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Furfural Degradation in Waste Water by Advanced Oxidation Process Using UV/H_2O_2

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Abstract

Furfural is one of the one of pollutants in refinery industrial wastewaters. In this study advanced oxidation process using UV/H_2O_2 was investigated for furfural degradation in synthetic wastewater. The results from the experimental work showed that the degradation of furfural decreases as its concentration increases, reaching 100% at 50mg/l furfural concentration and increasing the concentration of H_2O_2 from 250 to 500 mg/l increased furfural removal from 40 to 60%.The degradation of furfural reached 100% after 90 min exposure time using two UV lamps, where it reached 60% using one lamp after 240 min exposure time. The rate of furfural degradation k increased at the pH and initial concentration of furfural decreased, but different H_2O_2concentrations indicated no significant effects on the reaction rate. UV/H_2O_2 process is effective for furfural degradation in wastewater at neutral pH where the disposal of such effluents will be within the environmental limitations.

Key Words: Furfural, UV/H_2O_2, Degradation, AOP.

Introduction

Today water pollution is one of the most important environmental problems in the world. Industrial wastewaters containing toxic chemicals are the main sources for such problems. Petroleum refinery effluents are priority pollutants due to their high polycyclic aromatics content, which are toxic. They encompass a wide range of contaminants at varied concentrations that are harmful. Large amounts of water are used in petroleum refinery and significant volumes of wastewater are generated (0.4 – 1.6 times the amount of the crude oil processed) which need to be treated before disposal to water bodies [1, 2].

Among these contaminants found in petroleum refinery effluents is a compound known as furfural. Furfural is a toxic aromatic aldehyde with the chemical formula C_4H_3OCHO. It is pale yellow or colorless oily liquid and turns into brown or red in the presence of air or light [3, 4]. Furfural production is from a mixture of plant raw material (i.e corn seed hulls, cane bagasso and residues of olive extraction) with dilute sulfuric acid (acidic hydrolyaztion).Furfural is then recovered by steam distillation and fractionation with (98-99) % purity [5].

The main use of furfural is in the form of feed stock for furfural alcohol (FFA) this is used as an input for furan resin that is used for foundry binders[6]. Furfural and FFA are consumed by chemical industries as intermediate products such as nylons, lubricants and solvents, adhesives, medicines, plastics, urea furan resin synthesis; precision casts and dies [6]. Furfural is used as a solvent which has a high capability for separation of multi- components especially in the petroleum industry to separate sulfur and carbonaceous compounds [3].

Acute health effects (short-term) may occur shortly after exposure to furfural which may irritate the skin and eyes. Breathing furfural may irritate the nose and throat, also the lungs causing coughing and/ or shortness of breath. Higher exposure can cause fluid buildup in the lungs. High concentrations of furfural may cause the person to be dizzy, light headed and to pass out. The chronic health effects (long-term) may occur at some time after exposure to furfural and can last for months or years. This may cause skin itching and skin rash (skin allergy). Repeated exposure may cause loss in taste sense, numbness of the tongue, headache, tiredness, itchy throat, watery eyes and also may cause liver damage [4, 6, 7].Furfural is a very slow biodegradable material (27X 10^{-7} g/g biomass) which means that it has significant effects on the aquatic life and fishes [8].

The presence of furfural increase the toxicity of industrial effluents and its removal may be difficult or impossible by conventional treatment processes used in most industries. Many technologies have been developed to treat effluents containing furfural. Basheer et al., (2011) reviewed that petroleum refinery effluents were treated by coagulation, chemical oxidation, adsorption, biological techniques, membrane filtration and catalytic wet air oxidation [1]. Belay et al. (1997) investigated the metabolism of furfural by Methanococcus delta under anaerobic conditions; the results showed the ability of these micro organisms to transfer furfural to furfural alcohol [8]. Hassan et al. (2012) used activated sludge to provide micro organisms for furfural degradation [3]. Sulaymon and Abood, (2005) tested adsorption of furfural onto activated carbon [9], where Ghazi, (2012) used agricultural waste for furfural adsorption [6]. Sulaymon and Hayfa, (2014) used activated carbon and dead micro organisms from anaerobic sludge for adsorption/biosorption of furfural [10]. All these methods transfer the contaminants from one media to another therefore a second treatment process is required to eliminate these contaminants.

Several solutions have been proposed and compared with these traditional methods. In recent years the application of photo catalysis technique in wastewater treatment was tested. These techniques are known as advance oxidation processes (AOPs) which can completely degrade organic pollutants into harmless inorganic substances like CO_2 and H_2O under moderate conditions [2]. These processes are widely used in the decomposing of organic products in industrial wastewater and groundwater owing to their complete mineralization, produce no sludge, high reaction rates and operate under ambient temperature and pressure conditions [1, 8, 11, 12, 13].

AOPs are defined as potential processes that are capable of producing hydroxyl radicals ($^{\bullet}OH$), which are extraordinary reactive oxidations (oxidation potential 2.8 V) in sufficient quantity for mineralizing a majority of complex organic materials to carbon dioxide, water and inorganic ions. Majority of AOP processes like cavitation, photo catalytic oxidation and Fenton chemistry are performed by applying various combinations of homogeneous photo Fenton (Fe III), Ozone and TiO_2 such as UV/O_3, UV/H_2O_2, $UV/H_2O_2/O_3$, O_3/TiO_2, $TiO_2/H_2O_2/O_3$ and more. These combinations use energy to produce highly reactive intermediaries with high oxidation or reduction potential. The hydroxyl radicals may be obtained from powerful oxidants, such as H_2O_2 and O_3, combined with irradiation.[2,13, 14, 15]. Basheer et al. (2011) summarized several treatment producers for petroleum refinery effluents using AOPs; it was observed that the reduction in COD and DOC may reach 90% [1]. Kang et al. (2009) used UV/O_3 for the degradation of furfural wastewater. They achieved complete degradation within 3 hr under optimum conditions [13]. Nevak (2010) applied $Fe(III)/H_2O_2$/solar-UV process to petrochemical refinery wastewater, the reduction in COD reached 49% after 8 hr of exposure to solar radiation [2].

The objective of this study is to describe experimentally the feasibility of furfural removal from synthetic wastewater by UV/H_2O_2technology under different operational conditions, Furfural initial concentration, H_2O_2 dosage, number of UV lamps used and pH of the solution.

Experimental Work

Synthetic wastewater containing different concentrations of furfural was tested by UV/H_2O_2technology under different operational conditions in a photo reactor.

1- Materials

A. Furfural (C_4H_3OCHO) has a chemical structure shown in Fig. (1), of molecular weight 96.06 gm/mol, has synonyms of 2-furaldehycle, Furyl and 2 Furyl methanol [7].The physical properties of furfural are listed in Table (1).

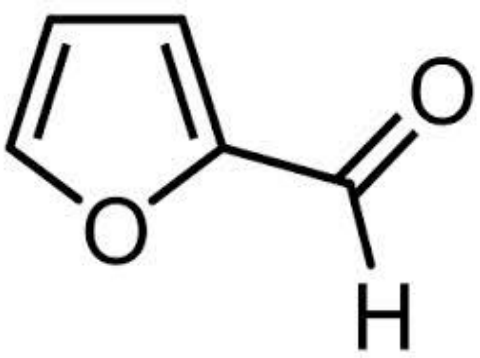

Fig. 1, Chemical structure of furfural [9]

Table (1), Recorded Physical properties of Furfural [9]

Color	Colorless to yellow and red-brown when exposure to light and air
Odor	Aromatic odor as benzaldehyde
Specific gravity 20°C	1.1598
Flash point, open cup °C	68.3
Heat of vaporization (kcal/mol) at 160 °C	9.22
Heat of combustion (kcal/mol)	560.2
Lower explosive limit in air at (125°C) vol.%	2.1%
Ignition temperature °C	39.3

B. Hydrogen peroxide (H_2O_2) 50% w/w was obtained in a plastic container of molecular weight 34.01 g/mol supplied by GCC Company. The stock solution is to be diluted by distill water for the preparation of different concentrations used in the tests.

2- Photo reactor units

A glass container 3 Liter in volume was used as the photo reactor. It is provided witha cooling jacket and a flexible sealed cover (rubber) with holes; two for UV lamps (model no. 5212RL manufactured by Sterilight copper company), one hole for supplying air and another for a thermometer. Sampling was achieved from a bottom valve as shown in Fig. (2) for interval times (30, 60, 90,120,180 and 240 min). Experiments were carried out at different operational conditions, furfural concentration (300, 200, 100 and 50) mg/l, H_2O_2 dosage (1000, 750,500 and 250) mg/l, UV lamps (one and two lamps) and pH solution (3, 7.5 and 11).

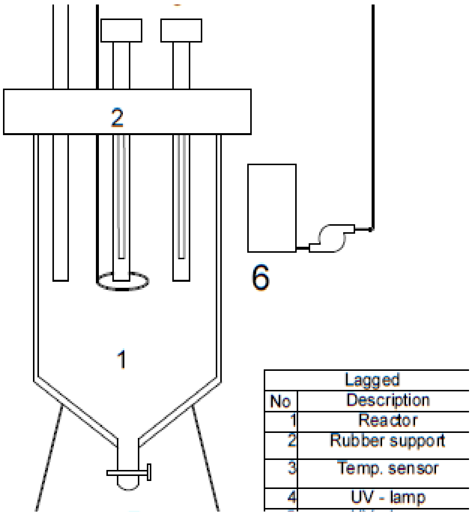

Fig. 2, Schematic representation of the photo reactor

3- Analyses method

For the determination of furfural concentrations in a solution, two methods that could be used: the colorimetric analyses by using a spectrophotometer at wave length 430 nm [16]. Another method using HPLC (High Performance Liquid Chromatography) was used. In this study HPLC (type CECIL, UK) was used for furfural concentration determination with operation conditions listed below [17].

Mobile phase : 5% acetic acid w/v in water methanol (80:20)
Column : C 18 (5 µm)
Flow rate : 1 ml/min
Injection volume : 285 nm

4- Removal Determination

Percentage of furfural removal was determined using eq.(1).

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} \times 100 \qquad \ldots (1)$$

Where: C_o is furfural initial concentration and C_t furfural concentration at time t during the treatment process.

Kinetic rate model

The progress of the reaction is observed to take place in a completely mixed batch reactor (CMBR), as complete mixing occurs uniformly throughout the reactor with an identical reaction rate (k).Common kinetic rate expressions can be evaluated to determine the correlation between the experimental data and the reaction kinetics. Most of the degradation processes follow a first order reaction [18] as expressed in eq. (2):

$$r = -kC = \frac{dC}{dt} \qquad \ldots (2)$$

Where: k= first-order rate constant,t^{-1}

Integrating this eq. (2) yields to

$$\frac{C_t}{C_o} = e^{-kt} \qquad \ldots (3)$$

Taking the natural logarithm of eq. (3)will obtain the following relationship:

$$\ln(C_t) - \ln(C_o) = -kt \qquad \ldots (4)$$

For a first-order reaction, the plot of ln(Ct) as a function of t, as shown in eq. (4), will result in a linear relationship.

Results and Discussion

1- Effect of Initial Furfural Concentrations

Four initial furfural concentration were investigated (50, 100, 200 and 300) mg/l at pH 7.5, H_2O_2 dosage 500 mg/l and one UV lamp.

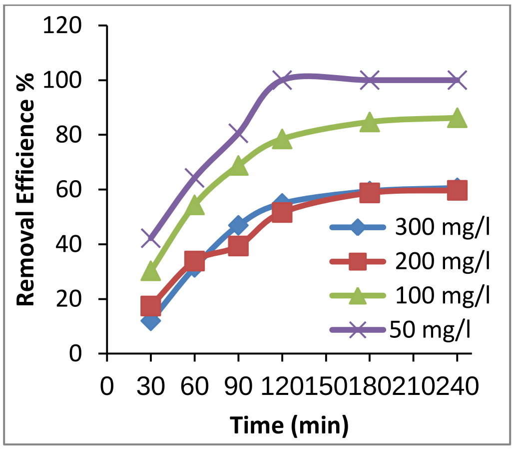

Fig. 3, Removal efficiencies of furfural at different concentrations for H_2O_2=500mg/l, 1 UV lamp and pH=7.5

The results in Fig.(3) show that the degradation of furfural decreases as its concentration increases, reaching 100% at 50mg/l furfural concentration at 120 min, but did not exceed 50% at 200 and 300 mg/l at 240 min. The dosage of 500mg/l H_2O_2 provided enough $^{\bullet}$OH radicals for complete degradation of 50 mg/l furfural but was not enough for the degradation of 200-300 mg/l. The use of H_2O_2 is more efficient in the presences of high concentrations of organic compounds (furfural), because the organic matter competes better with $H_2O_2$for the generation of $^{\bullet}$OH radicals [19]. From these results the optimum H_2O_2 dosage could be determined for economical purposes.

2- Effect of H_2O_2 dosage

Fig (4) shows the effect of various H_2O_2 concentrations (250, 500, 750 and 1000) mg/l on the furfural removal efficiency. Increasing the concentration of H_2O_2 from 250 to 500 mg/l increases the furfural removal from 40 to 60%.At higher concentrationsH_2O_2 will absorb more UV that will produce more •OH radicals which will degraded more furfural. But overdosing of H_2O_2 (more than 500mg/l) may cause simultaneous reactions that could: consume H_2O_2 or cause self decomposition of H_2O_2 to oxygen and water where this will reduce the generation of $^{\bullet}$OH radicals. It is also observed that the reaction of $^{\bullet}$OH with excess H_2O_2willform weak radicals $^{\bullet}HO_2$ (hydroperoxyl with oxidation potential 1.7 V). Hydroperoxyl radicals may react with H_2O_2 to produce also water and oxygen. So these radicals (•OH and $^{\bullet}HO_2$) will act as inhibiting agents and the removal efficiency of furfural decreases [20].These reactions are shown in the following equations:

$H_2O_2 + h\upsilon\ (\text{UV energy}) \rightarrow 2\ ^{\bullet}OH$
$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}HO_2 + H_2O$
$H_2O_2 + {}^{\bullet}HO_2 \rightarrow {}^{\bullet}OH + H_2O + O_2$
$2\ ^{\bullet}OH \rightarrow H_2O_2$
$2\ ^{\bullet}HO_2 \rightarrow H_2O_2 + O_2$
${}^{\bullet}OH + {}^{\bullet}HO_2 \rightarrow H_2O_2 + O_2$

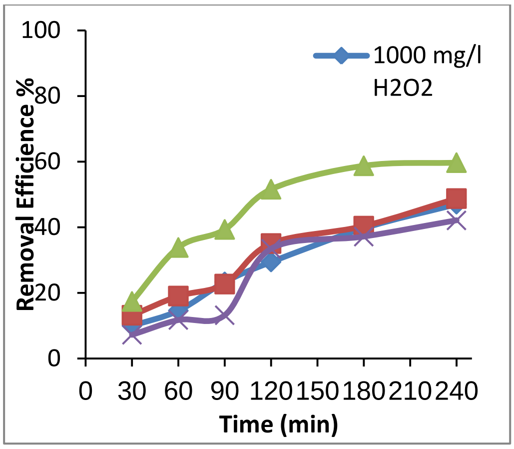

Fig. 4, Removal efficiencies of furfural at different H_2O_2 concentrations for furfural concentration= 200 mg/l, 1UV lamp and pH=7.5

3- Effect of Light Intensity

Fig. (5), shows the effects of light intensity on the degradation of furfural. The intensity of light was adjusted by using one or two lamps at constant furfural concentration of 200 mg/l, H_2O_2 dosage 500 mg/l and pH 7.5. As the intensity of light increased, the removal of furfural accelerated because more light intensity is available and more $^{\bullet}OH$ radicals are produced under the action of UV/H_2O_2.

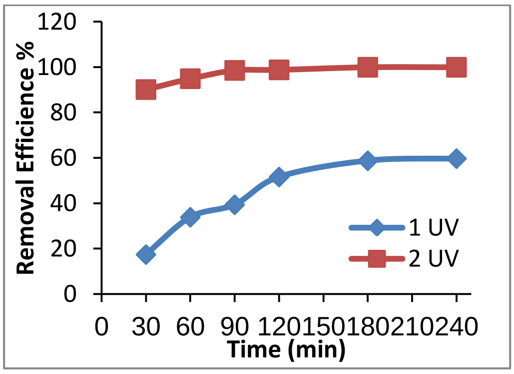

Fig. 5, Effect of UV intensity on removal efficiency of furfural 200 mg/l in concentration, H_2O_2 =500mg/l and pH=7.5

The rate of photolysis of H_2O_2 depends directly on the incident power. At low UV power the photolysis of H_2O_2 is limited. While, at high UV power more $^{\bullet}OH$ radicals are produced upon the photo dissociation of H_2O_2, hence furfural removal rate increases. It appears that the UV power lies within the linear range and hence all the photons provided were effectively used [21].

The degradation of furfural reached 100% after 90 min exposure time using two UV lamps, where it reached 60% using one lamp after 240 min exposure time.

4- Effect of Ph

Fig. (6) shows that the degradation rate of furfural was higher in acidic solution pH 3 (about 80% furfural removal).This pH value was the best for the UV/H_2O_2 process as $^{\bullet}OH$ radicals are free for reaction. At high pH values OH^- ions will increase in the solution and may react with $^{\bullet}OH$ radicals where this will decrease furfural degradation. Also in alkaline medium the oxidizing species hydroperoxy anion (HO_2^-) are formed and these anions react with $^{\bullet}OH$ radicals and residual H_2O_2 consequently lowering the removal rate of furfural. Hydrogen peroxide is most stable in the pH range 3-4, but its decomposition rate rapidly increases with increasing pH above pH 7.5 [21].

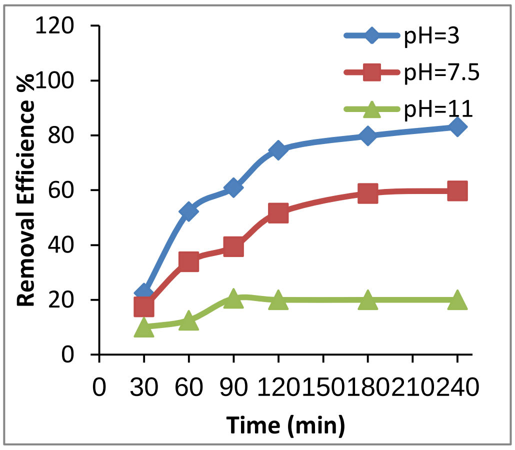

Fig. 6, Effect of pH on removal efficiency of furfural= 200 mg/l, 1UV and H_2O_2= 500mg/l

All the results in section 4 were at pH 7.5 and not 3. From these results furfural removal was observed at pH 7.5. Hence this could be considered if real wastewaters are to be treated by this process. No need to add chemicals to the wastewater to decrease its pH for furfural degradation. The wastewater then will be discharged to water bodies at neutral pH which is recommended for effluents disposal.

5- Kinetic Results

Eq. (4) was applied for all of the experimental results to find the rate of reaction (degradation of furfural by UV/H_2O_2). A plot of ln Ct/Co vs. time is illustrated in Fig. (7). The slope of the line in this plot is equal to the first-order rate constant k and the intercept is equal to In (C_0). The calculated values of k (min^{-1}) for the different operation conditions are listed in Table (2).

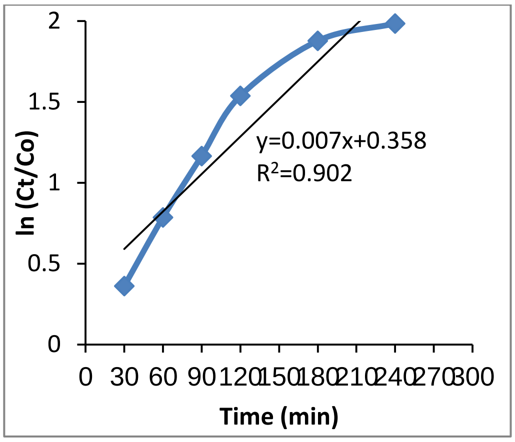

Fig. 7, First order Rate Constant of Furfural Removal by UV/H_2O_2 at 100 mg/l concentration, 500 mg/l H_2O_2 and 1 UV

Table (2) First Order Rate Constant k min^{-1} at Different Operation Conditions

Exp.	pH	Furfural Conc. mg/l	H_2O_2mg /l	No. of UV lamps	kmin^{-1}	R^2
1	3	200	500	1	0.007	0.905
2	7.5	200	500	1	0.0034	0.894
3	11	200	500	1	0.0024	0.652
4	7.5	200	500	1	0.0034	0.8937
5	7.5	300	500	1	0.0037	0.817
6	7.5	100	500	1	0.0077	0.902
7	7.5	50	500	1	0.0183	0.995
8	7.5	200	1000	1	0.0026	0.995
9	7.5	200	750	1	0.0026	0.705
10	7.5	200	500	1	0.0034	0.894
11	7.5	200	250	1	0.0024	0.894
12	7.5	200	500	2	0.0257	0.933

Table (2) shows that the rate of furfural degradation k increases as the pH decreases, 0.007, 0.0034 and $0.0024 min^{-1}$for pH 3, 7.5 and 11 respectively.

For different furfural initial concentrations the rate of degradation increased k 0.0037, 0.0034 0.0077 and $0.0183 min^{-1}$as the initial concentration of furfural decreased (300, 200, 100 and50) mg/l where k was nearly the same for 200- 300 mg/l furfural initial concentration.

The k values using different dosages of H_2O_2were 0.0024, 0.0034, 0.0026 and 0.0026 min^{-1} for 250, 500, 750 and 1000 mg/l respectively, indicating no significant effects on the reaction. All the above results had been achieved using one UV lamp, the k value increased using two UV lamps to 0.0257 min^{-1} which is higher than k value $0.0034 min^{-1}$using one UV lamp for the degradation of 500 mg/l furfural concentration

Conclusions

1- The degradation of furfural decreases as its concentration increases, reaching 100% at 50mg/l furfural concentration at 120 min, but did not exceed 50% at 200 and 300 mg/l at 240 min reaction time.

2- Increasing the concentration of H_2O_2 from 250 to 500 mg/l increased furfural removal from 40 to 60%. High concentrations of H_2O_2 (more than 500mg/l) act as a radical scavenger.

3- The degradation of furfural reached 100% after 90 min exposure time using two UV lamps, where it reached 60% using one lamp after 240 min exposure time.

4- The rate of furfural degradation k increased as the pH and initial concentration of furfural decreased, but different H_2O_2concentrations indicated no significant effects on the reaction rate.

From the above conclusions, UV/H_2O_2 process if effective for furfural degradation in wastewater at neutral pH where the disposal of such effluents will be within the environmental limitations.

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