

Comparison of furfural degradation by different photooxidation methods

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Abstract

In this paper, the degradation of C₅H₄O₂ “Furfural” in aqueous solution by photooxidation technology using UV, UV/H₂O₂, UV/H₂O₂/O₂, UV/H₂O₂/Fe²⁺, UV/O₂/Fe²⁺, O₃, UV/O₃ 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/H₂O₂ is a simple and effective process for furfural degradation and presence of Fe²⁺ ions (UV/H₂O₂/Fe²⁺) 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/H₂O₂ 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.

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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 TiO₂, titania-supported bimetallic catalyst, TiO₂/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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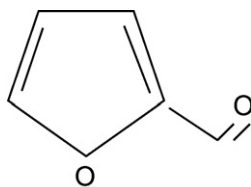


Fig. 1. Configuration of furfural (2-furaldehyde).

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·7H₂O, 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, C₂H₄O₂; molecular weight, 96.09 g mol⁻¹; characteristic, 254 nm; LD₅₀, 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 BOD₅, 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

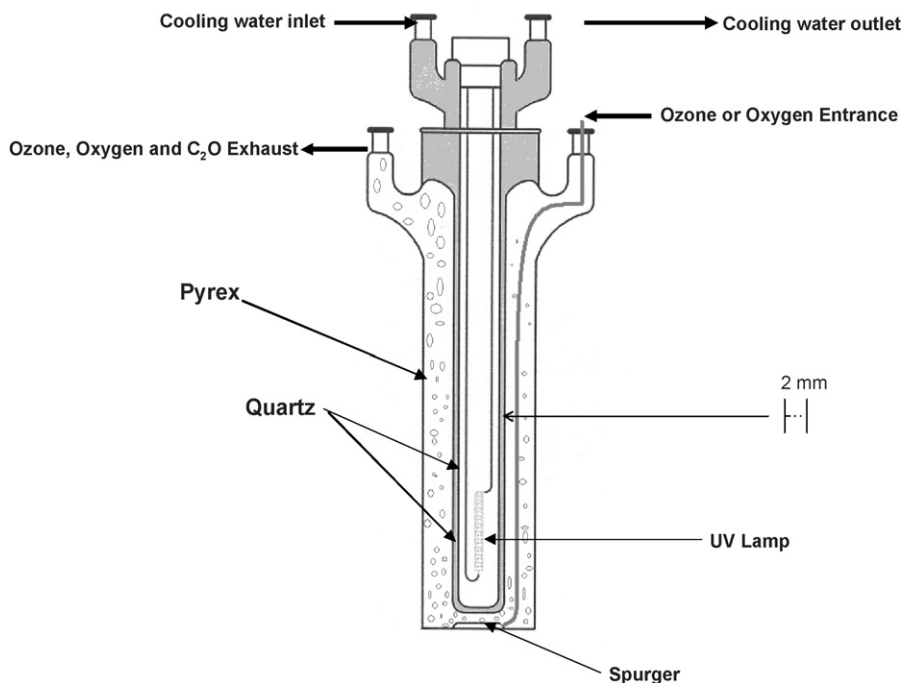


Fig. 2. The schematic of photo-reactor.

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