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Removal of Furfural From Wastewater Using Integrated Catalytic Ozonation and Biological Approaches

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Abstract: Furfural with a chemical formula of $C_5H_4O_2$ is a toxic compound which has several health problems for both humans and environment. It has a few exposure routes for entering the human body such as oral, dermal or nasal. In the present study, the efficacies of an integrated catalytic ozonation process (COP) and novel cyclic biological reactor (CBR) were explored for the removal of furfural from aqueous solutions. Activated carbon was purchased from Merck Company. It had a Brunauer, Emmett, and Teller (BET) specific surface area of 1100 m^2/g, with an average micropore volume and size of 0.385 cm^3/g and 595 μm, respectively. The results indicated that 30% pretreatment with COP could increase furfural and chemical oxygen demand (COD) removal efficiency with CBR 5.56% and 27.01%, respectively. With 70% pretreatment by COP, 98.57% furfural and 95.34% COD removal efficiencies happen in CBR. Generally, batch and continuous experiments showed that the integrated COP/CBR could be efficient in eliminating furfural from wastewater and thus may be a promising technique for treating furfural-containing wastewater.

Keywords: Furfural; Wastewater; Catalytic Ozonation Process (COP); Cyclic Biological Reactor (CBR)

1. Introduction

Humans' activities introduced hundreds of chemical substances into the environment. The production of harmful and toxic chemicals has had a rapid grow in the last century. These chemicals are released from many industries such as petroleum refining, oil refineries, oil processing, pharmaceutical industry, pulp and paper, and chemical plants into the environment (1). Obviously, some chemicals are useful, but many are toxic and their harm to the environment and our health far outweighs their benefits to our society. Furan compounds and their derivatives are commonly found in nature. Among different forms of furan, furfural is the most widespread one in the environment (2, 3). Furfural with a chemical formula of $C_5H_4O_2$ is viscous, colorless and liquid with a pleasant pungent aromatic odor; upon exposure to air, it turns dark brown or black (4). Furfural is toxic and causes several health problems for humans. Furthermore, it has a few exposure routes for entering the human body, including oral, dermal and nasal. Acute exposure can damage the liver and kidneys; if the exposures continue, they may cause tumors and mutations. The lowest concentration has been observed in the brain (5). Furfural is an organic compound derived from a variety of agricultural byproducts, including corncobs, oat, wheat bran and sawdust. It has properties similar to those of benzaldehyde. Furfural is used in solvent extraction processes in petroleum refining industry (it is the most common solvent to extract dynes from other hydrocarbons and is in great demand for separating saturated compounds from unsaturated ones for extraction of lubricating oils, gas oils and diesel fuels). It has a wide variety of other usages such an ingredient of phenolic resins, chemical intermediate (in the production of furan and tetrahydrofuran), and in the manufacture of pesticides and phenol furfural resins (either alone or together with phenol, acetone, or urea to make solid resins), and tetrahydrofuran. Tetrahydrofuran is used as a commercial solvent and is converted in starting materials for the preparation of nylon. It is also widely used in food spicery, as a dye, and as antiseptic, disinfectant, insecticide and rust remover (4-7). Furfural leakage causes not only pollution problems in the environment but also considerable economic losses. Regarding its effects on health and from the parsimonious point of view, there has been a growing interest for the removal or recycle of furfural from wastewater. Nowadays, furfural wastewater treatment commonly adopts several methods including physical, chemical and biological in the world (1). A few researchers investigated the degradation of furfural in aqueous solutions by photo-oxidation technology, adsorption technique with an activated

carbon, solvent extraction, etc. For instance, Anbia and Mohammadi investigated the nanoporous adsorbent of furfural from aqueous solutions (8). SM Borghei and SN Hosseini compared furfural degradation using different photo-oxidation methods (9). In this study, different types of reactions occurred, including the use of UV irradiation, alone or in combination with other oxidizing agents. However, its application to wastewater treatment is limited due to the high energy demand and ineffectiveness of UV transmission in wastewater. The influence of the bed height, inlet furfural concentration, flow rate, and column diameter on breakthrough curves have been investigated. Klasson et al. used agricultural residues for making activated biochar and successfully removed both furfural and hydroxyl methyl furfural (HMF) by adsorption process (10). However, there are a few limitations for these methods, including solvent recovery and solvent solubility problems in the water streams, as well as being time-consuming and costly (1). Therefore, to overcome some of its defects, we used catalytic ozonation process (COP), a new advanced oxidation process (AOP) (11) for pretreatment of a high concentration of furfural from wastewater. Transformations or degradation of furfural by microbial metabolisms can occur under aerobic and anaerobic conditions. For instance, furfural can be reduced to furfuryl alcohol by a few microbial transformations such as via *Saccharomyces* spp. Belay et al. showed that *Methanococcus deltae* can grow on H_2-CO_2 in the presence of various concentrations of furfural and transform furfural to furfuryl alcohol (2). Taherzadeh et al. investigated the effects of furfural on aerobic and anaerobic batch cultures of *S. cerevisiae* and found that furfural decrease both the specific growth rate and ethanol production rate after pulse additions in both anaerobic and aerobic batch cultures (12). Therefore, furfural has had toxic and inhibitory effects on anaerobic biological systems, especially in high concentration (2). Among these methods, biological processes are widely preferred because of their enormous and remarkable advantages, including flexibility and reliability, convenience of operation and maintenance, capability to eliminating a lot of contaminants, economic benefits, environmental friendly technology, degradation of contaminants to less toxic or harmful materials, potential for full-scale applications, etc. (13-15). However, biological systems have some deficits including disability to treat high concentration of pollutant and these techniques are time consuming (16). Furthermore, furfural has toxic and inhibitory effects on biological systems (2, 3, 17); thus, the use of single biological systems is impossible in treating furfural-containing wastewater. To overcome these deficits, we integrated the advanced oxidation process (catalyzed ozonation process) as a pretreatment step to degrade furfural to simple intermediate compounds (7) which can be used readily by biological microorganisms, with biological system as a final treating step. The aim of the present research was to explore the possibility of utilizing benefits of combined catalytic ozonation process (COP) and cyclic biological reactor (CBR) simultaneously. The more detention times needed in biological systems, much uses of catalysis in AOPs systems, can be ameliorated by using these combined systems.

2. Materials and Methods

Activated carbon was purchased from Merck Company. It had a Brunauer, Emmett, and Teller (BET) specific surface area of 1100 m^2/g, with an average micropore volume and size of 0.385 cm^3/g and 595 μm, respectively. Activated carbon with desired granule sizes was used as catalyst in this study. Before using it in the experiments, the granular activated carbon (GAC) particles were washed with deionized water and dried at 105˚C for eight hours in an oven. Other chemicals and reagents used in this research were furfural (molecular formula, $C_2H_4O_2$; molecular weight, 96.09 g mol^{-1}; LD50, 65 mg/kg; boiling point, 54-56˚C; density, 1.159 g mL^{-1}); sulfuric acid (98%), and those used in chemical oxygen demand (COD) analysis. All the chemicals were purchased in high purity analytical grade from Merck and no further treatment was performed and they were used as received. The solutions of furfural were prepared with distilled water.

2.1. Apparatus for Catalytic Ozonation Experiments

Batch experiments for COP were carried out with a glass sparger with 250 mL total volume, fitted with other components including an ozone generator, a sintered glass diffuser to distribute the ozone air stream to the solution, an air pump, an ozone off-gas destruction system, valves, and tubing. Gaseous ozone was generated by feeding air into a generator (ARDA, AEGCOG-5S model) with 5 g O_3/h capacity and regulated to the desired dose throughout the experiments. The catalyst was first added and then the ozone stream with a flow of 1 L/min and concentration of approximately 4.35 mg/min was introduced and continued for the required time. Magnetic stirrer was used to continuously mix the synthetic wastewater with the activated carbon. The ozone in the off-gas stream of the reactor was destroyed in a concentrated potassium iodide (KI) solution (Figure 1). The effluent of COP reactor entered into the feed tank of CBR for further continuous degradation of furfural with CBR.

2.2. Activated Carbons

GAC particles with -30 + 40 mesh (greater than 0.420 and smaller than 0.595 mm) were collected by the appropriate sieves (particles were retained by the sieve mesh No. 40, but were passed through the sieve mesh No. 30) and washed with boiling deionized water three times before drying at 105˚C for eight hours. This GAC was exposed to gas-phase ozone in an up-flow column-type reactor at a various flow rate to obtain the desired dosages of ozone.

2.3. Apparatus and Experiment Set-up for Cyclic Biological Reactor

The CBR used in this study consisted of the following accessories: a cylindrical glass column as the bioreactor (internal diameter = 20 cm; total height = 36 cm; total volume ~11 L), an aeration system with a stone diffuser supplying air to maintain the dissolved oxygen at around 2.5 mg L^{-1} in the mixed liquor during the aeration cycle time, a feeding system with a distributor installed at the bottom inside of the reactor, a decant system equipped with a time-control automatic operation system, tubing, valves, and other accessories (Figure 2). A decant automatic time-controlled valve was located at a height of 10 cm from the bottom of the column, giving a constant 3.1-L remaining volume (working volume or volume of mixed liquor remaining in the reactor at the end of the decant phase) in each operating cycle.

2.4. Analysis

Ozone concentration in the solution was measured by the Indigo method according to the standard methods for examination of water and wastewater (18) (method 2350 E). The concentrations of furfural in ozonated wastewater and cyclic biological reactor effluent were determined at 278 nm using a Unico-UV 2100 UV/vis spectrophotometer (7, 9). The initial and final COD were measured by closed reflux method (18) (method 5220 D). The pH values of the solutions were measured using an electrode (Sense Ion 378, Hack).

3. Results and Discussion

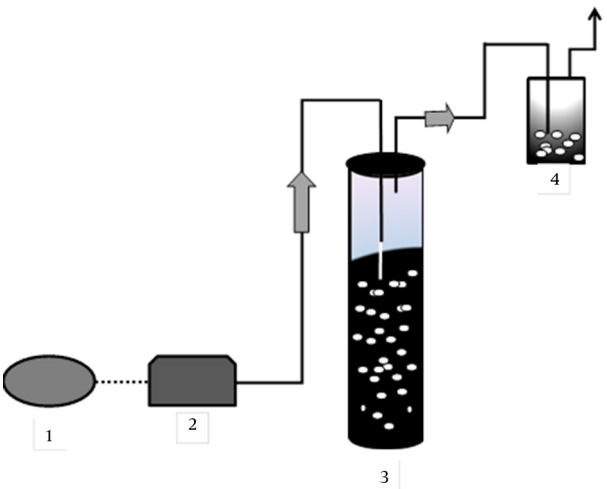
3.1. Single and Catalyzed Ozonation Processes

In the first phase of the study, the effects of various main operational parameters such as pH, ozone dosages, catalyst dosages and reaction time on furfural removal using single and catalyzed ozonation processes was assessed by the authors and the results were published (7). In this phase of the study, the experimentation was carried out using optimal conditions which were previously determined (Figure 3).

3.2. The Effect of 30% Pretreatment With Catalyzed Ozonation Processes on Cyclic Biological Reactor Performance

To achieve the operational objectives, combinations of the two reactors (COP and CBR) were used. In first step, the effect of 30% pretreatment by COP was assessed. For this purpose, furfural loading rate of 2.97 g/litre.day was selected as the higher limit of furfural loading rate; simple biological reactor could not degrade furfural readily with high efficiency (Figure 4). After 30% pretreatment via COP, furfural loading rate was decreased to 2.18 g/L.d and then enter to the feed tank of CBR to undergo degradation biologically for six days to attain a steady state with hydraulic retention time of 12.1 hours, previously determined as an optimum value. The means of furfural and COD removal efficiencies by CBR in this phase of study on pretreated wastewater was measured 98.52 % and 94.80 %, respectively (Figure 4 and 5). As seen in Figure 6, thirty percent pretreatment with COP could increase furfural and COD removal efficiencies by 5.56 % and 27.01 %, respectively. These results are important, especially for COD, because it shows that COP has broken the chain of furfural and converted it into simpler compounds which could readily be used by microorganisms. The results also showed that a CBR system containing acclimated microorganisms is a stable and good process to complete the treatment process in a short period of time. However, based on our literature reviews, the anaerobic process could not completely degrade pollutants to final harmless compounds and the intermediates produced during the process (13, 17) should be treated further.

Figure 1. Schematic Diagram of Ozonation Reactor



1, air pump; 2, ozone generator; 3, reactor column; 4, KI solution.

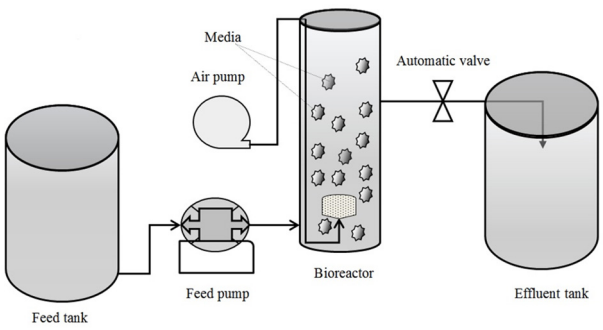
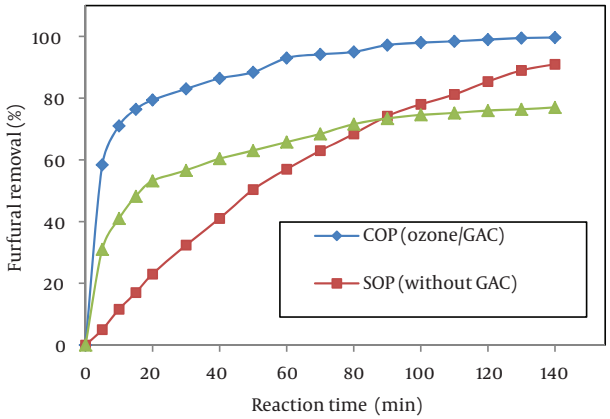


Figure 2. Schematic Diagram of Cyclic Biological Reactor

Figure 3. Synergistic Effect of Granular Activated Carbon on Ozonation Process



Ozone flow rate, 60 L/h; GAC concentration, 6 g/L (if added); reaction time, 20 minutes; furfural concentration, 500 mg/L.

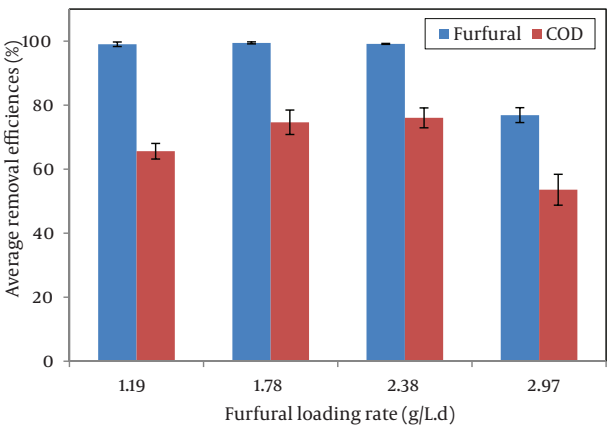


Figure 4. Average Furfural and Chemical Oxygen Demand Removal Efficiencies for Cyclic Biological Reactor at Different Furfural Loading Rates

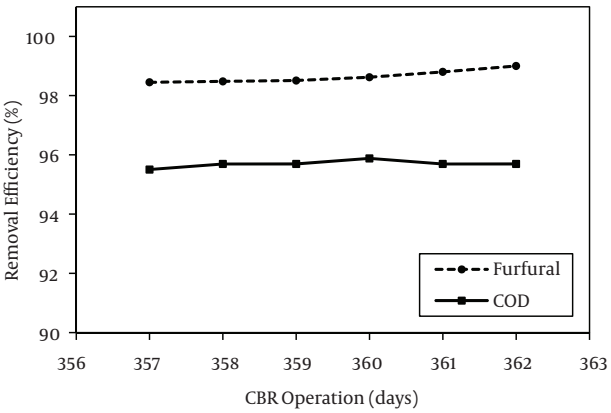
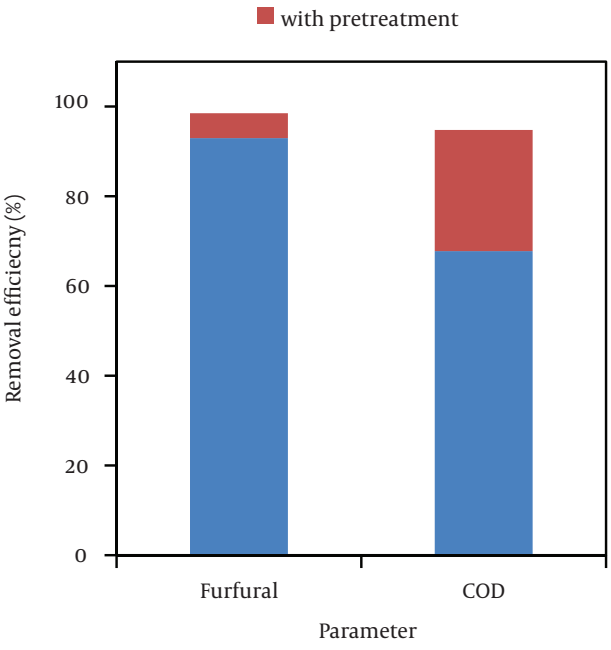


Figure 5. Average Furfural and Chemical Oxygen Demand Removal Efficiency With 30% COP Pretreatment for Cyclic Biological Reactor

Figure 6. The effect of 30% pretreatment with Catalytic Ozonation Process on Cyclic Biological Reactor Performance

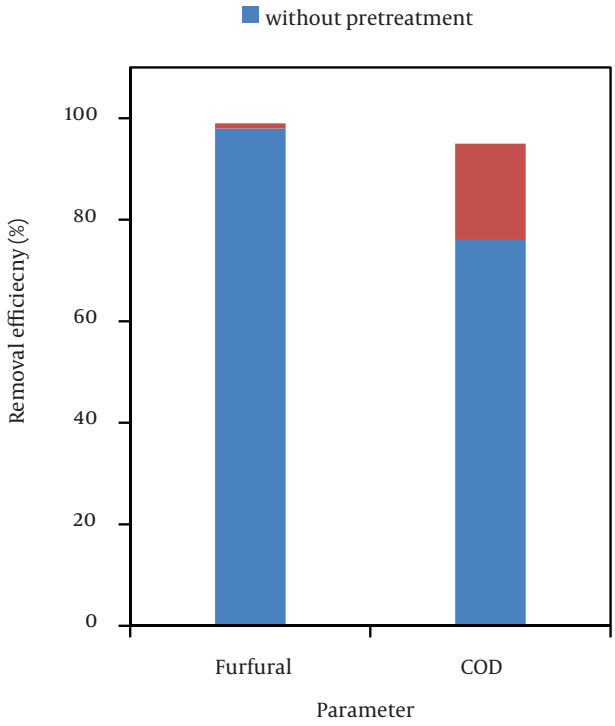


Hydraulic retention time Hydraulic Retention Time (HRT) = 12.1 hours.

3.3. The Effect of 70 % Pretreatment With Catalytic Ozonation Process on Cyclic Biological Reactor Performance

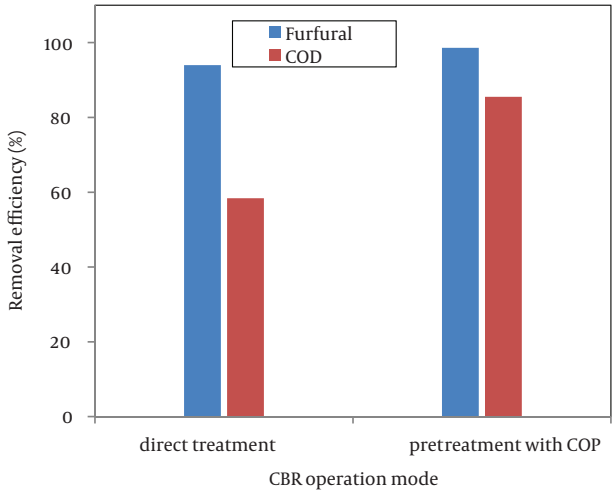
To further investigate the effect of COP on CBR performance and to decrease HRT, wastewater containing 1200 mg/L of furfural (Organic Loading Rate = 2.38 g/L.d) underwent pretreated with COP until 70% removal of furfural, the maximum amount that could be removed by the COP under optimum conditions. Afterwards, the effluent from the COP reactor entered the CBR feed tank and then underwent biological degradation via CBR to further decrease HRT. Firstly, the HRT of 12.1 hours was selected and the CBR operated for eight days to attain a steady state in furfural removal. The average furfural and COD removal efficiencies in this phase of operation were 98.57% and 95.34%, respectively. On the other hand, 70% pretreatment with COP could increase the CBR efficiency in furfural and COD removal 1% and 19 %, respectively (Figures 7 and 8). Given that an acceptable performance for CBR was achieved at this stage, the hydraulic retention time decreased to the minimum value (10.5 hours) which was used in the assessment of hydraulic retention time; but, a high efficiency was not obtained and the biological reactor operated for 13 more days until a steady state was observed. For this HRT, high removal efficiencies were obtained for both furfural (98.61%) and COD (85.51%) which were significant in comparison to the direct treatment mode with CBR, in which 4.62% and 27.42% increased

Figure 7. The effect of 70% Pretreatment With Catalytic Ozonation Process on Cyclic Biological Reactor Performance



HRT = 12.1 hours.

Figure 8. The effect of 70% Pretreatment With Catalytic Ozonation Process on Cyclic Biological Reactor Performance



HRT = 10.5 hours.

removal efficiencies were observed for furfural and COD, respectively. However, this low HRT can be of great value compared to the relatively high retention time required in anaerobic systems, designed to remove furfural from wastewater (2, 13). In fact, this modification allows exploitation of the unique advantages of the COP and intermittent-cycle extended-aeration activated sludge, used by Moussavi et al. (14). The upper limit of loading rate that effectively treated with relatively high removal efficiency in this study was higher than that obtained by other researchers through adsorption (1, 19), photo-oxidation (9, 20, 21), and biological (22) methods. Furthermore, the removal efficiencies for furfural loading rate up to 2.38 g L^{-1} d^{-1} (1200 mg L^{-1}) obtained in this study were also excellent and greater than 99%. The low COD removal at high furfural loading rate suggests the limitation of the furfural uptake and degradation by the bacterial culture.

4. Conclusions

In this study, we use the advantages of COP and CBR approaches. The effects of 30% and 70% pretreatment by COP were assessed in two distinct phases during the operational period. In the first 30% pretreatment phase, the means of furfural and COD removal efficiencies by CBR were 98.52 % and 94.80 %, respectively. The mean HRT of this phase was 12.1 hours. For decreasing the HRT in CBR, pretreatment was increased to 70% (this was the maximum amount that could be removed by COP under optimum conditions) in the second phase. Regarding the low HRT of 10.5 hours in this phase, the average removals of furfural (98.59%) and COD (90.42%) were excellent.

In conclusion, the capability of these developed systems to remove high concentrations of furfural in a relatively short HRT increases the value of the study and makes it a technically and economically feasible and promising technology for industrial applications.

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