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Comparison of furfural degradation by different photooxidation methods

S.M. Borghei [a], S.N. Hosseini [b,*]

[a] *Department of Chemical Engineering, Sharif University of Technology, Tehran, Iran*
[b] *Department of Environmental Engineering, Islamic Azad University-Hamadan Branch, Hamadan, Iran*

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Abstract

In this paper, the degradation of $C_5H_4O_2$ “Furfural” in aqueous solution by photooxidation technology using UV, UV/H_2O_2, UV/H_2O_2/O_2, UV/H_2O_2/Fe^{2+}, UV/O_2/Fe^{2+}, O_3, UV/O_3 process and also oxidation by sodium hypochlorite was investigated in a lab-scale batch photo-reactor.

To evaluate the performance of different processes, the efficiency of furfural degradation was studied by measuring the total organic carbon (TOC) throughout the experimentation. Results show that compare to other reactions studied in this research, the UV/H_2O_2 is a simple and effective process for furfural degradation and presence of Fe^{2+} ions (UV/H_2O_2/Fe^{2+}) enhanced removal of furfural in solution. The influence of experimental parameters such as hydrogen peroxide dosage, pH, temperature and UV input power on furfural degradation was investigated. The rate of TOC removal was positively affected by UV source intensity. Results indicated that the efficiency of UV/H_2O_2 system improves by increasing the solution temperature. Increasing the temperature of the reactor reduces the concentration of dissolved oxygen but has no significant effect on the rate of furfural degradation. The effect of solution pH is also studied and concluded that pH values near neutrality improves reaction speed.

Keywords: Photooxidation; UV/H_2O_2; Furfural; Oil refinery wastewater; Fenton process

1. Introduction

The release of complex chemicals from petrochemical industries, oil refineries, oil processing and chemical plants into the environment has been considered as a major source of air and water pollution [1,2]. Many of these materials are non-biodegradable or inhibitors for biological systems and often have a toxic effect on life systems. In natural environment they have a long life and are slow to decay and decompose. Some cyclic and aromatic organic compound such as phenols and furfural are good examples. Furfural is an aromatic aldehyde, with the cyclic structure shown in Fig. 1. It is an excellent organic solvent used in oil extraction unit of oil refineries and in petrochemical refining to extract dienes from other hydrocarbons.

Furfural is converted to furfuryl alcohol by enteric bacteria, which can also be formed by hydrolysis of furfuryl alcohol esters [3]. Furfural and the corresponding alcohol are rapidly taken from the gastric tract at doses of 0.1–200 mg/kg body weight and virtually totally excreted mainly in urine within 24 h [4,5].

The application of photo-oxidation techniques for decomposition of complex and heavy molecules have been considered in recent years. This type of reactions consists of the use of UV irradiation, alone, or in combination with other oxidizing agents and mineral catalysts [6–9].

Homogenous and heterogeneous chemical oxidation, photooxidation and photocatalysis have been developed over the last 10 years for efficient detoxification of wastewater, some of these processes, such as silica-modified TiO_2, titania-supported bimetallic catalyst, TiO_2/MgO, are reported as efficient processes to remove various chemical complexes from water and wastewater [10–13]. These methods provide an alternative for filtration, adsorption, reverse osmosis and incineration in environmental cleaning processes, dealing with complex non-biodegradable chemicals. The main objectives of this study were (1) selecting a simple and efficient method for degradation of furfural, (2) to compare the efficiency of different Advanced Oxidation Processes (AOPs) for furfural decomposition, and (3) to determine the effect of experimental parameters such as hydro-

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* Corresponding author. Tel.: +98 261 3400579; fax: +98 831 4240935.
E-mail address: seyyednezam@yahoo.com (S.N. Hosseini).

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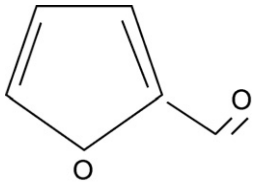

Fig. 1. Configuration of furfural (2-furaldehyde).

gen peroxide dosage, pH, temperature and UV input power on the rate of selected reactions.

2. Materials and methods

2.1. Materials

Chemicals used in this research included: hydrogen peroxide (30%, w/w), sulfuric acid (98%), sodium hydroxide, ferrous sulfate·7H_2O, ethyl alcohol, double distilled aniline, potassium iodide, sodium hypochlorite and sodium chloride. All named chemicals were laboratory grade (Merk Company) and no further treatment was required other than dilution to required level. Furfural (molecular formula, $C_2H_4O_2$; molecular weight, 96.09 g mol^{-1}; characteristic, 254 nm; LD_{50}, 65 mg/kg; bp (11 Torr), 54–56 °C; density, 1.159 g mL^{-1}) was used for experimentation and standardization of industrial grade, obtained from Tehran oil refinery.

2.2. Determination of furfural concentration

Samples taken from the effluent of oil extraction unit of Tehran refinery were analyzed for measuring the furfural concentration according to the following procedure. Fifteen millilitres of ethyl alcohol (50%) was added to 5 mL of wastewater and mixed completely. Then 0.5 mL of double distilled aniline and 5–10 drop of hydrochloric acid were added. After 5–10 min light absorbance was measured at 240 nm by spectrophotometer (UV/VIS spectrometer-Lambda from PERKIN ELMER). The results were compared with the standard furfural curves and so the concentration of furfural in wastewater was determined. According to average concentration of the samples obtained from oil refinery effluent, the synthetic sample with furfural concentration of 390 mg/L (4.06 mM) was made and used throughout the experimentations.

Quantitative determination of BOD_5, COD, TSS, TOC, sulfide, phenol and oil and grease were carried out according to standard methods [14].

Due to the fact that furfural was the main component in the samples taken from oil extraction unit effluents a direct correlation between furfural concentration and total organic carbon (TOC) of the samples existed. Therefore, the results of the efficiency of reactions are presented in terms of percent TOC converted, measured by TOC analyzer (ROSEMOUNT DC-190).

2.3. Pilot plant reactor

Experimental reactor included a pyrex (outer) and two quartz (inner) cells of 100 mL capacity. A medium pressure mercury UV lamp (OSRAM) was placed in the center of quartz cell in the photo-reactor (Fig. 2) and cooling water was introduced to the annulus, surrounding the lamp for cooling and maintaining a constant temperature during experiment.

Known quantity of synthetic wastewater with known concentration of furfural was injected into the reactor. Samples

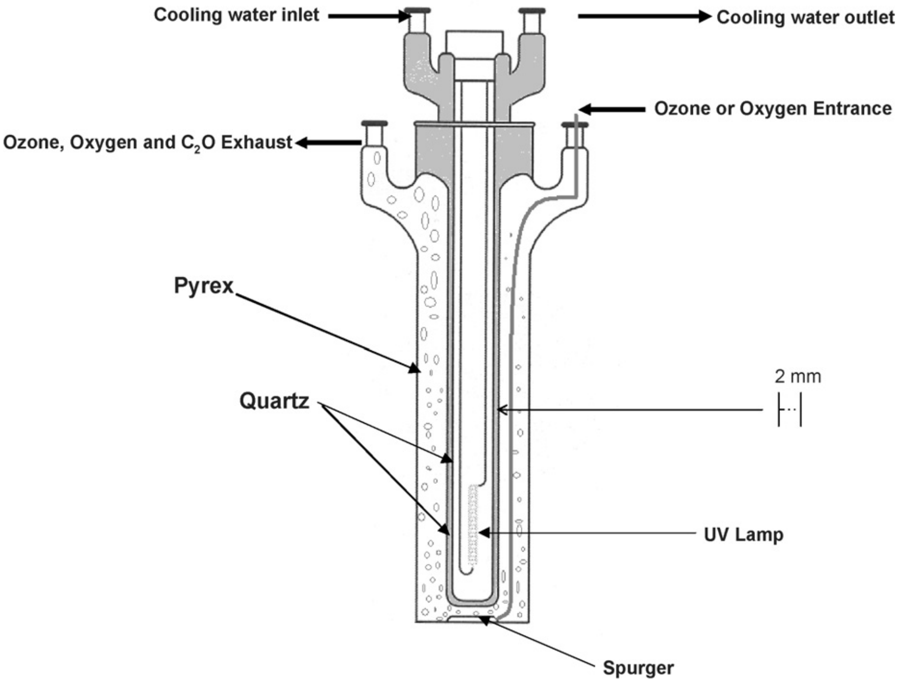

Fig. 2. The schematic of photo-reactor.

Table 1
Average characteristics of oil refinery effluent

Parameter (mg/L)	Range	Average
BOD_5	50–210	130
COD	250–510	380
TOC	90–245	182.5
TSS	155–230	192.5
Sulfide	6–15	10.5
Phenol	0.001–3	1.5
Furfural	250–900	575
Oil and Greases	50–370	210

were withdrawn from the photo-reactor for analysis at certain intervals.

3. Results and discussion

To determine the characteristics of the real wastewater, samples were taken from the effluent canal of the oil extraction unit of Tehran oil refinery over a 6 months period from December 2004 until July 2005.

In-plant studies showed that the main organic pollutant in this effluent is “Furfural” contributing to BOD_5, COD, and TOC of the discharged wastewater. All samples were degreased before analysis. Table 1 shows the wastewater characteristics of extraction unit of oil refinery.

The photooxidation of furfural, was investigated under different conditions and the results of furfural decomposition by reactions of UV, UV/H_2O_2, UV/H_2O_2/O_2, UV/H_2O_2/Fe^{2+}, UV/O_2/Fe^{2+}, O_3, UV/O_3, O_3/H_2O_2 and oxidation by active chlorine are summarized in Figs. 3 and 4.

The first set of experimentation was carried out by placing furfural solution exposed to UV irradiation alone in the absence of any oxidant and degradation of furfural (reduction in TOC) was studied. The removal of TOC under direct photolysis was found to be only 8.8% after 110 min of UV exposure (Fig. 3). Results show slow rate of oxidation of furfural, indicating very low capability of UV light in activating the organic molecule into more reactive radical species, which are responsible for further destruction process [15]. In direct photolysis, organic molecules become excited on absorption of UV photons. A large number of electronically excited organic molecules could transfer an electron to an acceptor present in its complex environment to form free radical ions. These active ions with subsequent recombination or hydrolysis form radicals ($C^\bullet$) which react with oxygen to form peroxy radicals, and on further photolysis are converted to partially oxidized intermediates [16].

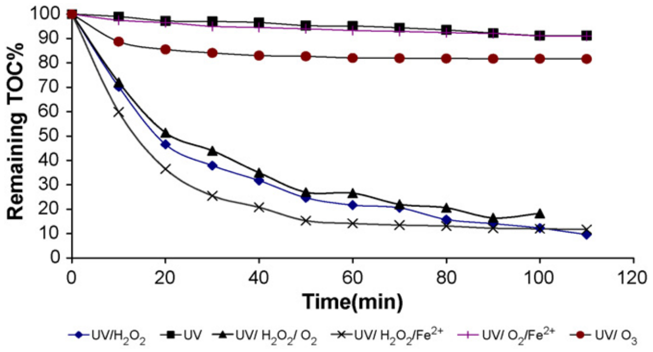

Fig. 3. TOC removal efficiency by photooxidation methods. Initial TOC 243 mg L^{-1}; pH 7.4; UV lamp electrical power 125 W; temperature 25 °C.

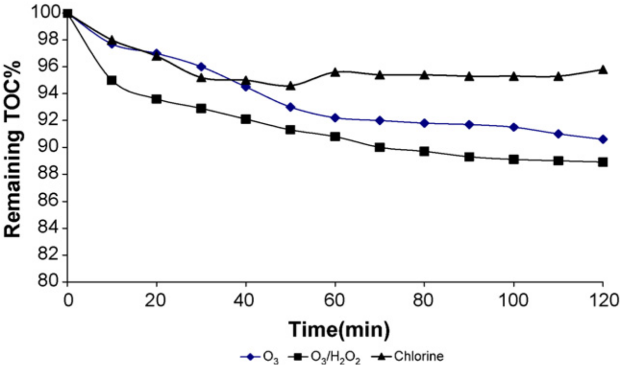

Fig. 4. TOC removal efficiency by chemical oxidation. Initial TOC 243 mg l^{-1}; pH 7.4; UV lamp electrical power 125 W; temperature 25 °C.

UV light may attack certain molecules by bond cleavage and free radical generation at a much lower rate than the UV/oxidant combination. Hence due to very low efficiency, this mode of photo-degradation was not extensively studied further. The main dominant reactions with UV system are as following:

$$R \xrightarrow{h\nu} R^* \tag{1}$$

$$R^* + O_2 \xrightarrow{h\nu} R^{\bullet +} + O_2{}^{\bullet -} \tag{2}$$

$$R^\bullet + O_2 \xrightarrow{h\nu} RO_2{}^\bullet \tag{3}$$

$$RO_2{}^\bullet \xrightarrow{h\nu} \text{Partially oxidizing intermediates} \tag{4}$$

here R is an organic compound in the solution as pollutant.

The second series of experimentation was carried out with hydrogen peroxide at 100 mM concentration used with a125 W medium pressure mercury lamp as a UV source for evaluation of photo-degradation behavior of furfural in the UV/H_2O_2 system. TOC reduction of furfural solution is shown in Fig. 3. Results show that degradation of furfural was much faster when UV alone was tested. TOC removal under photo-peroxide system was 90.4% after 110 min.

When the UV radiation is combined with a powerful oxidant, such as hydrogen peroxide the degradation of furfural is significantly enhanced due to $OH^\bullet$ radical production caused by photolysis of H_2O_2 [8]. ($OH^\bullet$) radical is one of the most reactive free radicals and is the strongest oxidant after fluoride [17]. Hydroxyl free radicals can abstract hydrogen atoms from any organic molecule, or add to any C=C double bond or accept an electron (electron transfer) producing a wide spectrum of products [18].

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet \tag{5}$$

$$HRH + OH^\bullet \xrightarrow{h\nu} RH^\bullet + H_2O \tag{6}$$

Depending on H_2O_2 concentration the following reaction may take place too

$$OH^{\bullet} + OH^{\bullet} \xrightarrow{h\nu} H_2O_2 \tag{7}$$

$$H_2O_2 + OH^{\bullet} \xrightarrow{h\nu} H_2O + HO_2{}^{\bullet} \tag{8}$$

$$HO_2{}^{\bullet} + OH^{\bullet} \xrightarrow{h\nu} H_2O + O_2 \tag{9}$$

The experimentations were continued to determine the effect of O_2 gas injection on efficiency of UV/H_2O_2 process by adding excess oxygen to photo-reactor, at flow rate of 50 L/h. Results show that the efficiency and the speed of this reaction is less than UV/H_2O_2 reactions. The reason of this phenomenon may be related to oxygen bubbles acting as a barrier of UV light inhibiting hydrogen peroxide molecular activity. It could also be attributed to reduction of H_2O_2 solubility in water due to presence of oxygen.

At next set of experimentation, the decomposition of furfural was explored by means of the very reactive and oxidizing hydroxyl radicals, which are generated by the Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions simultaneously, according to the reactions (5), (6), (10) and (11). Fenton reagent was prepared by mixing 1 mL of H_2O_2 (30%) and 2 mL of $FeSO_4$ (57 mM). The mixture was added to 97 mL of wastewater containing furfural in the reactor. After 110 min TOC was reduced to 11.7% of its original value (88.3% reduction in TOC) and 7 min was necessary for total disappearance of furfural color.

Obviously, in the photo-Fenton system the reactions (5), (10) and (11) are participating simultaneously in production of $OH^{\bullet}$ radicals. Therefore, there is a synergic effect of different reactions generating $OH^{\bullet}$ radicals and also $HO_2{}^{\bullet}$ anion production (reaction (10)), which enhances the efficiency of photo-Fenton system. $HO_2{}^{\bullet}$ anion would act as a hydroxyl radical scavenger in solution [19]. Even the photolysis of Fe(III)-organic intermediate quelates and $[FeOOH]^{2+}$ has been reported to contribute to this enhancement [20].

$$\begin{aligned} Fe^{2+} + H_2O_2 &\xrightarrow{h\nu} Fe^{3+} + OH^{\bullet} + OH^{-}/Fe^{3+} + H_2O_2 \\ &\rightarrow Fe^{2+} + H^{+} + HO_2{}^{\bullet} \end{aligned} \tag{10}$$

$$Fe(OH)^{2+} + h\nu \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet} \tag{11}$$

$$\begin{aligned} Fe^{2+} + H_2O_2 &\xrightarrow{h\nu} Fe^{3+} + OH^{\bullet} + OH^{-}/Fe^{3+} + H_2O \\ &\rightarrow Fe^{2+} + H^{+} + OH^{\bullet} \end{aligned} \tag{12}$$

Comparing the results obtained from the UV/H_2O_2 and $UV/H_2O_2/Fe^{2+}$ processes, it was found that the rate of TOC reduction in $UV/H_2O_2/Fe^{2+}$ process is faster. Remaining TOC reached to 20.6% of its initial value after 40 min, while in the former system (UV/H_2O_2) a further 30 min of reaction time is needed to reach the same stage. However, the final efficiency of furfural degradation (shown as TOC and after 110 min) is slightly higher at slower reaction rate, when UV/H_2O_2 is used (see Table 2).

To investigate the effect of direct photochemical reactions in the photo-Fenton system, the next experiment was performed by substitution of hydrogen peroxide by oxygen ($UV/O_2/Fe^{2+}$). Two millilitres of ferrous sulfate solution $FeSO_4{\cdot}7H_2O$ (57 mM) was added to 98 mL of wastewater containing 244 mg/L furfural aerated at a rate of 0.83 L/min (50 L/h) at 25 °C. Results of this reaction are shown in Table 2, indicating there is no significant reduction of wastewater's TOC after 100 min of reaction time. Visual observations also showed there was no significant change in the color of the solution during the test period. These results prove that Fe^{2+} ions without H_2O_2 do not produce radicals in reasonable concentration, therefore the decomposition of furfural do not take place as shown by results of remaining TOC in the solution.

In a following step, a degradation experiment of furfural by ozone as a highly oxidizing agent was investigated. In this experiment, 2 g/h of O_3 was generated by ozone generator apparatus (FISCHER-Type 302.00) and conducted into the batch photo-reactor without application of UV radiation. In this system, the decomposition of ozone, which initiated by the action of hydroxide ions [21,22], is too low and consequently the formation of hydroxyl radicals is limited. This decomposition of organic compounds by ozone can be represented by a single reaction as following

$$R + O_3 \rightarrow R_{oxide} \tag{13}$$

There was no change of color after 2 h of diffusing ozone into the solution and the TOC analyses showed very slight change in

Table 2

TOC removal by UV, UV/H_2O_2, $UV/H_2O_2/O_2$, $UV/H_2O_2/Fe_2{}^+$, $UV/O_2/Fe_2{}^+$, O_3, UV/O_3 process and NaClO reactions

Parameters														
Process						TOC% remained								pH_f
UV	100	–	97.2	97	96.6	95.3	95.1	94.4	93.5	92.2	91.2	91.2	–	6.5
UV/H_2O_2	100	70.2	46.6	37.9	31.8	24.7	21.7	20.6	15.8	16.1	12.3	9.6	–	5.2
$UV/H_2O_2/O_2$	100	–	51.4	–	41.4	–	26.6	–	20.6	–	18.3	18.1	–	6.3
$UV/H_2O_2/Fe^{2+}$	100	59.9	36.5	–	20.8	–	14.2	13.5	–	12.2	–	11.7	–	5.3
$UV/O_2/Fe^{2+}$	100	–	96.5	–	94.5	–	93.3	–	92.4	–	91.1	–	–	6.5
O_3	100	97.7	–	–	93	–	92.2	–	–	91.7	–	–	90.6	6.5
UV/O_3	100	88.7	85.5	84.1	–	82.7	–	81.9	–	81.7	–	–	81.5	6.5
NaClO	100	–	95.2	–	94.6	–	95.6	–	–	95.3	–	–	95.8	6.5
Time (min)	0	10	20	30	40	50	60	70	80	90	100	110	120	

TOC = 244 mg/L; UV lamp electrical power = 125 W; pH_0 7.4, T = 25 °C.

that period. The results tabulated in Table 2, shows TOC removal after 2 h is only 9.4%.

In a further experiment, the furfural degradation was tested by combination of UV radiation and ozone (UV/O_3). It was observed that this combined process accelerates the decomposition rate of furfural as can be expected compare to ozonation alone. Results shown in Table 2, indicates that the rate of degradation is much faster initially but no significant progress is made as the reaction goes on. After 60 min the reaction reaches some sort of equilibrium and the concentration of TOC stays at 79% of its original value.

Low TOC reduction rate might indicate depletion of H_2O_2 produced from reaction (14) or formation of compounds resistant to the oxidative processes or presence of intermediate products competing for the produced $HO^\bullet$ radicals.

This enhancement in the degradation rate (compare to ozonation alone) can be explained by considering the reaction that occurs in this system. Ozone absorbs UV radiation and produces hydrogen peroxide

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2 \qquad (14)$$

Then photolysis of hydrogen peroxide to generate hydroxyl radicals shown in reaction (5), takes place. In addition, hydrogen peroxide accelerates the ozone decomposition ion to $OH^\bullet$ radicals [22]. Therefore, radicals constitute an important active intermediate in the photolytic ozonation process which attack the organic compound R according to the reaction (13). The contribution of radical pathway in O_3/UV process explains the increase in the rate of furfural degradation at the early stages of the reaction.

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \qquad (15)$$

Oxidation by active chlorine constituted the next set of experimentation. Chlorine is a powerful oxidizing agent and is used for decomposition of some water pollutants such as cyanides and complex organics (dyes and coloring agents) [23]. The chlorine oxidation of furfural was investigated by addition of 10 mL sodium hypochlorite (5% active chlorine) to 50 mL wastewater at pH 9.57. Results of oxidation are shown in Table 2 indicating that chlorine has not any significant effect on furfural decomposition. Although the color of furfural in the solution disappeared completely in 5 min, but total organic carbon (TOC) of the solution was not affected.

The chlorination of wastewater was carried out in comparison with other photo-oxidation and other conventional oxidation methods used in this study. When applicable, the advantage of chlorination includes low operational cost, ease of application and availability of chlorine in many different forms. The disadvantage of this method is the presence of remaining active chlorine as a polluting substance and the possibility of THM (trihalomethane) formation, a well known carcinogenic compound.

3.1. *Effect of the H_2O_2 concentration on UV/H_2O_2 process*

Since UV/H_2O_2 reactions proved to be highly efficient in furfural decomposition, further experiments were carried out on this process. The initial concentration of H_2O_2 plays a very important role for generation of hydroxyl radicals in degradation of organic compounds. TOC reduction by UV/H_2O_2 process under various H_2O_2 concentrations including 0, 25, 50, 75, 100, 200 and 300 mM at different irradiation times are shown in Fig. 5. The observed pseudo-first order rate constants of reactions were plotted against concentrations of H_2O_2 shown in Fig. 6. The TOC removal efficiency at irradiation time of 60 min without hydrogen peroxide addition was only 4.9% and the observed first order rate constant was 0.0009 min^{-1}. The decomposition reaction of UV/hydrogen peroxide was extremely powerful compare to direct photolysis reaction. The increase in degradation rate follows a polynomial order of two by H_2O_2 concentrations. As the molar ratio of hydrogen peroxide to pollutant was increased, more hydroxyl radicals were available to attack the aromatic structure and the rate of reaction was increased. Beyond 200 mM, further addition of H_2O_2 slightly retarded the reaction rate due to the production of hydroperoxyl radicals when excess hydrogen peroxide is used. These hydroperoxyl radicals are much less reactive and do not appear to contribute to the oxidative degradation of organic substrate [16].

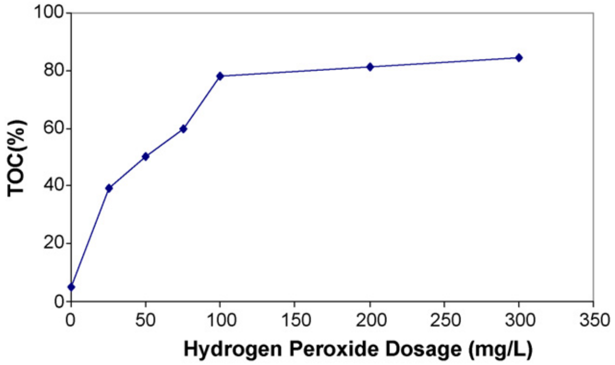

Fig. 5. TOC removal efficiency vs. hydrogen peroxide dosage by UV/H_2O_2 process. $[H_2O_2]_0$ = 0, 25, 50, 75, 100, 200 and 300 mM; UV lamp electrical power 125 W; initial pH 7.4; initial TOC 243.3 mg/L.

3.2. *Effect of UV source electrical power*

The effect of UV source electrical power on the decomposition of furfural with three different lamps including 125 W, 80 W

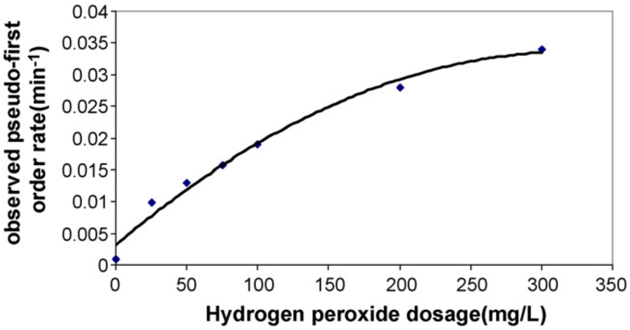

Fig. 6. Observed pseudo-first order rate vs. hydrogen peroxide dosage by UV/H_2O_2 process. $[H_2O_2]_0$ = 0, 25, 50, 75, 100, 200 and 300 mM; UV lamp electrical power 125 W; initial pH 7.4; initial TOC 243.3 mg/L.

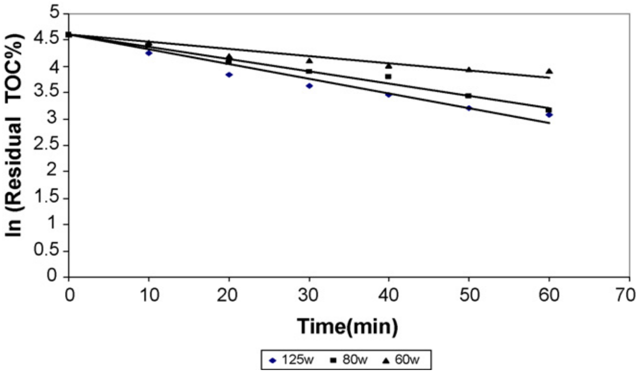

Fig. 7. Observed rate constant in UV/H_2O_2 process affected by different UV intensity. $[H_2O_2]_0 = 100$ mM; UV lamp electrical power 60, 80 and 125 W; initial pH 7.4; initial TOC 243.3 mg/L.

and 60 W by UV/H_2O_2 process was investigated, as shown in Fig. 7. Results show there is a significant relation between UV intensity and observed pseudo-first order rate constant of furfural degradation.

UV irradiation energy is absorbed by hydrogen peroxide molecules and generates the hydroxyl radicals. The magnitude of this energy is related to the amount of photons released so it is directly affected by UV intensity. The more reactive hydroxyl radical can react more readily with the pollutants molecules. TOC removal increased when electrical power of UV source was increased from 600 to 1250 W/L of polluted wastewater. The observed pseudo-first order rates for 60, 80 and 125 W lamps were obtained as 0.014, 0.023 and 0.028 min^{-1}, respectively. When UV intensity was doubled from 60 to 125 W, the first order rate constant was increased by a factor of 2. But when the UV intensity was changed from 80 to 125 W (1.56 times), the rate constant increased only by a factor of 1.2. While the UV intensity increased from 60 to 80 W (1.3 times), rate constant changed 1.65 times. Results show that at UV intensity higher than 120 W, only slight improvement in decomposition efficiency of furfural is observed indicating that the photons provided in the reaction may be too excessive.

3.3. *Influence of temperature on photo-oxidation of furfural in the UV/H_2O_2 process*

The influence of reaction temperature on the degradation of organic pollutants in aqueous solutions by UV/H_2O_2 process has been investigated by many researchers. While some have found that the solution temperature played a very important role in increasing the rate constant and subsequently the degradation of pollutants [16], others have suggested the rate of change is not very significant within the short range of experimental temperatures [24]. In this experiment, the efficiency of furfural decomposition by UV/H_2O_2 process was carried out at temperatures of 25, 40 and 60 °C. The observed pseudo-first order rate constants of reactions were calculated by linear regression that was plotted against time for different temperatures in Fig. 8. As it is seen, the influence of temperature is significant at 25–40 °C resulting in rate constant increase from 0.019 to 0.027 min^{-1}, while temperature increase from 40 to 60 °C increased the rate constant 7% only, from 0.027 to 0.029 min^{-1}. Higher temperatures adversely affect the activity of hydrogen peroxide and lowers free radical formation.

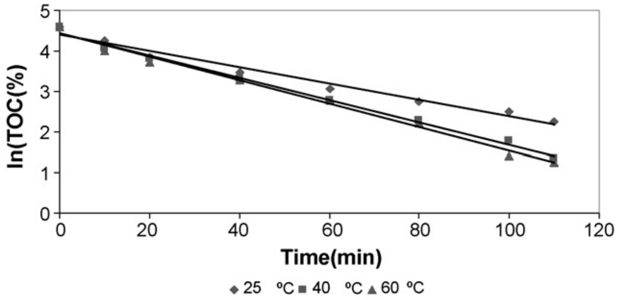

Fig. 8. The influence of temperature on the efficiency of furfural degradation by UV/H_2O_2 process. $[H_2O_2]_0 = 100$ mM; initial TOC = 234.4 mg/L; initial pH 7.4.

3.4. *Effect of pH*

It is well known that the reactions involving ionic solutions are pH dependent. In UV/H_2O_2 process, hydroxyl radical generation capacity is affected by pH [25,26]. The reactivity of H_2O_2 depends on the pH of the medium. Therefore, additional set of experiments was performed to determine the most effective initial pH for the furfural decomposition. The experiments conducted to study the effect of pH on TOC reduction in different initial solution at pH 3, 5, 7, 9 and 11 in the UV/H_2O_2 process during 60 min of irradiation time. The furfural solutions were adjusted to the desired pH with the addition of 0.1N sulfuric acid and/or 0.1N sodium hydroxide. Results presented in Fig. 9, show degradation increased with the increase in the pH value, from 70.3% TOC removal at pH 3, to 76.5% TOC removal at pH 7. With a further increase in the pH value, TOC removal was decreased to 72% at pH 11. The constant decrease in the TOC removal in high alkaline medium is due to the formation of oxidizing species such as hydroperoxy anions. This anion reacts with OH radical and residual H_2O_2 decreasing hydoxyl radicals and consequently the rate of reaction [26].

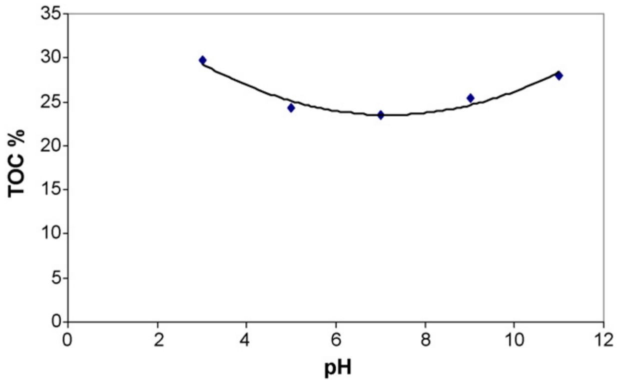

Fig. 9. Effect of pH on the UV/H_2O_2 process efficiency. $[H_2O_2]_0 = 100$ mM; initial TOC = 234.4 mg/L; temperature 25 °C.

4. Conclusions

In this study the effect of common chemical oxidation processes, with and without UV irradiation, on decomposition of furfural which is a well-known pollutant in oil industry wastewaters were compared. Result shows that UV irradiation process, where no oxidants are present, has little effect on decomposition of furfural. Ozone and sodium hypochlorite reactions without UV irradiation had also minimal effect on decomposition of furfural. Best results were obtained when UV was used in combination with hydrogen peroxide. Under the experimental conditions peroxide releases hydroxyl radicals which are powerful intermediates for destruction of furfural in solution. Addition of oxygen to the UV/H_2O_2 had a negative effect on reaction progress as oxygen slowed the reaction rate due to reduction of activity of peroxide. When ferrous ions were applied to the furfural solution as used in Fenton type reactions, Fe_2^+ ions without H_2O_2 did not produce radicals in reasonable concentration to affect the rate of reaction. However, in combination with UV and peroxide as in UV/H_2O_2/Fe^{2+} reactions, the speed of reaction was increased but the final efficiency was slightly less than UV/H_2O_2 process. This study demonstrated that TOC removal efficiency in the UV/H_2O_2/Fe^{2+} process is higher in comparison with UV/H_2O_2/O_2 process, especially in the early stages of reaction when concentration of reactants is high. The main problem in the UV/O_3 process is low solubility of O_3 in water and poor mass transfer rate resulting in failure of ozone to degrade furfural. Application of O_3, active chlorine, UV/O_2/Fe^{2+} process and UV irradiation alone has insignificant effect on the decomposition of furfural.

The best result for degradation of furfural was obtained in UV/H_2O_2 reaction. The reaction follows a first order rate kinetics where the rate constant is function of UV light intensity. Results showed that furfural decomposition efficiency was increased with increasing the spectral power of UV light source. The effect of temperature on the efficiency of degradation of furfural in UV/H_2O_2 reaction is only visible at 20–40 °C range and higher temperatures have little effect. The same reaction is faster under acidic condition while alkaline pH values have a negative impact on reaction progress.

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