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Degradation and mineralization of furfural in aqueous solutions using heterogeneous catalytic ozonation

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ABSTRACT

The main aim of this experiment was to study the degradation of furfural in wastewater using catalytic ozonation process with granular activated carbon as a catalyst. Influences of the following parameters were investigated on furfural degradation; initial furfural concentration, solution pH, GAC dosage, and reaction time. In order to gain an understanding of the mechanism, involved these experiments were done in the presence of some radical scavengers. A significant synergistic effect between ozone and activated carbon was obtained in the oxidation and mineralization of furfural compared to single ozonation and adsorption on GAC processes, thus verifying the positive effect of coupling ozonation and GAC to degrade toxic compounds such as furfural. Furthermore, this study demonstrated that the efficiency of furfural removal increased with a decreasing size of AC particles due to an increased surface area. Measurements of COD in SOP and COP showed that more degradation and mineralization of furfural occurred in COP (80.2%) compared to single ozonation process (42.4%). Desorption studies were performed and they showed that percentages for recovery of furfural from GAC used in COP and single adsorption processes were 3.5 and 85.4, respectively.

Keywords: Wastewater; Furfural; Catalytic ozonation process; Activated carbon

1. Introduction

Many chemicals are released into the environment daily through waste streams. These chemicals are mainly released by various industries such as petroleum refineries and processing plants, pharmaceutical production, pulp and paper processing, and chemical plants [1]. Many compounds in industrial effluents are non-biodegradable and/or inhibit biological processes. Furfural ($C_5H_4O_2$) is one of these chemical compounds which is frequently found in effluent from refineries of chemical and petrochemical industries [2]. Furfural is a viscous and colorless liquid with a pleasant pungent aromatic odor. It is highly soluble in most polar organic solvents, but has an only moderate solubility in water (about 83 g/L at 20°C) [3]. Furfural is used as a selective solvent in solvent extraction processes in the petroleum refining industry and has a wide variety of other uses: it is an ingredient of phenolic resins;

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a chemical intermediate in the food industry used for flavoring and is also used in the production of plastics, pesticides, and phenol-furfural resins. [4–8]. Hence, effluent from these industries contains considerable concentrations of furfural. For instance, furfural concentrations in the effluent from rubber, furfural manufacturing, and oil refinery plants have been reported to be 1,700, 600, and 500 mg/L [9–11], respectively.

Furfural is a toxic compound that can cause several problems for human and environment health. Acute exposure to furfural can damage the liver, kidney, and spleen. Furthermore, long-term exposure may cause tumors and mutations [3,12,13]. To prevent these harmful effects on humans and on the environment, furfural-laden effluent should be efficiently treated before its release into the environment. Several physical, chemical, and biological techniques have been investigated for the removal of furfural from wastewater. Due to their unique features of efficiency, cost-effectiveness, environmental friendliness, flexibility and reliability, as well as simplicity of operation and maintenance [14], biological treatment is the recommended method for treating wastewater containing biodegradable compounds. Although a few reports is available on anaerobic biodegradation of furfural [11,15,16], this is known to inhibit microbial metabolism particularly at high concentrations [15–17]. Therefore, another treatment option needs to be determined for these conditions. In this context, Anbia et al. [18] and Singh et al. [1] investigated the adsorption of furfural from aqueous solutions by surfactant-containing MCM-48 nanoporous material and activated carbon, respectively. The results show that adsorption was an efficient process to treat furfural containing wastewater. The use of activated carbon as an efficient adsorbent to remove the wide range of pollutants was investigated by many researchers [19–23]. The main challenge with the process of adsorption is that it is merely a phase transfer technique, which does not cause any change in the structure of the contaminant. Advanced oxidation processes (AOPs) offer an alternative method to degrade toxic and non-biodegradable organic contaminants through the generation of highly reactive hydroxyl radicals ($^{\cdot}$OH) [24]. Several varieties of AOPs including homogenous and heterogeneous AOPs have been successfully developed in recent decades and their potential for degrading various classes of contaminants has been evaluated [25,26]. For example, Chung et al. [27] investigated several AOPs including ozonation to remove refractory compounds from dye wastewater and found that ozonation in combination with H_2O_2/UV process attained the highest degradation rate. Accordingly, AOPs might be a suitable candidate for treating furfural-laden industrial effluent.

Catalytic ozonation process (COP) is an attractive and economically viable new AOP technology. In COP, a homogenous or heterogeneous catalyst is added to the ozonation reactor that can accelerate degradation reactions [28]. The ease of catalyst restoration and the presentation of high synergetic effects for heterogeneous COP are the main advantages of heterogeneous catalytic processes over homogeneous ones [29,30]. Several natural and synthetic materials have been used so far as catalysts in studies on COP. Application of activated carbon has attracted considerable attention due to its stability and durability as a key characteristic of any catalyst [31]. The activated carbon used in the COP has two functions: firstly to facilitate ozone decomposition and secondly for adsorption of a pollutant for subsequent oxidation [32,33]. The efficacy of COP with activated carbon as the catalyst for the degradation of several types of organic compounds has been investigated, and high efficacy of the COP for the target compound(s) has been reported. For instance, Comninellis et al. [24] reported that COP with granular activated carbon (GAC) catalyst can be an appropriate option to remove a micro-pollutant from water and wastewater. Moussavi et al. [28] investigated the capability of a COP in the presence of GAC to remove phenol from saline wastewater and found that an ozonation process catalyzed with activated carbon was a promising and economically viable technology to treat saline wastewater containing phenol. Khan et al. [32] investigated the homogeneous and heterogeneous catalytic oxidation using activated carbon as the catalyst for degradation of di-(2-ethyl hexyl) phthalate(DEHP) in aqueous phase and reported that on the generation of $^{\cdot}$OH in the process and its reaction with DEHP as an important factor to achieve high removal efficiency.

Although, only a few reports have been published on the efficient degradation of furfural in various UV-based AOPs [2,9,12], their application to wastewater treatment is limited due to high energy consumption and particularly the ineffectiveness of UV transmission in wastewater due to the presence of organic matter and/or suspended solids [34]. COP offers a feasible alternative to overcome some of these defects. To the best of the authors' knowledge, no report has yet been made available on furfural degradation using COP.

Accordingly, the aim of this study was to investigate some operational parameters on the efficacy of COP with GAC as a catalyst for degradation and mineralization of furfural. The influence of pH (2–12), GAC concentration (1–10 g/L), furfural concentration

(200–1,500 mg/L), and reaction time (5–140 min) was the parameters used to evaluate degradation and mineralization of furfural. Desorption experiments were also conducted to understand the mechanism of furfural degradation in the process.

2. Materials and methods

2.1. Materials

All chemicals used in the study were high purity analytical grade and purchased from Merck and used as received. Aqueous solution of furfural with desired concentration for the experiments was prepared by serial dilution of a 1% stock furfural solution. Activated carbon was also purchased from Merck. It had a BET specific surface area of 950 m^2/g, with an average micropore volume and size of 0.385 cm^3/g and 1.62 nm, respectively. Activated carbon with granule sizes of 0.4–0.6, 0.6–0.8, and 0.8–1 mm was used as the catalyst in this study. Before use in the experiments, GAC particles were washed with deionized water and dried at 105°C for 8 h in an electrical oven.

2.2. Apparatus and experiments

Batch experiments were carried out with a glass sparger, as the ozonation reactor, with 200 mL total volume equipped with an ozone generator, a sintered glass diffuser to distribute the ozone air stream to the solution, an air pump, a magnetic stirrer to evenly mix the solution with activated carbon, an ozone off-gas destruction system (a sparger containing 2% KI solution), valves, and tubing. Gaseous ozone was generated by feeding air into a generator (*ARDA, Model AEGCOG-5S*) with 5 g O_3/h nominal capacity and regulated to the desired dosage throughout the experiments. In each COP test, 100 mL of the solution with the specified furfural concentration and pH was poured into the reactor, GAC was added to the reactor, and then the ozone stream was introduced to the reactor. The flow rate of the ozone stream was kept constant throughout the experiment at 1 L/min with an average concentration of 4.35 mg/min and the reaction was allowed to continue for the predetermined time. When the reaction time was up, the reactor's content was filtered using a fiberglass filter with a pore size of 0.2 μm and the filtrate was analyzed for the residual furfural and chemical oxygen demand (COD). The same procedure was used for the single ozonation process (SOP) and the adsorption experiments except that no catalyst was added to the reactor for SOP and no ozonation in cases of adsorption. Several experimental phases were defined for the investigation of the influence of the selected variables on the removal of furfural. The phases and conditions of the experiment are given in Table 1. Some desorption experiments were also performed to describe the mechanism of furfural degradation and to demonstrate that real degradation instead of only adsorption had occurred [35]. To do this, an attempt was made to desorb furfural from the GAC used in the COP and adsorption processes with normal HCl and NaOH solutions and then to measure the remaining furfural according to mass balance analysis. About 0.2 g of GAC used in COP put in 50 mL HCl and 0.2 g dissolved in 50 mL NaOH, was then mixed and agitated for 1 h. At the end of the agitation period suspensions were centrifuged and amounts of desorbed furfural were determined spectrophotometrically. These steps were also taken for GAC used in the single adsorption process to desorb any furfural adsorbed on GAC. Finally, the amount of furfural that had degraded was determined via mass balance analysis.

2.3. Analysis

The concentration of furfural in the solution before and after the reaction was determined by measuring the absorption percentage at its maximum wavelength of 277 nm [9,10,36] using a Unico-UV 2100 UV/Vis Spectrophotometer. The wavelength scan (between 220 and 400 nm) of furfural solution before and after the treatment (SOP, COP, and single GAC) was done by spectrophotometer model *LAMBDA 25 UV/Vis PerkinElmer* to determine the maximum absorption wavelength (Fig. 1). As shown in Fig. 1, the maximum absorbance wavelength for furfural was 277 nm both before and after the reaction. By using this wavelength, a standard graph of absorbance vs. various concentrations of furfural was prepared. The initial and final COD were measured by closed reflux method [37] (method 5220 D). pH values of solutions were measured using an electrode (Sense Ion 378, Hack).

3. Results and discussion

3.1. Influence of solution pH on perfrmance of adsorption, SOP, and COP in the removal of furfural

Table 1, Fig. 2 shows the effect of a solution's pH value ranging from 2 to 12 on furfural elimination by adsorption, SOP, and COP under conditions given in the Table. The initial pH of synthetic wastewater was adjusted by additions of 0.1 N H_2SO_4 or 0.1 N NaOH.

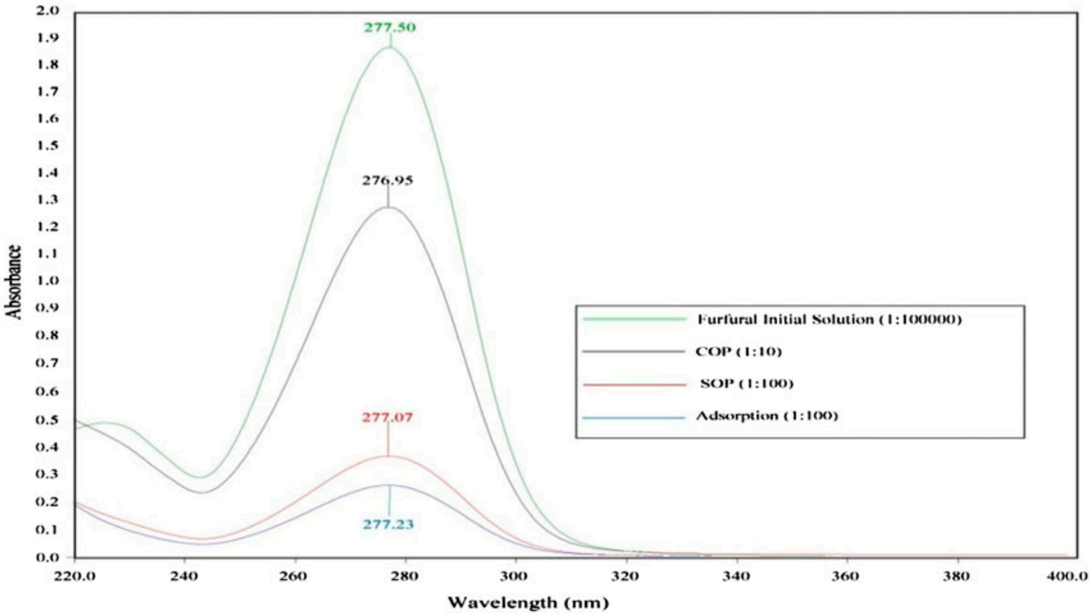

Fig. 1. Wavelenghth scan of furfural solution before and after reaction.

It is evident from the figure that a solution's pH value did not significantly affect the removal of furfural by adsorption onto GAC at the selected experimental conditions (Table 1). Moreover, as seen in Fig. 2, furfural degradation in both SOP and COP was higher in a strong acidic condition; the degradation percentages of furfural in SOP and COP were marginally decreased and relatively constant for the pH range of 4–8 [38]. Thus, the pH level of the solution in the subsequent experiment was set to eight because that was the initial pH of the synthetic wastewater and no adjustment was needed. For SOP, 37.5 and 34.7% of furfural could be degraded at pHs of 2 and 12, respectively, under the selected conditions. The degradation of furfural in the COP at pH levels of 2 and 12 were almost the same with the value of around 85%. The better performance was obtained in the acidic pH in both SOP and COP suggesting that the furfural degraded predominantly through direct oxidation with ozone [26,28,39]. Whereas, high degradation percentages of furfural at alkaline pHs can be attributed to indirect oxidation with $^{\cdot}$OH generated from ozone decomposition at the elevated solution pHs [30,39]. The higher amount of furfural removal in COP than that in SOP as well as in adsorption onto GAC indicates that GAC has significant potential to enhance the rate of oxidation; this topic will be discussed further in the text to follow.

3.2. Influence of GAC concentration

The degradation of furfural was studied in the COP with a constant pH of 8 and a furfural concentration of 500 mg/L but with various concentrations of GAC ranging from 1 to 10 g/L. Data on furfural removal obtained from the tests, as a function of reaction times at different GAC concentrations are shown in Fig. 3. As observed in Fig. 3, the efficiency of furfural removal increased with an increased GAC concentration up to 6 g/L and remained almost unchanged with the further increase of GAC concentration. For instance, for a given reaction time of 20 min, when GAC concentration increased from 1 to 6 g/L, the furfural degradation increased from 47.2 to 83.4% in the COP. A further increase of GAC concentration to 10 g/L, however, could not considerably improve the degradation percentage. One reason for the increase of efficiency with the increase of GAC concentration is greater surface area and increased availability of active sites for the ozonation reaction with the furfural that resulted in an enhanced rate of degradation [28]. Another possibility is that an increase in the activated carbon dosage led to a higher rate of ozone decomposition into $^{\cdot}$OH radicals [19,38], hence more efficient removal was achieved. Therefore, GAC dosage is an important factor to be considered in designing systems aimed to remove furfural from wastewater through COPs. Thus, the GAC dosage of 6 g/L was selected as the optimum dose for the next experiment.

Table 1
Experimental phases and conditions

Phase	Experiment	Conditions				
		$C_{furfural}$ (mg/L)	C_{GAC} (g/L)	pH	GAC size (mesh No.)	Contact time (min)
1	Effect of solution pH	500	6[a]	2–12	20–30	5–60
2	Effect of GAC dosage	500	1–10	8[b]	20–30	5–60
3	Effect of GAC particle size (mesh No.)	500	6	8	<20–>100	5–60
4	Furfural and COD removal under optimum conditions	500	6	8	20–30	20
5	Effect of radical scavengers (*t*-butanol, carbonate, sulfate, phosphate, methanol)	500	6	8	20–30	5–60
6	Desorption studies	500	6	8	20–30	20

Notes: [a]The same experiments were carried out for SOP (without GAC).
[b]Optimum pH in which the maximum furfural removal was obtained in COP.

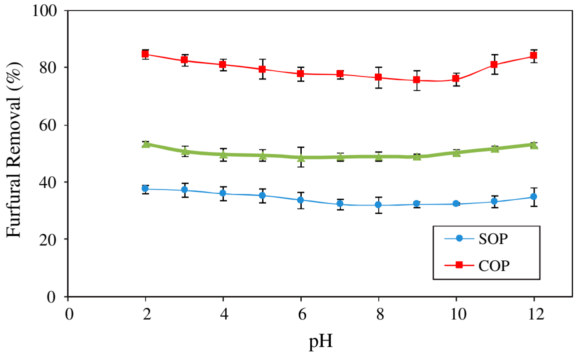

Fig. 2. Effects of initial pH on furfural removal from wastewater in the SOP, COP and GAC adsorption (ozone flow rate: 60 L/h; GAC concentration: 6 g/L (if added), reaction time: 20 min, furfural concentration: 500 mg/L).

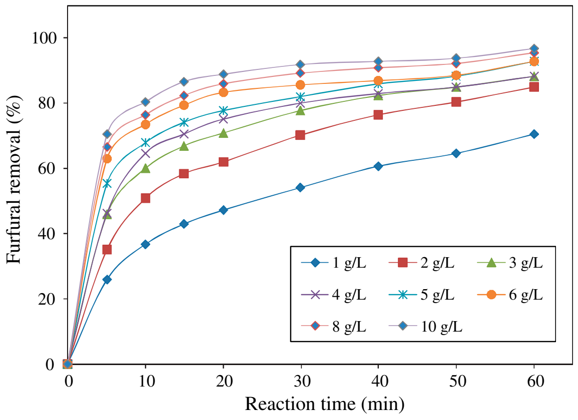

Fig. 3. Effect of GAC concentration on furfural removal in the COP (ozone flow rate: 60 L/h; GAC concentration: 6 g/L, reaction time: 60 min, furfural concentration: 500 mg/L).

3.3. The effect of contact time

Fig. 4 shows furfural removal as a function of reaction time by SOP, COP, and adsorption. As seen in Fig. 4, furfural removal increased in all three selected processes with an increased reaction time. Fig. 4 demonstrates that furfural removal in an integrated process was greater than removal in single ozonation and single adsorption on GAC systems. For instance, furfural removal percentage in COP, at a reaction time of 20 min was 79.4% that is a result greater than the sum of removals in those two other systems (76.2%) revealing that a synergistic effect occurred in the integrated activated carbon catalyzed ozonation process. It can be concluded, therefore, that GAC is likely to catalyze an ozone reaction through the generation of reactive radical species particularly ·OH. Indeed, furfural has been adsorbed onto the GAC and subsequently degraded through

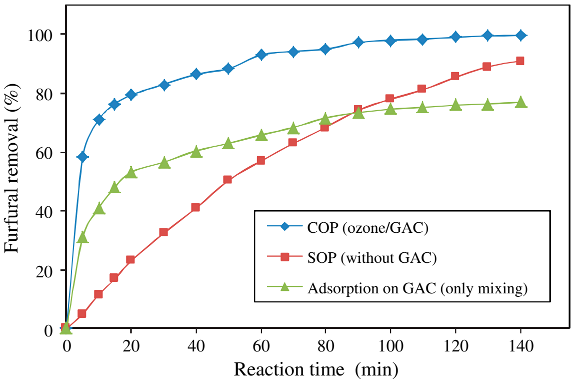

Fig. 4. Synergistic effect of GAC on ozonation process (ozone flow rate: 60 L/h; GAC concentration: 6 g/L (if added), reaction time: 20 min, furfural concentration: 500 mg/L).

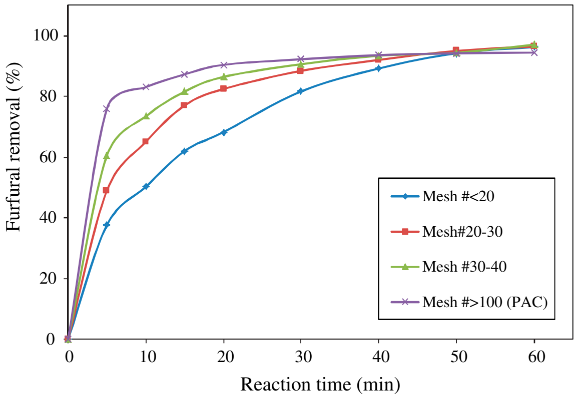

Fig. 5. AC particle size effect on furfural removal in the COP (ozone flow rate: 60 L/h; AC concentration: 6 g/L, reaction time: 20 min, furfural concentration: 500 mg/L).

indirect oxidation mainly by the generated radical species as well as by direct oxidation with molecular ozone [19,40]. Other researchers [28,30,41] have also demonstrated that activated carbon can initiate radical-type chain reactions that proceed in bulk solution and accelerate the transformation of ozone into secondary oxidants, such as OH-radicals that cause synergetic effects on removal efficiency. Fig. 4 also shows that no synergistic effect was observed at reaction times of over 20 min. Therefore, further experiments in the integrated ozonation process were conducted for 20 min contact times only; as the optimum reaction time.

3.4. Effect of GAC particle size

A study on the efficiency of different sizes of activated carbon particles on furfural removal in the COP was done to determine an optimum size of AC for the COP. As shown in Fig. 5, the furfural removal efficiency increased by decreasing the particle size of an AC particle. For instance, in a constant reaction time of 20 min, decreasing the GAC size from 0.841 to 0.15 mm, the removal percentage of furfural increased from 68.2 to 90.4% under the selected conditions of the experiment. It can therefore be determined that a decrease in size of the activated carbon catalyst improved performance of COP. This can be related to the fact that when the size of GAC was decreased, a larger external surface area was provided [42,43] for the reaction of ozone and furfural, hence the greater adsorption efficiency was obtained. As stated in the previous section, activated carbon accelerates the rate of ozone decomposition and a greater surface area facilitated quicker decomposition of O_3. The latter resulted in an enhanced rate of furfural degradation. Other researchers [43–45] have also demonstrated that a decrease in particle size resulted in an increased removal efficiency.

3.5. The degree of furfural mineralization in COP under optimum conditions

In order to determine the effectiveness of the COP for mineralization of furfural, the reduction of COD concentration of the furfural-laden solution was investigated in the COP under a pre-determined optimum pH (8) and a GAC concentration of 6 g/L. Fig. 6 illustrates the degradation and COD removal of furfural in SOP and COP. As illustrated in Fig. 6, after 60 min reaction time, about 57% of furfural degradation was obtained in the SOP but this value increased up to 99% in the COP under similar operational conditions. According to data given in Fig. 6, COD reduction in COP was 37.38% greater than that in SOP for a reaction time of 60 min. It is revealed that the COP was more efficient than SOP for effective mineralization of furfural under the selected conditions of this experiment.

According to Fig. 6, the removal of COD was lower than that of furfural in both SOP and COP. This result demonstrates that furfural has partly been degraded into organic intermediates. The drop in solutions' pH vs. reaction times (Fig. 6) suggests that these intermediates were most likely acidic compounds such as furoic acid [46]. Another point to be made from Fig. 6 is that, as the reaction preceded the difference between furfural and COD removal percentages became smaller showing that the degradation rate of COD was slower than that of furfural. Since COD is a gross measurement of the organic content in the sample, any reduction of this parameter denotes

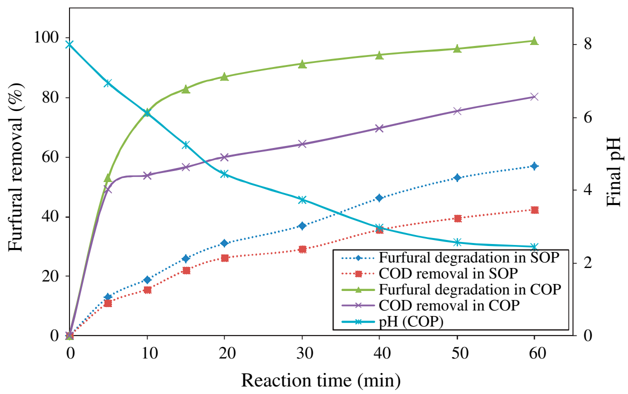

Fig. 6. Furfural and COD removal in the COP under the optimum operation conditions (ozone flow rate: 60 L/h; GAC concentration: 6 g/L, reaction time: 20 min, pH: 8, furfural concentration: 500 mg/L).

the degree of mineralization of a compound. Overall, it can be inferred that the COP, with activated carbon, induced a high degree of degradation and mineralization of furfural.

3.6. Effect of radical scavengers and mechanism of furfural degradation

The predominance of radical degradation of furfural in the COP was confirmed by the radical scavenger experiment under conditions defined in Table 1. Fig. 7 shows the furfural removal in the COP with and without tert-butanol and sulfate as examples of well-known radical scavengers. As seen in Fig. 7, the performance of COP in the degradation of furfural decreased in the presence of both tert-butanol and sulfate compounds. For instance, the removal percentage of furfural in the presence of *t*-butanol for a 20 min reaction time reduced from around 88 to 57%. Since *t*-butanol is a known ·OH scavenger that has very low reactivity with ozone molecules [31,47], this result verifies that ·OH was the dominant radical species working in the reactor, thus indirect radical oxidation was the predominant agent for the furfural degradation mechanism in aqueous solution in the GAC catalyzed ozonation process at the specified pH of the experiment. Moreover, furfural removal percentages also reduced in the COP in the presence of sulfate. As sulfate anions have a high affinity to bind with the functional groups on the surface of a catalyst [48,49], this finding indicates that the furfural degradation reaction in the COP occurred mainly on the surface of the catalyst rather than in the solution.

The generation of ·OH and the main mechanism of furfural degradation in the COP can be simplified in the following equations:

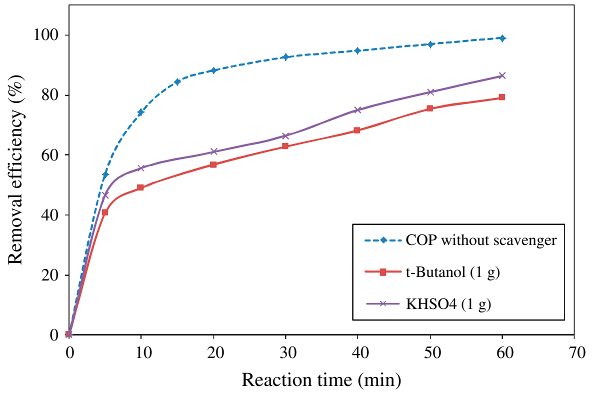

Fig. 7. Effect of radical scavengers (ozone flow rate: 60 L/h; GAC concentration: 6 g/L, reaction time: 20 min, furfural concentration: 500 mg/L).

- generation of ·OH:

$$C^{-S} + O_3 \rightarrow C^{-S-O_3} \rightarrow C^{-S-O^{\bullet}} + O_2, \qquad (1)$$

$$C^{-S-O^{\bullet}} + H_2O \rightarrow C^{-S-(^{\bullet}OH)_2} \qquad (2)$$

- degradation of furfural by ·OH:

$$C^{-S-(^{\bullet}OH)_2} + \text{furfural} \rightarrow C^{-S} + \text{oxidation products}$$
$$(CO_2 \text{ and } H_2O \text{ in complete oxidation}) \qquad (3)$$

where C^{-S}, $C^{-S-O^{\bullet}}$, and $C^{-S-(^{\bullet}OH)_2}$ are the Lewis sites on the carbon's surface, Lewis sites with atomic oxygen, and ·OH generated on the carbon's surface, respectively.

3.7. Desorption studies

In order to declare the contribution of adsorption in the furfural removal in the COP, furfural and intermediates (as COD) were adsorbed into the GAC at the end of the COP test was quantified according to the procedure detailed in section 2.4. It should be noted that these results were obtained under optimum conditions of pH 8, GAC concentration of 6 g/L, GAC particle size of 0.6–0.8 mm, and reaction time of 20 min. The fate of furfural was evaluated using a mass balance analysis around the reactor boundary based of the procedure explained in section 2. The results are given in Table 2. Information given in

Table 2
The fate of furfural in the COP under optimum conditions based on the desorption experiments

Fraction	M_{initial}	M_{removed}	M_{residual}	M_{desorbed}	M_{degraded}
Mass, mg (%)	50 (100)	42.95 (85.9)	7.05 (14.1)	1.5 (3.5)	41.45 (82.9)

Table 2 indicates that most of the furfural removed in the COP (85.9%) was degraded (82.9%). It should be noted that furfural degradation could be carried out either by direct oxidation with ozone after adsorption on GAC surfaces or through indirect oxidation processes via OH radical production. In both conditions, GAC accelerate the reaction rates and furfural removal efficiencies. Some degree of oxidation with non-decomposed ozone, however, might also be occurring both at the surface and in bulk solution. It is also possible that the adsorption on GAC could cause a higher concentration of furfural and ozone/ radicals on the surface of GAC and therefore enhance the degradation rates [31]. This confirms the previous conclusion that the GAC accelerated the decomposition of ozone into reactive radical species of hydroxyl instead of single adsorption on GAC.

Alvarez et al. [38] was done a regression analysis and showed that basic and hydroxyl surface oxygen groups of GAC favor the kinetics of the ozone decomposition process. Furthermore, they concluded that ozone transformation into $^{\cdot}OH$ radicals mainly occurred in the liquid bulk through a radical chain reaction that initiated by OH^- and $HO_2{}^-$ ions which arise from the formation of H_2O_2 on surface active sites of GAC and its further dissociation.

4. Conclusions

The present study examines an AOP of COP for furfural removal from an aqueous solution. The effect of GAC was investigated as a widely used catalyst on an ozonation process in order to increase the efficiency of single ozonation on the decomposition of furfural; one of the main contaminants found in effluent from the oil industry. The integration of ozonation and activated carbon had a synergistic effect in the removal of furfural when compared to single ozonation and the single adsorption processes, proving the existence of a catalytic reaction mechanism. Results showed that furfural decomposition efficiency was increased with an increased dosage of activated carbon and a decreased size of the activated carbon. Optimum GAC dosage and size were about 6 g/L and 0.841–0.595 mm, respectively. It was also found that the catalytic activity of GAC in the solution could have resulted from the decomposition of ozone into hydroxyl radicals that caused an improvement in the degradation and mineralization of furfural compared to those in the SOP. Results of desorption studies according to the mass balance analysis showed that degradation of furfural (about 83%) occurred in COP. It was concluded that the COP was an efficient technique for degradation and mineralization of effluent containing a high concentration of furfural.

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