Treatment of Furfural Wastewater by (AOPs) Photo-Fenton Method

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ABSTRACT

The objective of this study is to investigate the application of advanced oxidation processes (AOPs) in the treatment of wastewater contaminated with furfural. The AOPs investigated is the homogeneous photo-Fenton ($UV/H_2O_2/Fe^{+2}$) process. The experiments were conducted by using cylindrical stainless steel batch photo-reactor. The influence of different variables: initial concentration of H_2O_2 (300-1300mg/L), Fe^{+2}(20-70mg/L), pH(2-7) and initial concentration of furfural (50-300 mg/L) and their relationship with the mineralization efficiency were studied.

Complete mineralization for the system $UV/H_2O_2/Fe^{+2}$ was achieved at: initial H_2O_2 = 1300mg/L, Fe^{+2} = 30mg/L, pH=3, temperature =30°C and irradiation time of 60 min, for 300mg/L furfural concentration. The results have shown that the oxidation reagent H_2O_2 plays a very important role in the furfural mineralization.

Key words: Advanced oxidation process, UV, Furfural, Photo-Fenton process, H_2O_2.

معالجة المياه الملوثة بالفورفورال باستخدام عمليات الاكسدة المتقدمة(طريقة الفوتوفنتون)

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الخلاصة

الهدف من هذا البحث دراسة معالجة المياه الملوثة بمادة الفورفورال باستخدام احد طرق الاكسدة المتقدمة (AOPs). حيث تم استخدام نظام الاكسدة المتجانسة ($UV/H_2O_2/Fe^{+2}$, photo-Fenton process). التجارب تم اجرائها باستخدام مفاعل اسطواني مصنوع من الفولاذ المقاوم للصدأ يعمل بنظام الوجبات. تاثيرالمتغيرات المختلفة مثل: التركيز الابتدائي لل H_2O_2 (300- 1300mg/L) و Fe^{+2}(20-70mg/L) و pH (2-7) والتركيز الابتدائي للفورفورال(50-300 mg/L) تم دراستها ودراسة علاقتها مع كفاءة التحلل للفورفورال. بينت التجارب ان التحلل الكامل للفورفورال بتركيز 300 mg/L تم باستخدام H_2O_2=1300mg/L و Fe^{+2} =30mg/L وبظروف حامضية pH=3 ودرجة حرارة 30°C وبوقت 60 دقيقة . النتائج بينت ان تركيز العامل المؤكسد H_2O_2 له دور مهم في عملية الاكسدة.

1. INTRODUCTION

Many industries such as petroleum refining, petrochemical, pharmaceutical, pulp, paper and food industries involve processes that use or produce furfural, **Sahu, et al., 2008**. The discharge of untreated furfural wastewater can cause severe environment pollution. Therefore, there has been a growing interest for the removal of furfural from wastewater not only to counter its health effects but also to recover the furfural and recycle it back to the process. Most of the furfural on the world market is produced in China, **Win, 2005**. China is the dominant player in the world furfural market with 80% of global capacity and 72% of world consumption **Fig. 1**, **IHS, 2011**.

Furfural is irritating to eyes, skin and respiratory system. Inhalation may cause headache, nausea and central nervous system depression. It also may be absorbed through intact skin. It shows some limited carcinogenic effects, furfural has been classified as a category 3 carcinogen, **USEPA 2012.** Furfural actuate exposure can also damage livers and kidneys. The Permissible Exposure Limit (PEL) and the threshold limit value (TLV) for furfural was reported 5.0μg/ml and 2.0μg/ml, respectively, **ACGIH, 1994; OSHA, 1994**.

The presence of furfural, increase the toxicity of wastewater and makes biological treatment very difficult. Removal of this substance will require modifications or alternatives of the existing systems, **Yaghmaei et al., 2005**. This compound if discharge in open rivers, it can destroy the micro flora and has negative effect on human health.

Aerobic and anaerobic biological treatment have been used by many researchers for the degradation of furfural, **Wang, et al., 1994**. Also Adsorption technique is quite popular in the treatment of wastewater contaminated with furfural due to its simplicity as well as the availability of a wide range of adsorbents. Activated carbons are widely used as adsorbents for the treatment of furfural polluted water, **Sulaymon and Ahmed, 2006**.

Advanced oxidation processes (AOPs) are related to a nonconventional technologies that characterized by the generation of hydroxyl radicals, which are highly reactive and non-selective substances used to degrade toxic organic compounds present in a medium such as wastewater and soil. Some characteristics features of hydroxyl radical are shown in **Fig. 2**, **Oppenländer, 2007**. The hydroxyl radical has a high oxidation potential (E^0 = 2.8 V), as shown in **Table 1**, and is able to react with practically all classes of organic compounds, resulting in complete mineralization of these compounds, that is, the formation of carbon dioxide, water and inorganic salts, or their conversion into less aggressive products, **Bolton et al., 2001**.

Over a century ago, Fenton **,Fenton, 1894,** demonstrated that a mixture of H_2O_2 and Fe^{+2} in acidic medium had very powerful oxidizing properties. The classical mechanism is a simple redox reaction in which Fe^{+2} is oxidized to Fe^{+3} and H_2O_2 is reduced to hydroxide ion and the hydroxyl radical, Eq.(1) :

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + HO^{\bullet} + OH^{-} \quad (1)$$

In the conventional Fenton reaction, carried out in the absence of light, the ferric ion produced in Eq.(1) can be reduced back to ferrous ion by a second molecule of hydrogen peroxide forming the hydroperoxyl radical, according to Eq.(2). This reaction, referred to by **Neyens and Baeyens, 2003** as Fenton-like, occurs more slowly than reaction (1)

$$Fe^{3+}_{aq} + H_2O_2 + H_2O \rightarrow Fe^{2+}_{aq} + H_3O^{+} + HO_2^{\bullet -} \quad (2)$$

About two decades ago, it was found that the irradiation of Fenton reaction systems with UV light strongly accelerated the rate of degradation of a variety of pollutants, **Pignatello et al., 2006 and Malato et al., 2003**. This behavior upon irradiation is due principally to the photochemical reduction of Fe^{+3} back to Fe^{+2}, for which the net reaction can be written as, Eq.(3):

$$Fe^{3+}_{aq} + H_2O + hv \rightarrow Fe^{2+}_{aq} + HO^{\bullet} + H^{+} \quad (3)$$

The objective of this work is to study the effectiveness of the AOPs in the mineralization of furfural using batch experiments. The AOP selected to carry out this study is the photo-Fenton ($UV/H_2O_2/Fe^{2+}$) process.

2. MATERIALS AND METHODS

2.1 Furfural and Chemicals Used

Furfural commercial grade (Suzhou Alpha International Company, China) was obtained from AL-Dora refinery to simulate the wastewater used in the present experiments. Also **Table 2** shows all the chemicals that used. All the samples were prepared by dissolving requisite quantity in distilled water. The pH of the solution was adjusted by using H_2SO_4 solution.

2.2 Equipment

Batch experiments were carried out in the present work using laboratory scale system, **Fig. 3**, which consist of feed container, peristaltic pump and reactor. The cylindrical reactor is made of stainless steel, 2.4 Litter volume. Irradiation was achieved by using low-pressure mercury vapor lamp, 4-pin single end, 40W, UV-C 254 nm (Philips Company) which was sheathed in glass sleeve for protection and fixed inside along the reactor. The feed container was mounted on a magnetic stirrer with heater (MSH-300N, BOECO. Germany) to maintains the desired temperature and provide a well mixing. Valves 1, 2 and 3 were utilized to control the flow direction through the system. Peristaltic pump (BT300-2J), of medium flow rate 0.07-1140 mL/min from Longer Company, China was used to maintain the desired flow. The pH of solution was monitored using pH meter from (WTW Co., German. INOLAB 720).

2.3 Experimental Procedure

Batch experiments were conducted in the present work to find the best conditions for AOP treatment. The procedure was performed maintaining valve No.1 and No.2 opened and valve No.3 closed, **Fig.3**. For each experiment, simulated furfural wastewater with desired concentration was added to the feed container. A well mixing was maintained using a magnetic stirrer, and the pH value of the solution was adjusted before adding the reagents by adding a dilute H_2SO_4 in the feed container. The desired quantity of Fe^{+2} was added to the feed container and mixed very well. The peristaltic pump was switched on and the solution was allowed to flow from the feed container through the peristaltic pump to the UV reactor, the solution was re-circulated for 5 minutes. The desired quantity of H_2O_2 300-1300 mg/L was added to the feed container, and immediately the UV lamp was turned on. The solution was circulated at a flow rate of 600 mL/min. Regular samples 10ml volume was taken from the feed container after 0, 20, 40 and 60 min for analyses.

2.4 Analysis

Chemical Oxygen Demand of samples was analyzed by COD Photometer system. Appropriate amount of sample (2ml) was introduced into commercially available digestion solution (MR-Rang: 0-1500mg/L) containing potassium dichromate, sulfuric acid and mercuric sulfate. The mixture was then incubated for 120 min at 150°C in a COD reactor (model RD-125, Lovibond Company, Germany). After oxidation was complete, the COD concentration was measured colorimetrically at 605 nm using a DR/2010 spectrophotometer (model MD100, Lovibond, Germany).

3. RESULTS AND DISCUSSION

3.1 The Effect of Initial H_2O_2 Concentration

The effect of initial concentration of H_2O_2 (300, 500, 700, 900, 1100 and 1300 mg/L) on photo-Fenton process was tested to optimize the amount of H_2O_2 required to treat the furfural. Fixed initial amount of Fe^{+2} (40 mg/L) was maintained through the experiments. Initial pH equal to 3 was used and the temperature was maintained at 30^oC through all the experiments. Initial furfural concentration 300 mg/L was used in the experiments. **Fig. 4** shows the relation between the removal efficiency and the irradiation time for different initial concentration of H_2O_2. From this figure it can be noticed that the degradation of furfural increased as the concentration of H_2O_2 increased from 300 to 1300mg/L reaching a maximum removal efficiency of 100% at 1300 mg/L after 40 minutes of irradiation time. The mineralization of furfural increased with the increasing of initial concentrations of hydrogen peroxide was related to the fact that the solution was additionally produced hydroxyl radicals for mineralization process as mentioned by many researchers, **Tang, et al., 2011**.

3.2 The Effect of Initial Fe^{+2} Concentration

The amount of Fe^{+2} used in the experiment is one of the critical parameters, which influences the efficiency of photo-Fenton processes and it plays an important role in the minimization of the amount of H_2O_2 dosage. The effect of initial Fe^{+2} concentrations on photo-Fenton process was tested by carrying out experiments with different concentrations of Fe^{+2} (20, 30 and 40 mg/L). The best H_2O_2 concentration (1300 mg/L) from the previous section was used in these experiments. The pH=3, the furfural concentration=300mg/L and the temperature was maintained at 30^oC through the experiments. From **Fig. 5** it can be observed that the mineralization rate of furfural increased when Fe^{+2} amount was increased from 20 to 30 mg/L, and the removal efficiency increased from 58.17 % to 100% respectively after about 40 min of irradiation time. At 40mg/L Fe^{+2} the removal efficiency was observed to be 71.33% . This finding is in agreement with the previous observation, **Zhang and Yang, 2011**. The negative effect can be explained as: the addition of ferrous ions increases wastewater turbidity during the photo-treatment, which hinders the absorption of the UV light, required for the photo- Fenton process, excess ferrous ions can react with hydroxyl radical decreasing the attack of hydroxyl radical on organic substrates, also excess ferrous ions can react with OH radical producing compound which inhibit reaction rate, **Dincer et al., 2008**.

3.3 Effect of Initial pH

The photo-Fenton reaction is strongly affected by the pH-dependence. The pH value has a decisive effect on the oxidation potential of hydroxyl radical. Therefore, additional set of experiments were performed to determine the most effective initial pH for the furfural decomposition. Different initial solutions at pH 2, 3 and 7 for H_2O_2 initial concentration of 1300 mg/L were examined, keeping the other parameters and dosage constant (Fe^{+2}=30 mg/L, temperature =30°C, irradiation time =60min and furfural concentration =300 mg/L). **Fig. 6** shows that the mineralization of furfural was significantly influenced by the pH value. The removal efficiency increased when pH increases from pH=2 (63.10%) to pH=3 (100%). Then a decreased in the efficiency was noticed at pH=7 (62.5%) after 60min of irradiation time. The best pH, as observed, was 3 which is in agreement with previous studies using photo-Fenton process, **Tony et al., 2012**.

3.4 Effect of the Initial Furfural Concentration

Pollutant concentration is an important parameter in wastewater treatment, for that a set of experiments with different concentrations of furfural 50, 150 and 300 mg/L were performed. The initial concentration of H_2O_2=1100 mg/L, Fe^{+2}=30 mg/L, pH=3, Temp. =30^{o}C and irradiation time=40 min. The results were plotted in **Fig. 7**. As noticed from this figures, the removal efficiency increases as the initial concentration of furfural decreases. A complete mineralization of furfural was reached after 20 min of irradiation time for 50 mg/L furfural concentration, while for 150 mg/L a complete mineralization was achieved after 60 min of irradiation time. For 300 mg/L furfural concentration, 94.22 % removal efficiency was reached only after 60 min of irradiation time. This can be explained as: when the concentration of H_2O_2 was fixed throughout these set of experiments, the OH radical that generate in to the photo-Fenton treatment will be more available to attach the furfural molecules in solution of low concentration. This finding is in agreement with the previous observation of, **Tang et al., 2011**.

4. CONCLUSIONS

The main conclusions that can be drawn from the experimental work of this study are as follows:

1- The results indicated that a complete mineralization for $UV/H_2O_2/Fe^{+2}$ system, for furfural concentration of 300 mg/L, was obtained at H_2O_2 = 1300 mg/L, Fe^{+2} = 30 mg/L, pH = 3, Temp. = 30^{o}C, irradiation time = 60 min.

2- H_2O_2 plays a very important role in the furfural mineralization, high consumption (1300mg/L) of H_2O_2 was required in photo-Fenton system to attain complete mineralization.
3- The best pH value for homogeneous system was found to be equal to 3.

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Table 1. Oxidation potentials of some oxidants in volts compared with the normal hydrogen electrode (NHE, E0 = 0V).

Oxidant	**Oxidation Potential (V)**
Fluorine	3.03
Hydroxyl radical ($HO^\bullet$)	2.80
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Potassium permanganate ($KMnO_4$)	1.68
Chloride dioxide (ClO_2)	1.5
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09

Table 2. List of chemicals used.

Compound	**Formula**	**Vender**	**Assay**
Hydrogen peroxide	H_2O_2	Hopkin and williams	>35 %
Ferrous sulphate	$FeSO_4.7H_2O$	Panreac	99.9 %
Sulfuric acid	H_2SO_4	Riedel-deHaën	97 %
Sodium hydroxide	NaOH	BDH	99%
Acetonitrile HPLC grade	C_2H_3N	Sigma-Aldrich	99.9%

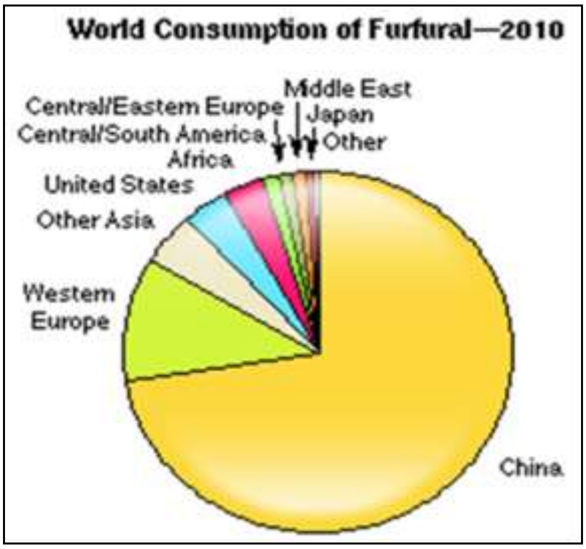

Figure 1. World consumption of furfural at the year 2010.

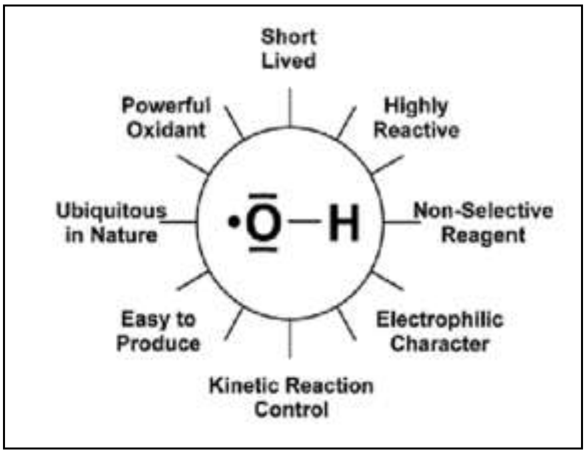

Figure 2. Some characteristics feature of hydroxyl radical.

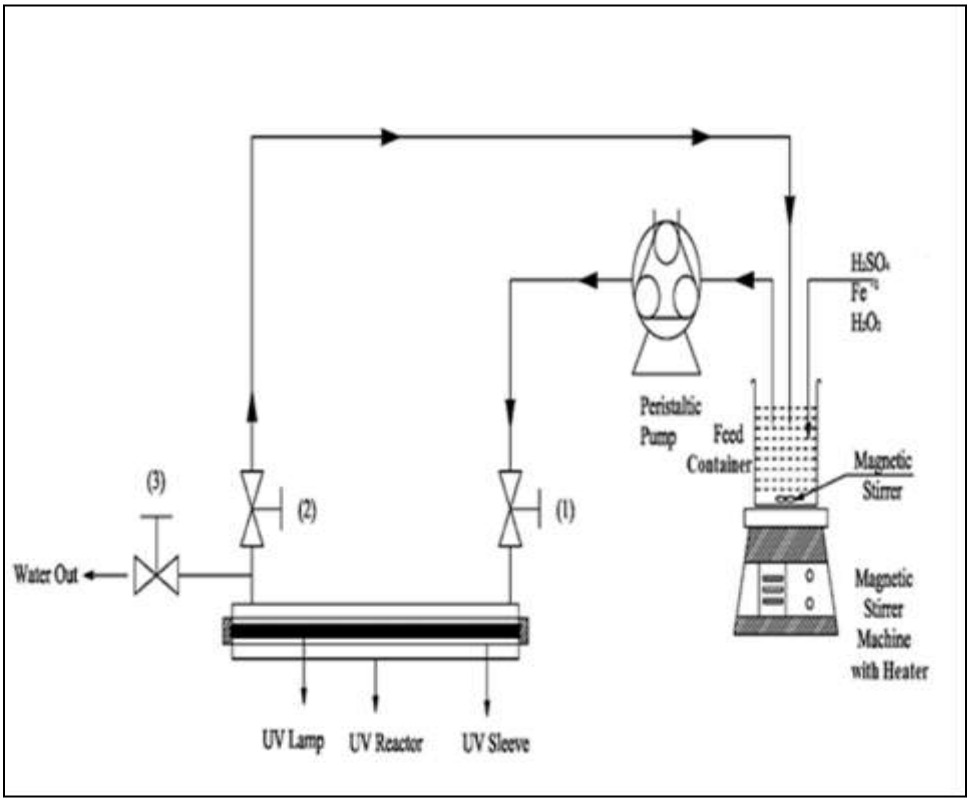

Figure 3. Schematic diagram of AOP system experimental set-up.

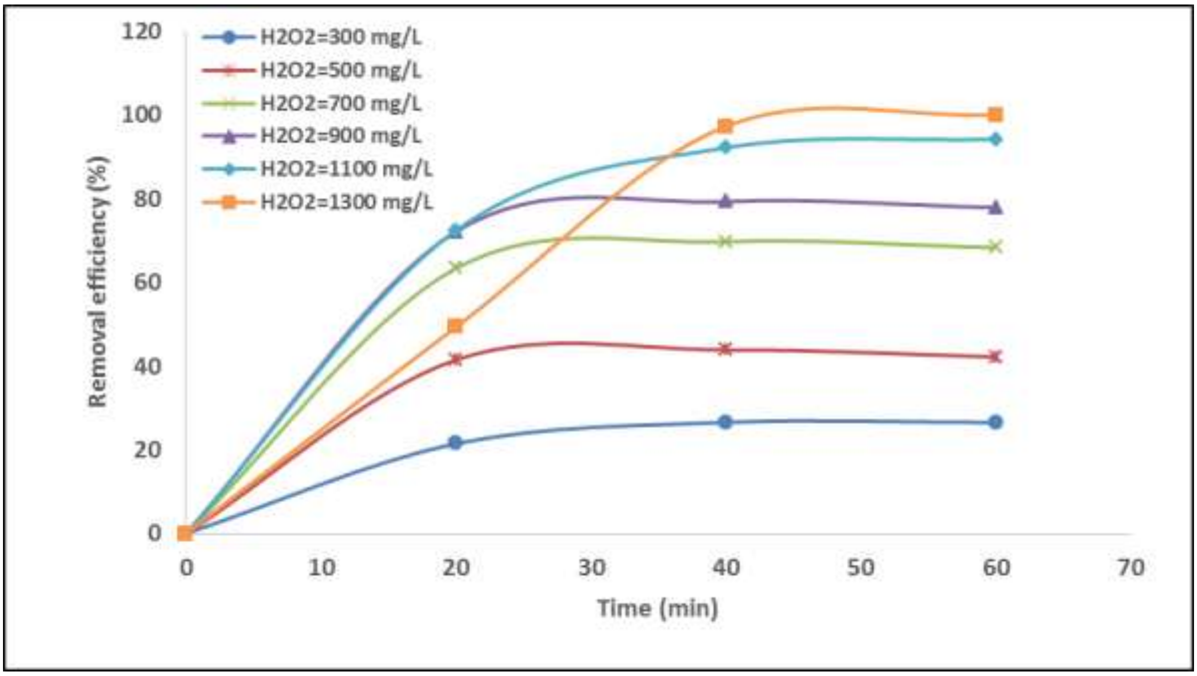

Figure 4. Effect of initial H_2O_2 concentration on the mineralization of furfural by photo-Fenton system at Fe^{+2}=30 mg/L, pH =3, Temp. =30°C and furfural conc. =300mg/L.

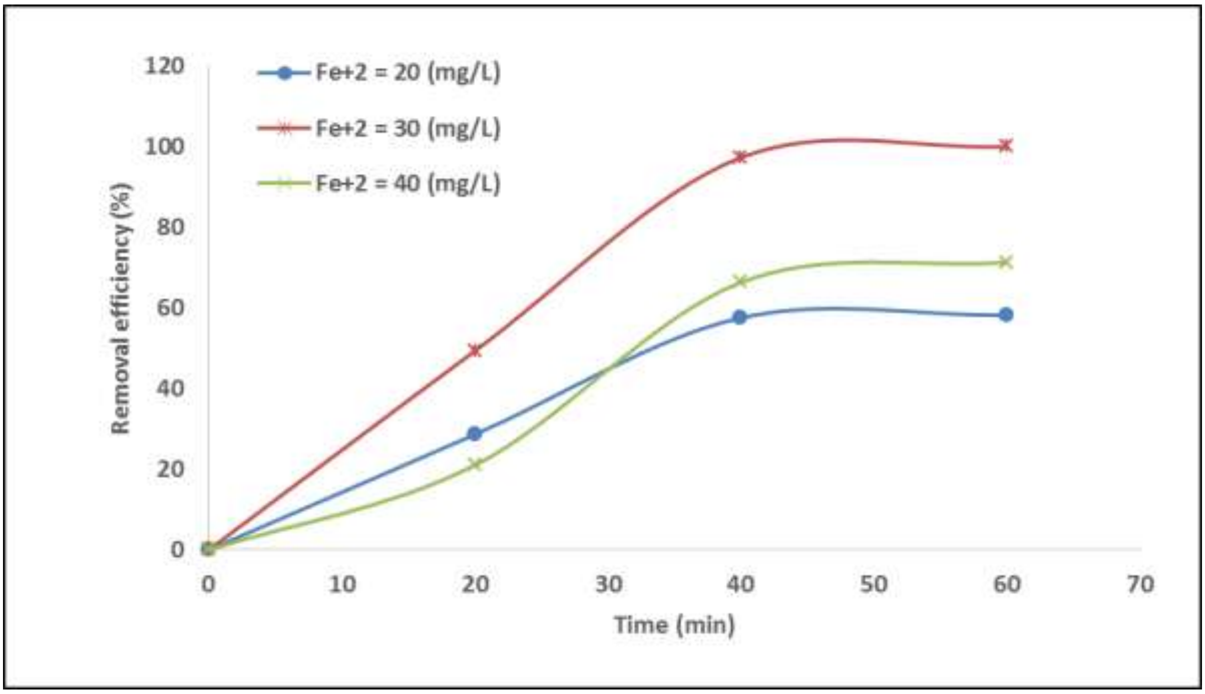

Figure 5. Effect of initial Fe^{+2} concentration on the mineralization of furfural by photo-Fenton system at H_2O_2=1300 mg/L, pH=3, Temp =30°C and furfural conc. = 300 mg/L.

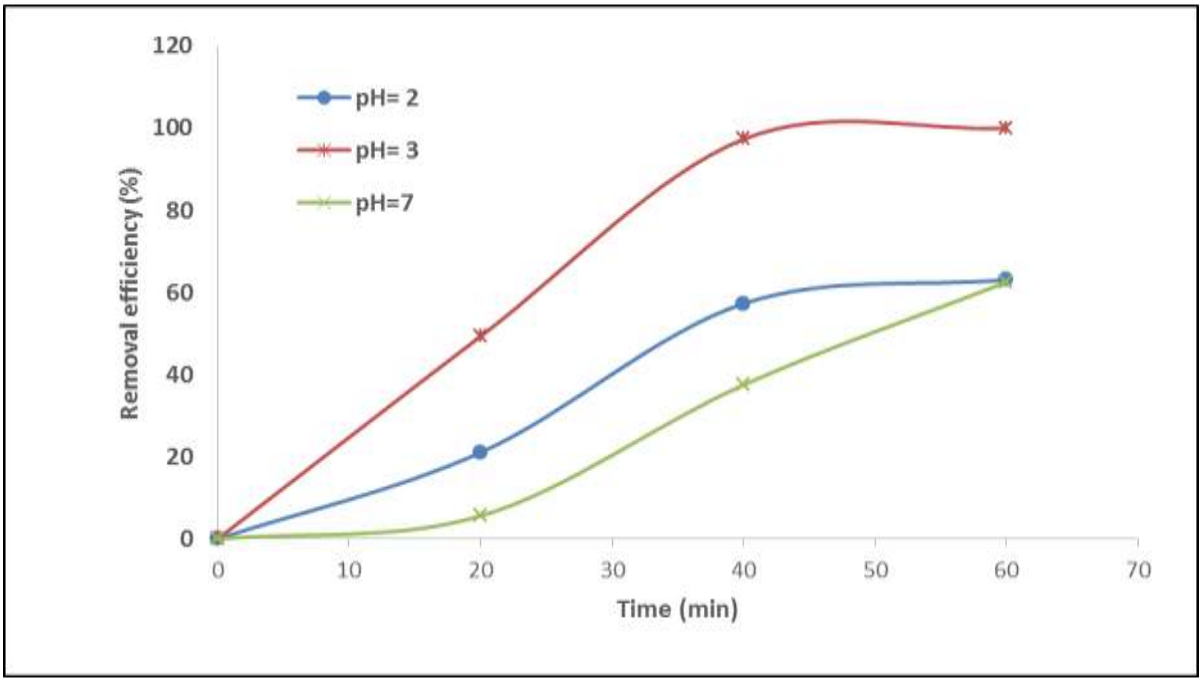

Figure 6. Effect of different pH on mineralization of furfural using photo-Fenton system at H_2O_2=1300 mg/L, Fe^{+2} = 30 mg/L, Temp. =30°C and furfural conc. =300 mg/L.

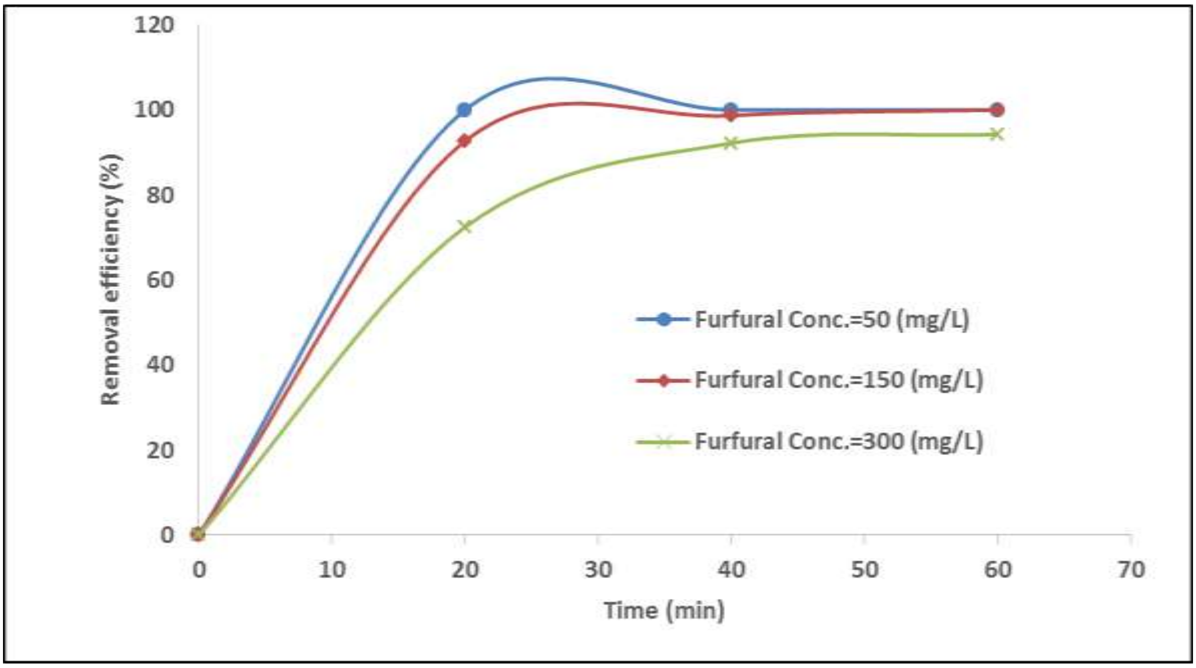

Figure 7. Effect of initial furfural concentrations on the mineralization of furfural by photo-Fenton system at H_2O_2=1100 mg/L, Fe^{+2}=30 mg/L, pH=3 and Temp. = 30^{o}C.