

Research Article

Catalytic Ozonation of Phenolic Wastewater: Identification and Toxicity of Intermediates

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A new strategy in catalytic ozonation removal method for degradation and detoxification of phenol from industrial wastewater was investigated. Magnetic carbon nanocomposite, as a novel catalyst, was synthesized and then used in the catalytic ozonation process (COP) and the effects of operational conditions such as initial pH, reaction time, and initial concentration of phenol on the degradation efficiency and the toxicity assay have been investigated. The results showed that the highest catalytic potential was achieved at optimal neutral pH and the removal efficiency of phenol and COD is 98.5% and 69.8%, respectively. First-order modeling demonstrated that the reactions were dependent on the initial concentration of phenol, with kinetic constants varying from 0.038 min^{-1} ($[\text{phenol}]_0 = 1500 \text{ mg/L}$) to 1.273 min^{-1} ($[\text{phenol}]_0 = 50 \text{ mg/L}$). Bioassay analysis showed that phenol was highly toxic to *Daphnia magna* ($\text{LC}_{50} 96 \text{ h} = 5.6 \text{ mg/L}$). Comparison of toxicity units (TU) of raw wastewater (36.01) and the treated effluent showed that TU value, after slightly increasing in the first steps of ozonation for construction of more toxic intermediates, severely reduced at the end of reaction (2.23). Thus, COP was able to effectively remove the toxicity of intermediates which were formed during the chemical oxidation of phenolic wastewaters.

1. Introduction

phenol is a hazardous contaminant and classified as a toxic and priority hazardous contaminant in the list of USEPA [1], which can be found in aqueous effluents from various industries such as the petrochemical plants, petroleum refineries, manufacturing of resins and plastics, steel production, coal conversion, surface runoff from coal mines, dyestuff, tanning, paint stripping operations, pulp and paper, pesticides, pharmaceuticals, medications, and food processing industries [2, 3]; Environmental Protection Agency has limited this contaminant concentration in surface waters to less than 1 ppb [4]. Due to its toxicity and hazardous character and an increasing social concern on environment, it is required to be removed prior to discharging to the environment. Therefore,

because the traditional methods of treatment of phenolic wastewaters such as physical and biological processes are not sufficient and have their own limitations, there is a need to use effective strategies of treatment.

Many investigations are available regarding the use of advanced oxidation processes (AOPs) such as ultrasonic, photooxidation, photocatalytic oxidation plasma, Fenton, photo-Fenton, wet oxidation, and ozone/ultraviolet (UV) for the degradation and mineralization of various classes of biorecalcitrant organic compounds [5] that, based on economic consideration and their complexity, rarely selected as a possible process.

Ozonation is one of the oxidation processes widely used for industrial wastewater pretreatment in which ozone molecules (as a strong oxidant) break down recalcitrant and

toxic organic compounds into smaller molecules. However, ozonation has some limitations such as the following: (1) high energy consumption for ozone generation which could be costly; (2) in some cases ozonation is selective; (3) incomplete oxidation and low efficiency due to low reaction kinetics and limited mass transfer [4, 6]; and incomplete mineralization of recalcitrant organics [7].

In recent years, significant attention has been paid on the catalytic ozonation process (COP). Indeed, COP is a new AOP in which a catalyst is applied to increase the soluble ozone decomposition, as result, producing highly reactive hydroxyl radicals [8]. These nonselective radicals are capable of oxidizing the refractory and toxic organic compounds into final inorganic and less toxic products [9].

Many studies have reported that the treatment process can be improved by combining ozonation with other agents such as UV, H_2O_2 , and homogeneous catalysts, for instance, Mn^{+2} , Fe^{+3} , Fe^{+2} , Ag^+ , Zn^{+2} , and Co^{+2} [10, 11].

But, due to high consumption of the catalyst and complexity of these technologies, it is rarely selected as a promising method.

Recently, heterogeneous catalytic ozonation processes, as a powerful treatment method, have been investigated to increase the efficiency of ozonation process. In this process, a synthesized catalyst is applied to increase the ozone decomposition and thereby form highly reactive free radicals. Many catalysts including metals and metal oxides such as CO_3O_4/CeO_2 , TiO_2 , Pt/carbon nanotube (CNT), Ru/ Al_2O_3 , Mn/ TiO_2 , Au/AC, Mn/Co, Fe_3O_4/CoO , ZnO, Fe_2O_3 , Fe_2O_3/CeO_2 , CNT, Ru/ CeO_2 , Cu/ZrO, $CuFe_2O_4$, and activated carbon (AC) are widely used for enhancing the activation of the ozonation process [12–15].

The coupling of ozone and activated carbon was proven to be an effective method to degrade organic contaminants [9, 16]. In this method, carbon can act as an adsorbent, a reactive support, and free-radical initiator [6, 14], but irreversibility and high consumption still remain the main disadvantages of this catalyst.

In this study, carbon nanocomposite was applied as a catalyst for heterogeneous ozonation. This catalyst has superparamagnetic properties that could be recovered from effluent by magnetic field and reused for several times.

Hence, this research is focusing on the degradation and detoxification of phenol and intermediates by COP, and the influences of some operational conditions such as initial pH of the solution, reaction time, and initial concentration of phenol on the degradation and the COD removal efficiencies were evaluated.

For control and optimization of this treatment method, it is necessary to understand the role of this catalyst and the nature of the reactions. Accordingly, in this research, the physical and chemical properties of the nanocomposite, such as specific surface area, pH_{Zpc}, and its composition were determined and later discussed in detail.

Also, toxicity of phenol stream and identification of intermediates in the various reaction time of COP were carried out using *Daphnia magna* and GC/MS, respectively. In this study, the LC₅₀, which is considered as the concentration of toxic

compound which results on average in a 50% mortality of the test organisms at a specific exposure time, was investigated.

In order to determine changes in effluent acute toxicity during the COP, toxicity values (LC₅₀) were converted to toxic unit values (TU) and then considered as an indication of the comparison.

2. Materials and Methods

2.1. Chemicals. Phenol (purity $\geq 99.5\%$; CAS number 108-95-2) was purchased from Merck Co. (Germany). Then standard solutions were prepared with distilled and deionized water, protected from light, and stored at 4°C. Except for HPLC-grade acetonitrile, all other chemical agents such as (KI), ($Na_2S_2O_5$), (Na_2SO_3), sulfuric acid, nitric acid, sodium hydroxide, (KCr_2O_7), (Ag_2SO_4), ($HgSO_4$), NaH_2PO_4 , and $Fe(NO_3)_3 \cdot 9H_2O$ were of analytical reagent grade. A commercial powder activated carbon (CAS number 1.02183.1000) supplied by Merck Co. was used in this study as a precursor of the catalyst.

2.2. Preparation and Characterization of the Catalyst. The nanocomposite catalyst was prepared from activated carbon (AC) via a modified impregnation method by using Fe_3O_4 . Firstly, the AC was treated with nitric acid (37%) and the resulting mixture was kept at 80°C and stirred for 3 h to make it hydrophilic. Then, it was washed with water, filtered, and dried at 105°C over night. 25 g of the modified AC was dispersed in 200 mL aqueous solution containing 100 g $Fe(NO_3)_3 \cdot 9H_2O$ as a Fe_3O_4 precursor by sonication using an ultrasonic bath. The resulting particles then filtrated and dried and the thermal treatment was performed at 700°C for 1 h in the presence of pure nitrogen flow for the formation of Fe_3O_4 magnetic nanoparticles.

The specific surface area of the prepared catalyst was determined using the BET equation and its mineralogical characterization was specified by X-ray diffraction (XRD) patterns carried out on an XRD diffractometer at room temperature. The distribution of elements on the catalyst was determined by dispersive X-ray spectroscopy (EDS) and its morphology was characterized by scanning electron microscopy (SEM) analysis. The pH of the zero point of charge (pH_{Zpc}) of the catalyst was measured by acid-base titration of catalyst suspension method, which is detailed by Altener et al. [17].

2.3. Catalytic Ozonation Treatment. The ozone was generated from pure oxygen via corona discharge using an ozone generator (ARDA, Model COG-1A) with 5 g O_3/h capacity. The ozone inlet flow rate was controlled via a gas rotameter (capacity, 3.5 L/min) at 0.5 L/min.

The ozone was regulated at a constant mass flow rate of 33 mg/(L·min) throughout the experiments, measured by the standard potassium iodide (KI) absorption method [18] and finally destroyed in the off-gas stream of the reactor in a concentrated KI solution.

The samples containing phenol were prepared from the stock solution (5000 mg/L) and their residual concentrations

TABLE 1: Experimental steps and conditions.

Phase	Experiment	Conditions			
		C_{Phenol} (mg/L)	C_{Catalyst} (g/L)	pH	Time (min)
1	Effect of pH	100	0.5	4–10	5
2	Effect of initial concentration of phenol	50–1500	2	8 ^a	0–60
3	Phenol and COD removal at optimal condition	500	2	8	0–60
4	Toxicity of effluents	200	2	8	0, 10, 30 and 60
5	Identification of intermediates	500	2	8	15

^aOptimum pH in which the maximum phenol removal was obtained in COP.

in the samples were analyzed by HPLC (Cecil CE 4100) using a Hypersil C18 column (250 mm × 4.6 mm i.d, with 5 μm particle size) with a UV detector (Cecil CE 4200) at 254 nm. The mobile phase consisted of a mixture of 50 mM buffer solution (NaH₂PO₄) and acetonitrile (50 : 50, v : v) at a flow rate of 1.0 mL min⁻¹.

The experiments regarding the catalytic ozonation were carried out in a semibatch cylindrical stainless steel reactor with 1 L total volume fitted with other elements including an ozone generator, a sintered diffuser to distribute the ozone stream into the solution, a cylinder of pure oxygen (99.9%), an ozone off-gas trap system, and gas rotameter. For each catalytic ozonation test, the following procedure was made.

- (1) A 1 L solution of phenol with a certain initial concentration was transferred into the reactor.
- (2) The initial pH of the solution was adjusted at the desired value by the addition of either NaOH or HCl (1 M).
- (3) The required amount of catalyst was added to the solution.
- (4) The ozonation was started at a certain time (see Table 1).

At given time intervals, 2 mL of the sample was immediately introduced into 100 μL of sulphite solution (0.1 M) to remove the dissolved ozone. The magnet and filter (0.22-μm) were used to remove the catalyst and then 60 μL of the recovered sample was injected to the HPLC for analysis of the residual phenol. The condition of experiments was optimized using one factor at a time method.

The extent of mineralization of the organic matter was measured by COD experiment via digestion of the treated sample in COP with KCr₂O₇ solution [18].

2.4. Kinetic Studies. The kinetic study in both COP and single ozonation process (SOP) was carried out with different concentrations of catalyst and phenol. The following first-order kinetic expression was used to determine the phenol removal reaction rate, given by

$$-\ln\left(\frac{C}{C_0}\right) = kt, \quad (1)$$

where k is the first-order rate constant and C and C_0 are the phenol concentrations at reaction time t and initial phenol concentration, respectively.

2.5. Toxicity and Intermediates Identification of COP Effluent. Acute toxicity of phenol and its intermediate products after degradation by COP were investigated with infants of *Daphnia magna* as detailed in standard methods for the examination of water and wastewater [18].

Daphnia is a very sensitive organism to phenol [19]; therefore, toxicity tests were done using this animal.

Dilution water was taken from spring with the chemical properties of pH = 7.9, electrical conductivity = 987 μS/cm, total hardness = 285 mg/L as CaCO₃, total alkalinity = 125 mg/L as CaCO₃, chloride = 38 mg/L, and nitrate = 5.7 mg/L. *D. magna* was maintained in a 20 L glass vessel containing dilution water in temperature of 23 ± 2°C and a 14/10 light-dark cycle. In each experiment, 10 infants (<24 h old) were transferred to the test volume of 200 mL in a 500 mL glass beaker with a Pasteur pipette.

In order to determine the toxicity of phenol and its intermediates, the initial concentration of this contaminant was 200 mg/L, which ozonated with the catalyst at the reaction times of 0, 10, 30, and 60 min, and the effluents were diluted to 100, 75, 50, 25, 12.5, 5, 2.5, 1, 0.5, and 0.25% with dilution water.

After the exposure times (24, 48, 72, and 96 hours), the number of immobilized and dead infants was recorded and LC₅₀ values were calculated by usage of PROBIT program in the SPSS (version 21) software and the toxic unit (TU) of each effluent was determined by [20]

$$TU = \frac{100\%}{LC_{50}}. \quad (2)$$

The intermediates formed during the degradation were monitored using a gas chromatograph-mass spectrometer (GC-MS) supplied by Agilent, USA, and a temperature program was as follows: the temperature of the column was initially set at 50°C for 2 min, then increased by 10°C per min to 280°C, and maintained at this isothermal temperature for the final 5 min. Injector temperatures were set at 250. Helium was used as a carrier gas at a flow rate of 1.0 mL/min and the injections were made in the split mode with a split ratio of 1 : 2.

3. Results and Discussion

3.1. Characterization of Catalyst Particles. The modification by HNO₃ can cause enhancement of surface area and pore volume of activated carbon. The surface area and the total

pore volume (at $P/P_o = 0.992$) of the catalyst were $814 \text{ m}^2/\text{g}$ and $0.26 \text{ cm}^3/\text{g}$, respectively. The surface area of magnetic catalyst was reduced from $907 \text{ m}^2/\text{g}$ to $814 \text{ m}^2/\text{g}$ (10% reduction), attributing to the formation of nanoparticles of Fe_3O_4 inside the pores. Nanoparticles of Fe_3O_4 bonded on the surface of activated carbon by hydroxyl groups [21, 22]. The functional groups of catalyst surface can be modified by ozone [23], by increasing the specific surface area of the pores, and by significant decreasing of the total volume of the catalyst [24]. However, once the activated carbon was ozonated, its specific surface area was slightly decreased, and the total volume of the pores remained unchanged [25]. Therefore, the influence of ozonation on the structure of the carbon-based catalyst is dependent on its origin and nature. X-ray diffraction (XRD) patterns of carbon nanocomposite were assigned to the synthesized carbon nanocomposites at $2\theta = 24^\circ$ indicating that the AC structure was not destroyed after the calcination of the catalyst, and magnetic nanoparticles in the composite were actually pure Fe_3O_4 . The result regarding the EDS analysis, shown in Table 2, reveals that around 90% of the synthesized catalyst contains pure carbon and 5% of the total weight consists of iron and oxygen. The SEM results represent the nanoparticles of Fe_3O_4 with the particle sizes of 25–30 nm. The result of catalyst characterization is summarized in Table 2.

3.2. Parameters Affecting Ozonation

3.2.1. Effect of pH_{zpc} of the Catalyst and Initial PH of the Solution. The catalyst surface will be charged negatively when $\text{pH} > \text{pH}_{zpc}$, positively when $\text{pH} < \text{pH}_{zpc}$, and neutrally when $\text{pH} \approx \text{pH}_{zpc}$. The pH of the solution can greatly affect the structural properties of the pollutant. Changes in the pH can alter the ions in solution, the ionic state of the phenol, and the surface properties of the catalyst.

The pH_{zpc} of catalyst was measured 7.7, falling in the range of 6.08–7.7, reported by various researchers for similar catalysts [9, 26, 27]. It is demonstrated that the catalyst surface has slightly basic properties allowing the catalyst to induce ozone decomposition followed by the generation of reactive radical species [16].

Studies have shown that contribution of ozone molecules and modified activated carbon can cause to production of phenolic and hydroxyl groups. as the major functional groups on the surface of the catalyst, contributing acidic properties and low value of pH_{zpc} [28].

These functional basic groups located on the surface of the catalyst are thought to be responsible for ozone decomposition, resulting in the generation of reactive radical species [16].

As observed in Figure 1, the rate of phenol degradation in SOP increased from 48% at pH of 4 (almost linearly) to 73% at the pH of 10 during a 5 min reaction time. This increase can be attributed to the effect of pH value on the ozone transfer rate from the gas flow to the liquid phase [16] and increase the concentration of OH anions (decomposition of ozone to reactive oxidizing radical species with the much higher oxidation potential than ozone molecules in the solution) [29].

TABLE 2: Specifications of nano- Fe_3O_4 coated on activated carbon.

	PAC	$\text{Fe}_3\text{O}_4/\text{AC}$
Parameters		
Specific surface area (m^2/g)	907	814
Pore volume (cm^3/g)	0.42	0.26
pH _{zpc}	8.9	7.7
Average particle size as Fe_3O_4	—	25–30
Elements		
Fe (%)	—	5.04
O (%)	—	5.76
Assay (%) as carbon	99.99	89.20

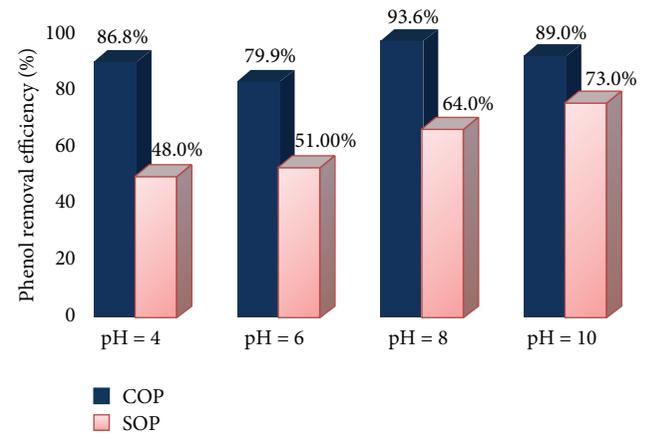


FIGURE 1: Effect of initial pH on removal efficiency of phenol. [Phenol]₀: 100 mg/L; catalyst concentration of 0.5 g/L; reaction time: 5 min.

In COP, due to the properties of the catalyst surface, the maximum degradation (93%) was obtained at pH of 8 and above this pH ($\text{pH} = 10$), as other studies were reported, the degradation was decreased (89%) [6, 30]. As shown, at higher pH, a negative effect on phenol degradation was observed, and the degradation rate of phenol was decreased under strong alkaline conditions (Figure 1). This result could be interpreted by considering both the property of phenol ($\text{pK}_a = 9.9$) and the surface nature of the catalyst, with respect to the pH of the solution and catalyst pH_{zpc}.

Since the pH_{zpc} of catalyst is 7.7, a negative charge is developed on its surface at this pH (>8). Phenol ($\text{pK}_a = 9.9$), on the other hand, is mostly dissociated to its ionic form (the phenolate anion) at this basic pH value [31]. The effect of pH value on the adsorption of phenol can be explained by the electrostatic interaction between the surface of the catalyst and the target material.

We found out, as expected, that the optimal pH was in $\text{pK}_{ZPC}^{\text{Catalyst}} < \text{pH} < \text{pH}_a^{\text{Phenol}}$ range. At this pH, the negatively charged catalyst and positively charged phenol molecules should readily attract each other.

The affinity of catalyst toward phenolate through adsorption under strong alkaline condition is limited, leading to the reduction of phenol degradation rate [16]. Hence, under neutral and weak alkaline conditions (pH 7–8), negative

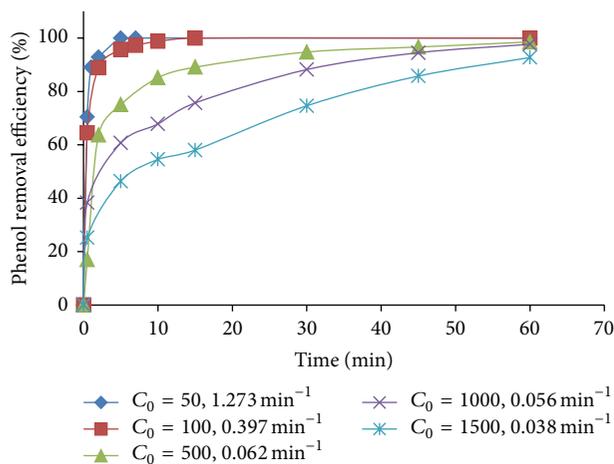


FIGURE 2: Effect of initial concentration of phenol on degradation efficiency in COP. Catalyst concentration of 2 g/L; initial pH of 8 : 0.

charge is the predominant surface charge for the catalyst and the positive charges are the primary species of the phenol contaminant. Therefore, both of them are easily attracted toward each other through hydrogen bonding and, consequently, the amount of phenol adsorption and its decomposition rate rise [30].

As Zhao et al. [32] pointed out, an increase was observed in the degradation rate of nitrobenzene in COP using a Mn catalyst with an increase in the pH of solution from 3 to 11.

In further developments, some researchers have found out that a decline in the mineralization of phenolic compounds, was a function of pH of the solution from 3 to 10 [33].

It is also reported that the optimum pH for decolorization and mineralization of azo dye in COP using MgO nanocatalyst was found to be at alkaline pH over 8 [34].

It can be deduced that the process in which the pH of solution affects the degradation of a contaminant in COP depends on the structure, the type of the reacting compound, and the properties of the catalyst. Hence, the optimum pH of the COP must be selected for each specific condition.

Nonetheless, the maximum degradation rate in the COP was obtained at pH of 8.0 and the phenol degradation rate was remarkably higher in the COP than that of the SOP regardless of pH. It is reported that increase in the reaction efficiency can be due to the fact that ozone reacts indirectly with organic molecules at alkaline pHs [35].

3.2.2. Effect of Initial Concentration of Phenol. As illustrated in phase 2 of Table 1, it can clearly be seen that the degradation of phenol, as a function of contaminant concentration (Figure 2), shows a significant declining effect of initial concentration of phenol on the ozonation process and kinetic constant, particularly in the first minutes of the reaction time.

For example, at a given reaction time of 5 min, the degradation of phenol increased from 46.3% in the initial phenol concentration of 1500 mg/L to 99.9% at the phenol concentration of 50 mg/L, representing the strong effect of

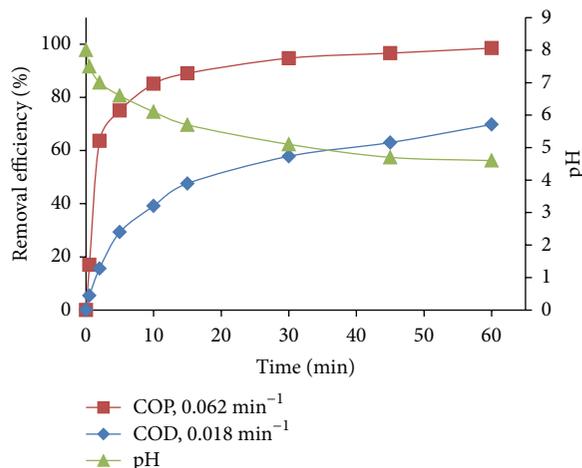


FIGURE 3: The degree of phenol degradation and COD removal in the COP, $[\text{phenol}]_0 = 500 \text{ mg/L}$; catalyst concentration of 2 g/L; initial pH of 8 : 0.

contaminant concentration on ozonation. Also, the reaction rate constant increased from 0.038 min^{-1} in phenol concentration of 1500 mg/L to 1.273 min^{-1} with catalyst concentration of 2 g/L, indicating the 33-fold increase in the reaction rate constant by decreasing of the initial contaminant concentration.

Based on the literature, the most likely mechanism of phenol degradation is as follows.

Ozone molecules are first adsorbed on the functional groups of the catalyst surface followed by decomposition by AC [6, 12] and metal oxides including Fe_3O_4 [36]. Afterwards, the generation of hydroxyl radicals and surface oxygenated radical species take place [37–39].

This result can be attributed to the expansion of surface area of the catalyst and the availability of more active sites for ozone decomposition leading to the enhancement of the following events: the available contact surface area for the reaction of phenol and ozone molecules [28], generation of reactive species of radicals [40–42], and the improvement of the phenol degradation efficiency.

3.3. Phenol and COD Removal at Optimal Condition. On completion of this investigation, the effect of the COP on the removal of COD from a phenolic sample was studied under the conditions defined in phase 3 of Table 1.

Since COD is a general measurement of the organics in the sample, its reduction denotes the amount of mineralization of the compounds [9]. As reported in the literature, the AOP causes a drastic reduction of COD of recalcitrant organics [7]. Our findings indicate that the COP is not exempt from this general principle. As shown in Figure 3, the phenol degradation efficiency was approximately 85% after 10 min of the reaction. But, approximately 39% of the COD of phenol were removed after the same reaction time, and it increases up to 70% after 60 min, while in other similar studies, with other catalysts, COD removal efficiency from phenolic samples was lower than that of the above-mentioned values [43].

Although a further decrease (88%) was reported by Moussavi et al. [9] in the COP of phenolic sample ($C_0 = 1200 \text{ mg/L}$) at the end of reaction time (60 min), applying a 10-fold increase in the concentration of AC catalyst will overshadow its economic superiority.

The results show that the efficiency of COD removal and the reaction rate constants are lower than phenol degradation and its COD removal, particularly in early minutes of the reaction. This phenomenon can be illustrated in such a way that phenol molecules are converted to some intermediates prior to complete oxidation, especially at the initial steps of degradation.

The quick drop in pH value versus the reaction time confirms that acidic intermediates were generated during the oxidation of phenol (Figure 3). In addition, as the oxidation process is promoted by COP, the gap between COD and phenol removal percentage curves is narrowed. This could be due to the fact that intermediates are more efficiently mineralized in COP than their corresponding parent compounds. Overall, these results inferred that the COP with this catalyst could cause a high degree of degradation and mineralization of phenol compared to the other processes such as single ozonation [9, 44], Fenton and photo-Fenton [45], adsorption, TiO_2 -photocatalytic, wet air oxidation, and catalytic-based wet air oxidation [46].

Although the COP in the presence of nanocomposite catalyst was able to degrade almost completely all the phenol (98.5%) and removed significant amounts of COD (70%) after 60 min of reaction time, the rather long time of ozonation would impose high operational cost for the generation of required ozone on the treatment system.

As other studies reported [44], catalytic ozonation process improved the biodegradability at BOD_5/COD ratio of phenolic compounds from only 0.3 to 0.52 and slightly reduced toxicity of the intermediate solution.

The results also showed that the COP not only efficiently degraded the phenol as a recalcitrant compound, but also prompted a high degree of COD removal and, consequently, the mineralization of its derivative intermediates.

3.4. Toxicity of COP Effluents. Results showed that *Daphnia* is very sensitive bioindicator to phenol [12], so that LC_{50} 96 h of row waste was 2.78% v/v, which, with initial concentration of 200 mg/L, was equal to 5.6 mg/L. As can be seen in Figures 4 and 5, acute toxicity of phenol and its intermediates were reduced significantly after being treated by COP. For instance, toxicity unit of phenol (according to LC_{50} 96 h) by treatment with COP was reduced from 36 to 2.3, which represents that the acute toxicity is reduced ~16 times at the end of reaction time (60 min). As results showed, the toxicity of effluent after the first stages of COP slightly increased, which can be due to formation of more toxic intermediates such as catechol, hydroquinone, and benzoquinone [47].

Generally, the reduction of effluent toxicity was obtained by phenol and its intermediates to aliphatic and low chain carboxylic acids products.

Results of this research showed that the catalytic ozonation was able to eliminate effectively the toxicity of aqueous

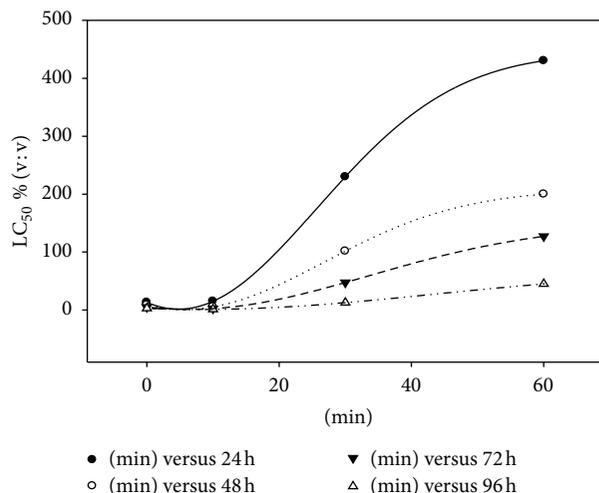


FIGURE 4: The change of LC_{50} of treated phenolic stream versus reaction time of COP, $[\text{phenol}]_0 = 200 \text{ mg/L}$; catalyst concentration of 2 g/L; initial pH of 8:0.

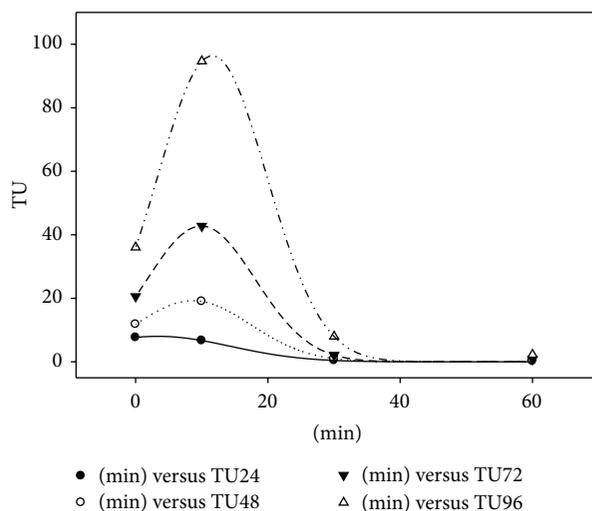


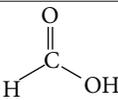
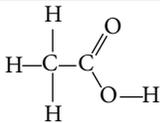
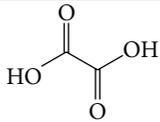
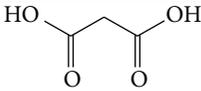
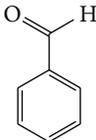
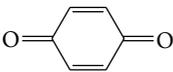
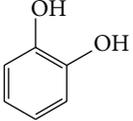
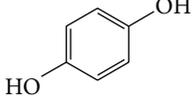
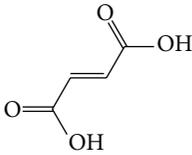
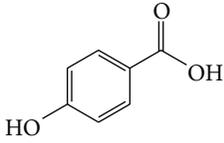
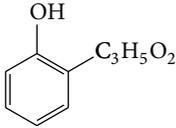
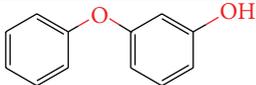
FIGURE 5: The change of toxic unit of treated phenolic stream versus reaction time of COP, $[\text{phenol}]_0 = 200 \text{ mg/L}$; catalyst concentration of 2 g/L; initial pH of 8:0.

phenol and this technique can be used as a reliable method to detoxification of industrial phenolic effluents.

3.5. Identification of Intermediates. In this study, aromatic and aliphatic oxidation intermediates of phenol degradation were identified by GC/MS analysis as listed in Table 3 and shown in Figure 6.

Results showed that, after 1 h catalytic ozonation, phenol almost removed, while hydroquinone, benzoquinone, and catechol were present in small amount. At the end of reaction time carboxylic acids such as oxalic, fumaric, and acetic acids were formed as the main products of phenol degradation. Accordingly, at the end of reaction time, the pH value decreased from initial value of 8.0 to ~4.5 (Figure 3).

TABLE 3: Identified compounds by GC/MS.

Compound	Formula	Structure	Molar mass (g/mol)
Formic acid	CH_2O_2		46
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$		60
Oxalic acid	$\text{C}_2\text{H}_2\text{O}_4$		90
Malonic acid	$\text{C}_3\text{H}_4\text{O}_4$		104
Benzaldehyde	$\text{C}_7\text{H}_6\text{O}$		106
p-Benzoquinone	$\text{C}_6\text{H}_4\text{O}_2$		108
1,2-Dihydroxybenzene (catechol)	$\text{C}_6\text{H}_6\text{O}_2$		110
1,4-Dihydroxybenzene (hydroquinone)	$\text{C}_6\text{H}_6\text{O}_2$		110
Fumaric acid	$\text{C}_4\text{H}_4\text{O}_4$		116
4-Hydroxybenzoic acid	$\text{C}_7\text{H}_6\text{O}_3$		138
2-Propylphenol	$\text{C}_9\text{H}_{12}\text{O}_2$		152
Phenoxy-phenol	$\text{C}_{12}\text{H}_{10}\text{O}_2$		186

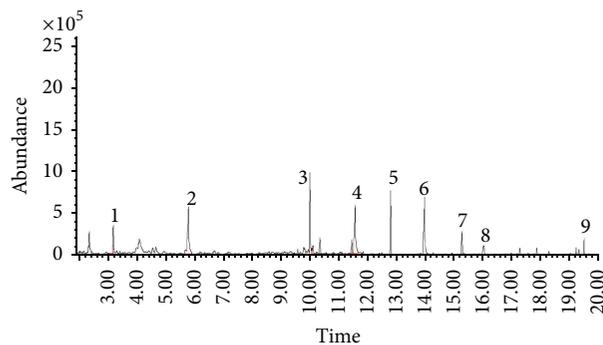


FIGURE 6: GC/MS chromatogram of phenol solution after being treated by COP for 15 min (peaks 1 and 2: lower carboxylic acids; peak 3: oxalic acid; peak 4: phenol; peak 5: 1,2-dihydroxy benzene; peak 6: 1,4-dihydroxy benzene; peak 7: 4-hydroxy-benzoic acid; peak 8: propylphenol; peak 9: phenoxyphenol), $[\text{phenol}]_0 = 500 \text{ mg/L}$; initial pH of 8 : 0.

Also, the formation of coupling by-products such as phenoxyphenol with molecular weights higher than phenol was evidenced in this study, as it has been observed for other AOPs [48].

According to some findings [9, 43, 49], major intermediates of phenol oxidation in AOPs can be categorized as readily biodegradable compounds (acetic, fumaric, propionic, formic, and succinic acids), nonbiodegradable compounds but without inhibitory or toxic effect over the biomass (maleic, oxalic, and malonic acids), toxic (p-benzoquinone and hydroquinone), and finally inhibitory compounds (cathol) for the biodegradation [43, 50].

4. Conclusions

In this study, the preparation of AC/nano- Fe_3O_4 composite used as a catalyst in the catalytic ozonation and detoxification of phenol has been investigated. This superparamagnetic nanocomposite exhibited a catalytic effect on the reactive radical generation.

The findings indicated that the removal efficiency and the constant rate of degradation increased with decreasing initial concentration of phenol and the optimum pH of solution was observed at pH of 8.0. At the initial concentration of 500 mg/L of phenol and the optimal conditions as well as O_3 dosage of 33 mg/(L·min), 98.5% and 69.8% of phenol and COD were removed in the COP, respectively.

Despite more toxicity of effluent in the early stage of the catalytic ozonation, the toxicity of treated phenolic wastewater at the end of reaction was very low.

Accordingly, it is concluded that this nanocomposite is an efficient and active catalyst in the degradation and detoxification of phenol solution.

In spite of the high removal efficiency of phenol and low toxicity of effluent, the mineralization was incomplete.

Therefore, it is concluded that the combination of the biological process followed by COP is an effective and economic technique for the treatment of industrial wastewaters containing phenolic compounds.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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