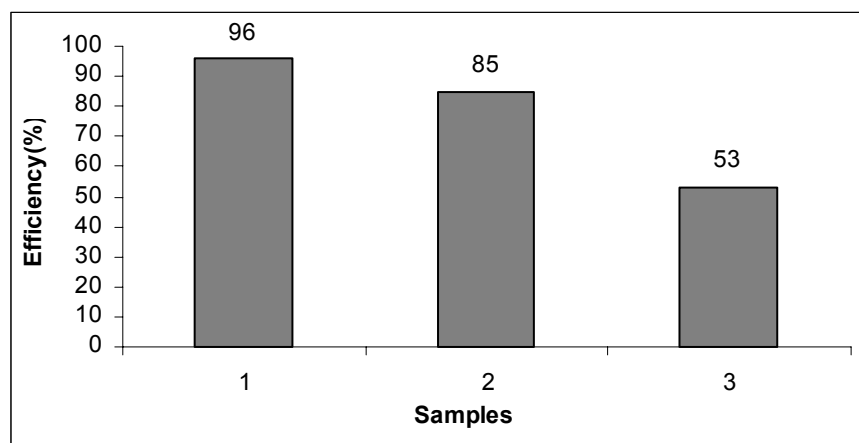


Fig. 1: The effect of shaking on benzene removal efficiency (H₂O₂=140ml/l · FeSO₄=1g/l, Total reaction time= 120min) (Sample1: intensive shaking in 5 minutes and then shaking in 100 rpm; Sample 2: shaking in 100 rpm; Sample 3: without shaking)

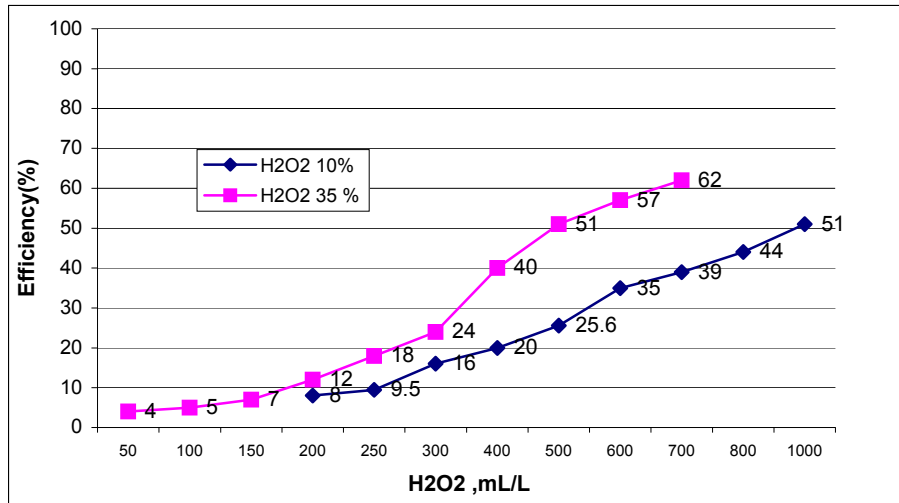


Fig. 2: The changes in benzene removal efficiency with change in purity of H₂O₂. In presence of ethanol (ethanol=50ml/l, benzene=870mg/l, FeSO₄= 1g/l).

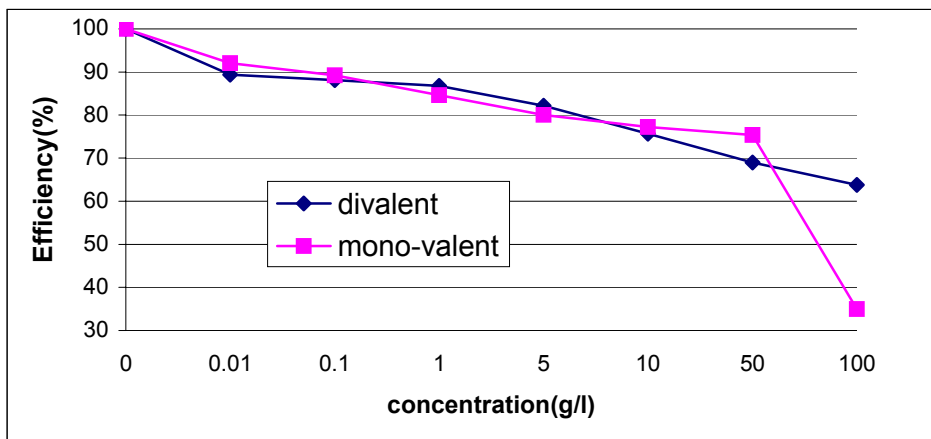


Fig. 3: The effects of equivalence and two valance ions on benzene removal efficiency in Fenton reaction.

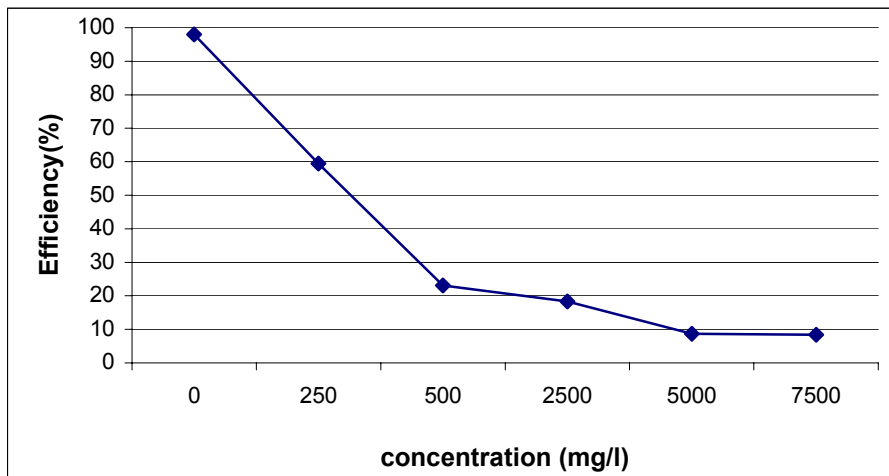
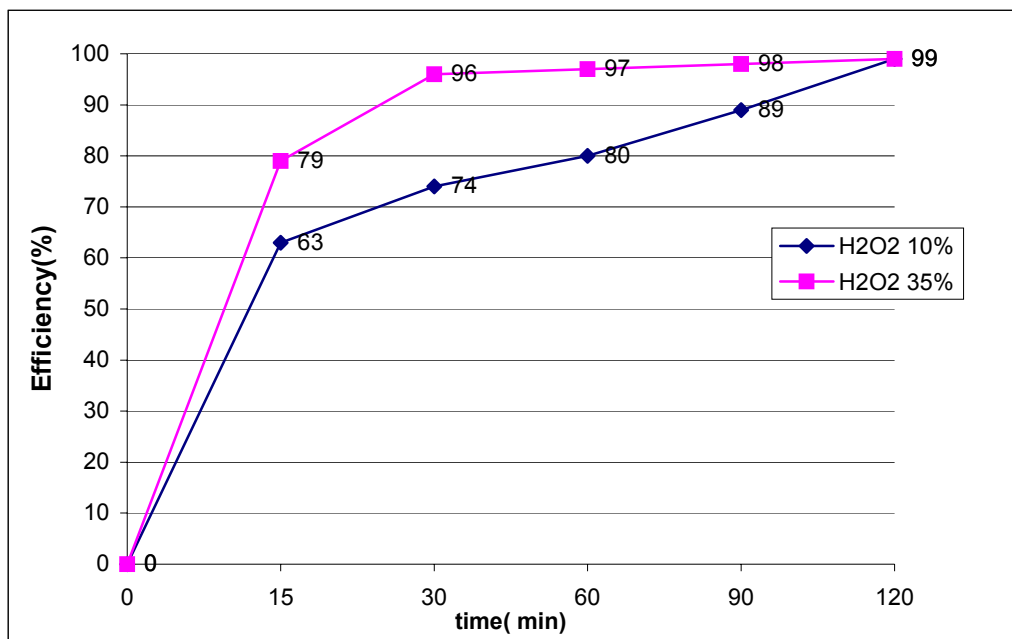
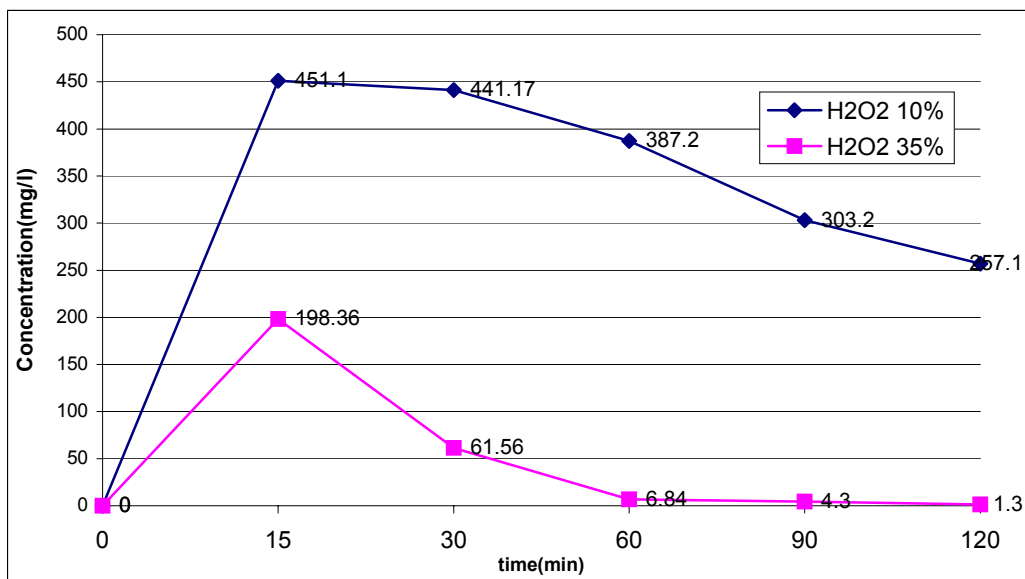


Fig. 4: The effects of hardness on benzene removal efficiency in Fenton reaction (H₂O₂=200ml/l, benzene=878mg/l, FeSO₄=0.01g)



(a)



(b)

Fig. 5: Comparison between 10% and 35% purities of H₂O₂ on benzene removal efficiency (a) and remaining phenol concentration (b).

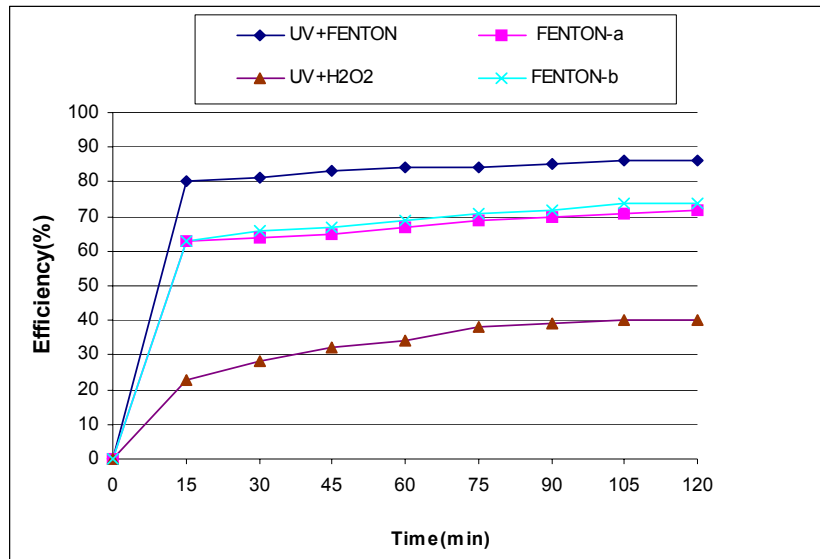


Fig. 6: Degradation of benzene by different Fenton process (All samples maintained in 100rpm shake; Fenton-a: Fenton reaction in glassy vials Fenton-b: Fenton reaction in sunless vials).

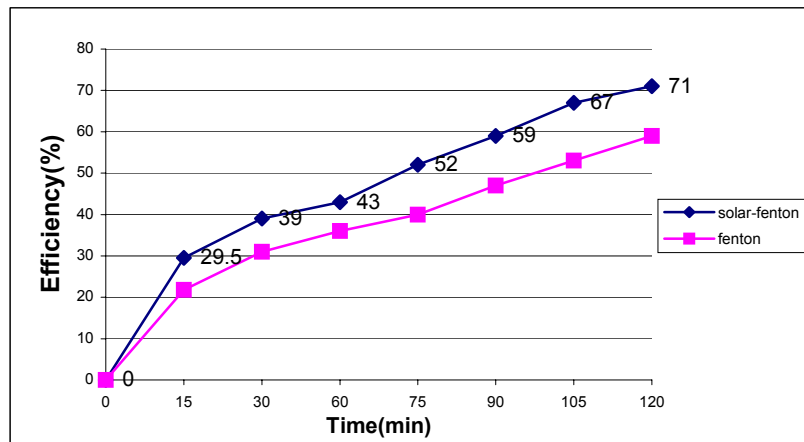


Fig. 7: Comparison of benzene removal efficiency between Solar-Fenton and Conventional Fenton processes in different times.

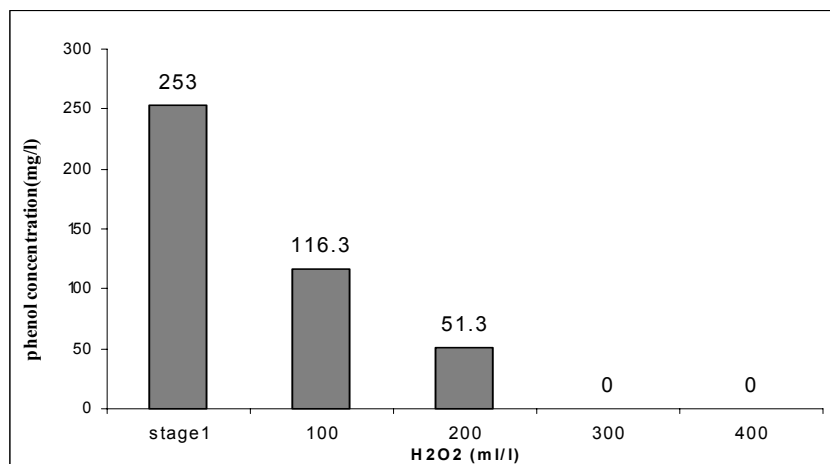


Fig. 8: The phenol concentration in different volumes of H₂O₂ 10 %. (In second stage of Sequence-Fenton reaction)

DISCUSSION

In Fenton process, when hydrogen peroxide was added to the solution containing benzene and ferrous salts, the color of the solution changed from yellow to brown and became turbid within 2 minutes that indicates phenol production (Wanga et al., 2001). The chemical reactions of the hydroxyl radical in aqueous solutions are of four types, which one of them is addition (Eq. 5):

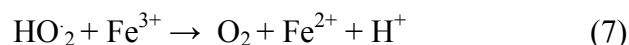


Where the hydroxyl radical is added to an unsaturated compound, aliphatic or aromatic, to form free radical products (Wanga et al., 2001). In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can be added to the benzene rings, and then produce phenol and other aromatic compounds (Neyens and Baeyens, 2003). Hereupon direction of reactions to less phenol is valuable, because phenol is as toxic as benzene. When ferrous ion was added to an aqueous solution of H_2O_2 , hydroxyl radicals ($\cdot\text{OH}$) are generated by Fenton reaction as shown in Eq. (1).

The generated $\cdot\text{OH}$ radicals attacked the "P" system of the aromatic benzene ring in a rapid manner resulting in conversion of benzene to phenol (Kavitha and Palanivelu, 2004).

Aromatic compounds are mainly interested in participating in substitution reactions; OH is substituted with H in benzene structure. In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic (benzene) rings (Isoshi et al., 2000). In all states, the pH of the treated solution decreased to 2.3–2.5, it might be due to the formation of carboxylic acids like acetic acid, oxalic acid, formic acid, etc. It is evident that shaking is one of the important elements in Fenton process. The benzene removal efficiency decreased when reducing shack of samples, because reactants do not complete mixing. Oxygen is an important element in reactions. Kavitha and Palanivelu (2003) reported that the

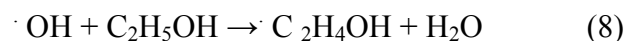
dissolved oxygen (DO) profile in degradation of phenol by Fenton process, dropped immediately within 60s after the addition of H_2O_2 . As the reaction progressed, the DO in the solution accumulated and found to be 6.38, 7.30 and 7.38 mg/l at 10 min, 1 and 2 h, respectively. Increase in DO was mainly due to slow consumption of hydroxyl radicals for oxidation process and rapid production of O_2 by the breakdown of peroxides catalyzed by ferric ion as shown in Eqs. (6) And (7).



As shown in Fig.6, more than 60% of benzene was degraded primary in 60 minutes and then the oxygen concentration dropped in time. The oxygen concentration after reaction was 6.5 - 7.5, respectively.

The results revealed that the highest conversion of benzene was obtained in ethanol, but phenol was not produced (Hosseini Monfared and Amouei, 2004)

Results showed that more than 95% of benzene decreased and the quantity of phenol produced was 41 mg/l ($\text{FeSO}_4 = 1 \text{ g/l}$, benzene= 870 mg/l and H_2O_2 (10%)= 400 ml/l, ethanol= 100ml/l) In the presence of alcohols the consumed H_2O_2 was increased respectively (400 ml/l). Fig.7 shows that benzene removal efficiency in the presence of ethanol (50ml/l) decreased (even with H_2O_2 35%), because H_2O_2 consumes ethanol like as benzene (Eq. 8).



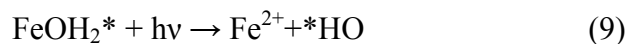
In this reaction (hydrogen abstraction) an organic free radical and water are formed (Bishop, 1968). In the presence of ethanol, benzene removal efficiency decreased, but the remained phenol decreased.

The data shows that hardness had important effects in Fenton reaction as the removal efficiency closed to zero in high dose of calcium carbonate. As shown in Fig. 3, the efficiency of reaction decreased, if the concentration of

mono-valance and divalent ion increased. Mono-valance ions had greater effect than divalent ion on removal efficiency.

The result shows that UV-Fenton had highest efficiency and UV/H₂O₂ was not effective as other processes. Almost Fenton-a was similar to Fenton-b and had the same efficiency.

The rate of degradation of the organic pollutants by Fenton reaction increases when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photo reduction of Fe (III) to Fe (II) ions; a step that produces new OH radicals and regenerates Fe (II) ions that can further react with more H₂O₂ molecules. The photo reduction of Fe (III) follows the following equation (Torrades et al., 2003):



Recently, it has been proven that the irradiation of Fe (III) +H₂O₂, also called Fenton-like reaction, enhances the rate of oxidant production, through the involvement of high valence Fe intermediates responsible for the direct attack to organic matter. Absorption of visible light by the complex formed between Fe (III) and H₂O₂ seems to be the cause of formation of such high valence Fe-based oxidants (Torrades et al., 2003). The Solar-Fenton process has higher efficiency than conventional Fenton process (Fig. 4). In Solar-Fenton process the temperature of vials was 32-35 °C. Cause of less efficiency in both methods was quietness of vials that revealed shaking was main parameter in Fenton process

It is evident that H₂O₂ 35%, decreases more concentration of benzene and phenol than H₂O₂ 10%. The volume of consumed H₂O₂ 10% was 200 ml/l, but H₂O₂ 35% was 180 ml/l. It is expected that less volume of H₂O₂ 35% was consumed but the difference between them was 20 ml/l. It seems that preliminary reactions conducted to phenol production, and then phenol degraded too. In H₂O₂ 35% this reaction was stricter and faster than H₂O₂ 10%. Step injec-

tion of H₂O₂ (sequence Fenton) affects the mineralization of benzene and then phenol.

The sequence-Fenton processes found to be successful with almost complete mineralization of benzene and then phenol, but the time of reactions and volume of H₂O₂ was greater than conventional Fenton reaction.

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