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Enhanced Oxidation of Phenol by Copper-catalyzed Fenton-like Reaction in the Presence of Bicarbonate

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Abstract

In this study, the copper-catalyzed Fenton-like reaction in the presence of bicarbonate (i.e., the Cu(II)/HCO₃⁻/H₂O₂ system) was examined for the phenol degradation. The rate of phenol degradation by the copper-catalyzed Fenton-like reaction ([Cu(II)]₀ = 0.1 mM, [H₂O₂]₀ = 10 mM, pH = 10) was accelerated by 17-fold in the presence of 50 mM HCO₃⁻. The rate of phenol degradation by the Cu(II)/HCO₃⁻/H₂O₂ system increased with increasing doses of Cu(II) and HCO₃⁻, but showed an optimal value for the H₂O₂ dose and pH at 5 mM and 10, respectively. The Cu(II)/HCO₃⁻/H₂O₂ system was selective in degrading phenolic compounds; benzoic acid was resistant to degradation. Cu(III) species (likely complexed forms with carbonate) are believed to be the reactive oxidants responsible for the phenol degradation by the Cu(II)/HCO₃⁻/H₂O₂ system. Meanwhile, aerating CO₂ gas successfully accelerated the phenol degradation by the copper-catalyzed Fenton-like reaction, implying that CO₂ aeration can be a practical option to supply bicarbonate when implementing the Cu(II)/HCO₃⁻/H₂O₂ system.

Keywords

Copper; Fenton-like Reaction; Phenol; Hydrogen Peroxide; Bicarbonate

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Introduction

For decades, the use of pharmaceuticals and personal care products (PPCPs) has increased tremendously with increasing concerns about hygiene and health care with population growth [1]. Phenol and its derivatives have been widely used as essential precursors in the manufacturing of PPCPs [2]. However, many PPCPs and phenolic compounds are not effectively degraded by conventional water treatment, including biodegradation. Trace amounts (a few ng/L) of these compounds are frequently detected in surface water [3, 4], causing concerns about potential contamination of drinking water.

Advanced oxidation technologies (AOTs) based on the Fenton and Fenton-like reactions have been extensively studied as effective tools to degrade recalcitrant organic compounds in wastewater [5]. Recently, copper-catalyzed Fenton-like reactions (i.e., the Cu(II)/H₂O₂ system and its modifications) have been shown to degrade organic

compounds under neutral and basic pH conditions [6–8]. These systems also have been suggested as effective methods to inactivate microorganisms [9, 10] and control membrane biofouling [11]. The cupryl (Cu(III)) species were proposed as the reactive oxidants dominantly produced by the copper-catalyzed Fenton-like reactions [8].

Meanwhile, several recent studies have reported that copper-catalyzed Fenton-like reactions can be enhanced in by the presence of bicarbonate (HCO_3^-), demonstrating successful degradation of organic compounds, such as dyes [12] and an antimicrobial agent [13]. The enhanced reactions in the presence of HCO_3^- are believed to result because Cu(II)-carbonate complexes are more reactive in the catalytic decomposition of H_2O_2 into reactive oxidants than the Cu(II) species without H_2O_2 (e.g., Cu(II)-hydroxo complexes or Cu(II) oxide). Cu(III) species [12] and hydroxyl radical ($\cdot\text{OH}$) [13] were suggested as major oxidants responsible for the degradation of organic compounds. However, despite these references [12, 13], little information is available for the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system. Phenolic compounds have not been examined as target contaminants in the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system. In addition, information about factors such as pH and doses of reagents (Cu(II), HCO_3^- , and H_2O_2), as well as the efficiency of H_2O_2 use, have not been clearly reported. Moreover, further discussion is needed on the major oxidant produced by the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system; the reactive oxidants suggested by the two previous studies contradict each other [12, 13].

The objectives of this study are (i) to assess the potential of the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system for degrading phenol by investigating factors that affect the phenol degradation rate, and (ii) to discuss the reactive oxidants mainly responsible for the phenol degradation by the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system. For these purposes, we examined phenol degradation by the Cu(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system with various levels of pH and doses of reagents. The Cu(II)/ $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system was compared to the Co(II)/ $\text{HCO}_3^-/\text{H}_2\text{O}_2$ system, a similar Fenton-like system enhanced by HCO_3^- [14–16]. The degradation of several other organic compounds, such as benzoic acid, bisphenol A, and 4-chlorophenol, was also examined. To gain insight into the reactive oxidants produced by the system, experiments using scavengers and a probe compound of reactive oxidants were performed. In addition, aerating CO_2 gas was tested as a means of supplying HCO_3^- to the Cu(II)/ H_2O_2 system.

Materials and methods

Reagents

All chemicals were of reagent grade and used without further purification. Acetonitrile and 2,9-dimethyl-1,10-phenanthroline (DMP, Neocuproine) were from J.T. Baker® (USA) and TCI Co. (Japan), respectively, and all the other chemicals were obtained from Sigma-Aldrich Co. (USA). 18.2 M Ω -cm Milli-Q water from a Millipore system was used to prepare solutions. CuSO_4 was used to prepare the Cu(II) stock solution (10 mM). The stock solution of sodium bicarbonate (NaHCO_3) (0.5 M) was prepared freshly prior to the experiment.

Experimental Setup and Procedure

All experiments were conducted in a 125 mL Erlenmeyer flask open to the atmosphere at room temperature ($22 \pm 2^\circ\text{C}$). For some experiments, the solution was aerated with ultrapure CO_2 gas using a diffuser for saturation (for 30 min prior to the experiment). The solution pH was adjusted using a 1 N HClO_4 and 1 N NaOH solution. The solutions for pH 7 and 8 were buffered with 5 and 1 mM phosphate, respectively. In all experiments, pH variations were less than 0.3 units during the reaction. The reaction was initiated by adding hydrogen peroxide (H_2O_2) to the prepared solution containing Cu(II) and the organic compound (and HCO_3^-). Samples were withdrawn using a 10 mL glass syringe at predetermined times and filtered through a 0.2- μm hydrophilic PTFE filter. The possible reactions of Cu(II) in samples were immediately quenched by adding 20 μL of 200 mM ethylenediaminetetraacetic acid (EDTA). All experiments were carried out at least in triplicate, and the average values and standard deviations (error bars) were presented. Main experimental conditions include: $[\text{Cu(II)}]_0 = 0.1 \text{ mM}$, $[\text{HCO}_3^-]_0 = 50 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Phenol}]_0 = 0.1 \text{ mM}$, and $\text{pH} = 10$. For some experiments, the doses of Cu(II), HCO_3^- , H_2O_2 , and pH were varied in the ranges of 0.001–0.1 mM, 1–100 mM, 1–100 mM, and 7–12, respectively. All the experimental conditions were summarized in Table S1 in the supplementary data.

Analytical Methods

The concentration of organic compounds was measured by high-performance liquid chromatography (HPLC; Dionex Ultimate 3000; Thermo Fisher Scientific Inc., USA) with UV absorbance detection (at 277, 230, 230, 227 nm for phenol, 4-chlorophenol, bisphenol A, and benzoic acid, respectively). Separation was performed on an Agilent - Eclipse XDB - C18 column (150 mm $\times$ 4.6 mm, 5 μ m) using a binary mixture of 0.1 % (w/w) phosphoric acid solution and acetonitrile as an eluent at a flow rate of 1.5 mL/min. H_2O_2 was analyzed using the titanium sulfate method on a UV/Vis spectrophotometer (S-3100; Scinco Co., Korea) [17]. Reactive Black 5 (RB5) was analyzed by measuring the absorbance at 597 nm. Chemical oxygen demand (COD) was analyzed by the KMnO_4 method using a COD analysis kit (COD-Mn-L; Humas Co., Korea).

Results

Phenol Degradation by the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ System: Comparison to the $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ System

The $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system degraded phenol (approximately 90% degradation in 2 h) much better than the $\text{Cu(II)/H}_2\text{O}_2$ system (10% degradation in 2 h) (Figure 1a); the phenol degradation by Cu(II)/HCO_3^- and $\text{H}_2\text{O}_2/\text{HCO}_3^-$ was negligible. The COD removal was 38% in 2 h during the phenol degradation (Figure S1 in the supplementary data) The decomposition of H_2O_2 was also greater in the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system than in the $\text{Cu(II)/H}_2\text{O}_2$ system (Figure 1b), indicating that HCO_3^- accelerates the Cu(II) -catalyzed decomposition of H_2O_2 to increase the production of reactive oxidants that can degrade phenol.

FIG. 1 DEGRADATION OF PHENOL AND DECOMPOSITION OF H_2O_2 BY THE $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ SYSTEM (a, b) AND BY THE $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ SYSTEM (c, d) ($[\text{PHENOL}]_0 = 0.1 \text{ mM}$; $[\text{Cu(II)}]_0 = [\text{Co(II)}]_0 = 0.1 \text{ mM}$; $[\text{HCO}_3^-]_0 = 50 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $\text{pH} = 10.0$)

The $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system (a similar HCO_3^- -enhanced Fenton-like system) led to 72% degradation of phenol under the same conditions (Figure 1c); phenol was not degraded by other combinations, such as Co(II)/HCO_3^- , $\text{Co(II)/H}_2\text{O}_2$, and $\text{H}_2\text{O}_2/\text{HCO}_3^-$. Like the Cu(II) -catalyzed systems, the $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system exhibited greater H_2O_2 decomposition than the $\text{Co(II)/H}_2\text{O}_2$ system (Figure 1d).

Comparing the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ and $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ systems (Figures 1a and 1b versus Figures 1c and 1d), the rates of phenol degradation and H_2O_2 decomposition were higher in the $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system than in the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system. However, the degree of phenol degradation was greater in the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system (90% degradation in 60 min) than in the $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system (72% degradation in 30 min). As a result, the H_2O_2 use efficiencies (i.e., $\Delta[\text{Phenol}]/\Delta[\text{H}_2\text{O}_2]$, calculated from the results of Figure 1) were higher in the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system than in the $\text{Co(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system (Figure S2 in the supplementary data).

Effects of Cu(II) , HCO_3^- , H_2O_2 Doses, and Solution pH

The effects of Cu(II) , HCO_3^- , and H_2O_2 doses on the degradation of phenol were examined in the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system (Figure 2). The rate of phenol degradation was presented by the pseudo-first order rate constant (k), which was determined using the data points that satisfy $R^2 > 0.9$ (those for 50–70% phenol degradation depending on the condition). The k value increased with increasing doses of Cu(II) and HCO_3^- . However, when the H_2O_2 dose was adjusted, the optimal rate of phenol degradation was observed at 5 mM H_2O_2 .

FIG. 2 EFFECTS OF Cu(II) , HCO_3^- , AND H_2O_2 DOSES ON THE PHENOL DEGRADATION RATE BY THE $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ SYSTEM ($[\text{PHENOL}]_0 = 0.1 \text{ mM}$; $\text{pH} = 10.0$; $[\text{Cu(II)}]_0 = 0.1 \text{ mM}$ FOR VARIOUS DOSES OF HCO_3^- AND H_2O_2 ; $[\text{HCO}_3^-]_0 = 50 \text{ mM}$ FOR VARIOUS DOSES OF Cu(II) AND H_2O_2 ; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$ FOR VARIOUS DOSES OF Cu(II) AND HCO_3^-).

The phenol degradation by the $\text{Cu(II)/HCO}_3^-/\text{H}_2\text{O}_2$ system was optimal at pH 10 (Figure 3a); the k value increased with increasing pH from 7 to 10, then drastically decreased under alkaline pH conditions. However, the rate of H_2O_2 decomposition continued to increase with increasing pH from 7 to 12 (Figure 3b). In addition, RB5 (believed to be more vulnerable to oxidation [6, 7]) was employed as a reference target compound to investigate the pH effect. Contrary to phenol, RB5 was degraded faster under alkaline pH conditions (Figure 3c), exhibiting a similar trend to the H_2O_2 decomposition (Figure 3b).

FIG. 3 RATES OF PHENOL DEGRADATION (a), H₂O₂ DECOMPOSITION (b), AND RB5 DEGRADATION (c) AS A FUNCTION OF pH ([PHENOL]₀ = 0.1 mM; [H₂O₂]₀ = 10 mM; [RB5]₀ = 50 mg/L; [Cu(II)]₀ = 0.1 mM; [HCO₃⁻]₀ = 50 mM)

Degradation of Selected Organic Compounds

Several organic compounds (benzoic acid, bisphenol A, and 4-chlorophenol) were also tested for degradation by the Cu(II)/HCO₃⁻/H₂O₂ system (Figure 4). Benzoic acid was resistant to degradation, whereas the other compounds were successfully degraded, exhibiting degradation kinetics similar to that of phenol.

FIG. 4 DEGRADATION OF SEVERAL ORGANIC COMPOUNDS BY THE Cu(II)/HCO₃⁻/H₂O₂ SYSTEM ([BENZOIC ACID]₀ = [PHENOL]₀ = [BISPHENOL A]₀ = [4-CHLOROPHENOL]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [HCO₃⁻]₀ = 50 mM; [H₂O₂]₀ = 10 mM; pH = 10.0)

Effects of Oxidant Scavengers and Copper-chelating Agents

Effects of oxidant scavengers (methanol and *tert*-butanol) on the rate of phenol degradation were examined in the Cu(II)/HCO₃⁻/H₂O₂ system (Figure 5). The addition of methanol inhibited phenol degradation; the *k* value gradually decreased from 0.034 min⁻¹ to 0.020 min⁻¹ when the input concentration of methanol increased up to 1 M. On the other hand, *tert*-butanol did not inhibit the phenol degradation; in fact, the *k* value increased with the increasing concentration of *tert*-butanol.

FIG. 5 EFFECTS OF OXIDANT SCAVENGERS (*tert*-BUTANOL AND METHANOL) ON THE PHENOL DEGRADATION RATE BY THE Cu(II)/HCO₃⁻/H₂O₂ SYSTEM ([PHENOL]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [HCO₃⁻]₀ = 50 mM; [H₂O₂]₀ = 10 mM; pH = 10.0)

The addition of copper-chelating agents such as EDTA, DMP, and citrate significantly inhibited the phenol degradation by the Cu(II)/HCO₃⁻/H₂O₂ system (Figure 6). EDTA completely stopped the phenol degradation, and DMP and citrate led to less than 10% of phenol degradation in 2 h.

FIG. 6 EFFECTS OF COPPER-CHELATING AGENTS ON PHENOL DEGRADATION BY THE Cu(II)/HCO₃⁻/H₂O₂ SYSTEM ([PHENOL]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [EDTA]₀ = [DMP]₀ = [CITRATE]₀ = 10 mM; [H₂O₂]₀ = 10 mM; [HCO₃⁻]₀ = 50 mM; pH = 10.0)

Aeration of CO₂ in the Cu(II)/H₂O₂ System

To explore the potential of CO₂ for supplying HCO₃⁻, the phenol degradation by the Cu(II)/H₂O₂ system was examined by aerating CO₂ into the solution. As shown in Figure 7, the Cu(II)/H₂O₂ system with CO₂ aeration degraded phenol better than that without CO₂ aeration, indicating that CO₂ aeration is indeed effective in supplying HCO₃⁻ to the Cu(II)/H₂O₂ system. The measured alkalinity of the CO₂-aerated solution was equivalent to that of the 43.3 mM HCO₃⁻ solution.

FIG. 7 DEGRADATION OF PHENOL BY THE Cu(II)/H₂O₂ SYSTEM WITH CO₂ AERATION ([PHENOL]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 10 mM; pH = 10.0)

Discussion

Production of Reactive Oxidants by the Cu(II)/HCO₃⁻/H₂O₂ System

The Cu(II)/H₂O₂ system is known to produce reactive oxidants via the Fenton-like reaction mechanism [7, 18, 19]. Cu(II) is reduced to Cu(I) by the reaction with H₂O₂, producing superoxide radical anion (O₂^{•-}) (reaction 1). Then, the reaction of Cu(I) with H₂O₂ produces reactive oxidants, i.e., [•]OH and Cu(III) (reaction 2); [•]OH and Cu(III) are produced by the one-electron and two-electron transfer reactions, respectively. Reaction 1 is believed to be slower than reaction 2, becoming the rate-determining step (RDS) for the production of reactive oxidants [7].

The addition of HCO₃⁻ can change the kinetics of the reaction of Cu(II) with H₂O₂ by forming Cu(II)-carbonate complexes. In the presence of HCO₃⁻ (50 mM), Cu(II)-carbonate complexes form in the pH range of 4–11 (Figure S3 in the supplementary data). These complexes are believed to have higher reactivity with H₂O₂ than those in the absence of HCO₃⁻ (e.g., Cu(II)-hydroxo complexes and Cu(II) oxide); the decomposition of H₂O₂ was indeed accelerated in the presence of HCO₃⁻ (Figure 1b). When strong Cu(II)-chelating agents, such as citrate, EDTA, and DMP, were added to the Cu(II)/HCO₃⁻/H₂O₂ system (to replace Cu(II)-carbonate complexes with the Cu(II) complexes of added ligands), the phenol degradation was almost completely blocked (Figure 6 in the supplementary data), confirming the critical roles of Cu(II)-carbonate complexes.

On the other hand, it has been reported that HCO₃⁻ can directly react with H₂O₂ to produce peroxymonocarbonate (HCO₄⁻) (Reaction 3) [20, 21]. HCO₄⁻ as a strong oxidant ($E^\circ[\text{HCO}_4^-/\text{HCO}_3^-] = 1.8 \text{ V}_{\text{NHE}}$ [20]) is known to oxidize

sulfides [20], dyes, and 4-chlorophenol [21].

However, phenol degradation by the $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system was negligible under the conditions employed in this study (Figure 1). It appears that much higher concentrations of HCO_3^- and H_2O_2 may be required to generate a significant level of HCO_4^- .

Compared to the $\text{Co(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system (a similar Fenton-like system), the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system appears to have lower catalytic activity for decomposing H_2O_2 into reactive oxidants; the rates of both phenol degradation and H_2O_2 decomposition were lower (Figure 1). However, the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system used H_2O_2 more efficiently (Figure S2 in the supplementary data), implying that the yields of reactive oxidants are higher or that reactive oxidants that are more selective toward the reaction with phenol are generated.

Nature of Reactive Oxidants

Earlier studies suggested that Cu(III) species are the major reactive oxidants produced by the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system under neutral and alkaline pH conditions [6, 7, 19], and that $\cdot\text{OH}$ may be dominantly produced under lower pH conditions [6, 7]. However, more recently, Lee et al. suggested that Cu(III) species are dominantly produced regardless of pH in the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system, and that they exhibit $\cdot\text{OH}$ -like reactivity [8].

In the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system, discrepant views were presented about the identity of the reactive oxidants [12, 13]. Cheng et al. [12] and Peng et al. [13] suggested Cu(III) and $\cdot\text{OH}$ as the major reactive oxidants, respectively. This discrepancy appears to result mainly from different observations of the effects of radical scavengers, which did not inhibit the degradation of the target compound in Cheng et al.'s study, whereas Peng et al. observed significant inhibitory effects by radical scavengers. However, the inhibitory effects by typical $\cdot\text{OH}$ scavengers, such as 2-propanol and *tert*-butanol, do not necessarily identify $\cdot\text{OH}$ as the major reactive oxidant, because the $\cdot\text{OH}$ scavengers can also react with Cu(III) [8, 19]. Various Cu(III) species of different reactivity can exist, depending on their ligands, and some of them can have high reactivity with 2-propanol and *tert*-butanol.

Experimental results in this study present evidence against $\cdot\text{OH}$, supporting the production of Cu(III) species as major reactive oxidants in the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system. First, the failure of excess *tert*-butanol to quench the phenol degradation is not explained by the reaction of $\cdot\text{OH}$ (Figure 5); the rate of phenol degradation instead increased, for which no clear explanation can be provided. Although the addition of methanol somewhat inhibited the phenol degradation (Figure 5), the degree of inhibition (40% decrease of k at 1 M methanol) is far from the observation anticipated from the reaction of $\cdot\text{OH}$. The concentrations and second-order rate constants of the compounds present in the solution were as follows:

$$[\text{Phenol}]_0 = 0.1 \text{ mM}, k(\cdot\text{OH} + \text{phenol (at pH 10)}) = 8.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1};$$

$$[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}, k(\cdot\text{OH} + \text{H}_2\text{O}_2) = 3 \times 10^7 \text{ M}^{-1}\text{s}^{-1};$$

$$[\text{HCO}_3^-]_0 = 50 \text{ mM}, k(\cdot\text{OH} + \text{HCO}_3^-/\text{CO}_3^{2-} \text{ (at pH 10)}) = 1.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1};$$

$$[\text{Methanol}] = 1 \text{ M}, k(\cdot\text{OH} + \text{methanol}) = 9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1} [22],$$

Given these concentrations, almost complete quenching of $\cdot\text{OH}$ by 1 M methanol would be anticipated. Second, the negligible degradation of benzoic acid (Figure 4) also weighs against the reaction of $\cdot\text{OH}$; in fact, the second-order rate constant of benzoic acid (benzoate, $k(\cdot\text{OH} + \text{benzoate}) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) is comparable to that of phenol ($k(\cdot\text{OH} + \text{phenol (at pH 10)}) = 8.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [22].

The reactivity of Cu(III) species (likely present as Cu(III) complexes) is believed to vary with the ligands coordinated to Cu(III) . Different Cu(III) species including Cu(III) -carbonate complexes can be produced by the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system, and the speciation of these Cu(III) complexes is determined by several parameters, such as pH and concentrations of Cu(III) and HCO_3^- . Therefore, the reactivity of Cu(III) species formed in the $\text{Cu(II)}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ system can vary depending on these parameters.

The different trends in the pH-dependency of phenol and RB5 degradation by the Cu(II)/HCO₃⁻/H₂O₂ system (Figures 3a and 3c) may be attributed to the pH-dependent Cu(III) speciation. At pH > 10, weaker oxidizing species (which can degrade RB5 but hardly phenol) appear to be formed; these species may be Cu(III)-hydroxo complexes with high coordination numbers, e.g., Cu(OH)₃, Cu(OH)₄⁻, etc.

The discrepant effects of oxidant scavengers observed by previous studies [12, 13] are also likely due to the occurrence of Cu(III) species of different reactivities. Cheng et al. [12] used higher concentrations of Cu(II) and HCO₃⁻ than Peng et al. [13]; this difference may have affected the speciation of Cu(III), producing Cu(III) species of different reactivities with the oxidant scavengers.

Factors Affecting the Production of Reactive Oxidants

In the Cu(II)/HCO₃⁻/H₂O₂ system, factors such as pH and doses of Cu(II), HCO₃⁻ and H₂O₂ affect the production of reactive oxidants and the resultant phenol degradation. Increasing doses of Cu(II) and HCO₃⁻ increased the rate of phenol degradation (Figure 2). The increase in the dose of Cu(II) (as a catalyst) accelerates the catalytic decomposition of H₂O₂ into reactive oxidants. In addition, the increase in the dose of HCO₃⁻ leads to increased formation of Cu(II)-carbonate complexes that are believed to have higher reactivity with H₂O₂ than those in the absence of HCO₃⁻ (e.g., Cu(II) oxide). According to the calculation using MINEQL+ 4.6, more Cu(II)-carbonate complexes, such as CuCO₃ and Cu(CO₃)₂²⁻, evolved under mild alkaline conditions when the dose of HCO₃⁻ increased from 1 mM to 100 mM (Figure S4 in the supplementary data).

For the H₂O₂ dose, the rate of phenol degradation was maximized at 5 mM H₂O₂ (Figure 2). The inhibitory effect at [H₂O₂] > 5 mM is attributed to the scavenging of reactive oxidants by excess H₂O₂. Considering that the phenol degradation was not inhibited (or slowed down) by an excess amount of HCO₃⁻, the reactions of reactive oxidants (likely Cu(III)-carbonate complexes) may be more selective to H₂O₂ than HCO₃⁻. Note that, for [•]OH, the reaction with HCO₃⁻ is even faster than that with H₂O₂ (refer to $k(^{\bullet}\text{OH} + \text{H}_2\text{O}_2) = 3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and $k(^{\bullet}\text{OH} + \text{HCO}_3^-/\text{CO}_3^{2-} \text{ (at pH 10)}) = 1.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [22]).

The phenol degradation was optimized at pH 10 (Figure 3a). The degradation of phenol at pH < 10 accelerates because the catalytic decomposition of H₂O₂ into reactive oxidants accelerates with increasing pH (Figure 3b). The reduction of Cu(II) by H₂O₂ (reaction 1, RDS) accelerates with increasing pH because the reaction proceeds via the complexation of Cu(II) with a deprotonated form of H₂O₂ (HO₂⁻, pK_a of H₂O₂ = 11.75) as the primary step. As described in Section 4.2, at pH > 10, weaker Cu(III) species that hardly degrade phenol may arise.

Applications of the Cu(II)/HCO₃⁻/H₂O₂ System

The Cu(II)/HCO₃⁻/H₂O₂ system can potentially be used to oxidize refractory organic contaminants in water and wastewater. For practical application, Cu(II) needs to be immobilized in order to recycle the catalyst and minimize the (eco)toxic impacts of released copper ions. Particularly for treating drinking water, the concentration of released copper ions should be controlled at less than 1 mg/L; the regulation levels of copper in Korea and the United States are 1 mg/L (15.7 μM) and 1.3 mg/L (20.5 μM), respectively [23, 24].

In addition, as demonstrated in Figure 7, aeration by CO₂ gas is an effective alternative for supplying HCO₃⁻ into water to implement the Cu(II)/HCO₃⁻/H₂O₂ system. When the Cu(II)/HCO₃⁻/H₂O₂ system is used to treat industrial wastewater, waste CO₂ discharged by neighboring industries may be used for this purpose.

Conclusions

The Cu(II)/HCO₃⁻/H₂O₂ system was shown to effectively degrade phenolic compounds, better than the Cu(II)/H₂O₂ system. Cu(II)-carbonate complexes formed in the presence of HCO₃⁻ appear to have higher catalytic activity for decomposing H₂O₂ into reactive oxidants. Cu(III) species (likely complexed forms with carbonate) may be the major reactive oxidants responsible for the phenol degradation. Several parameters, such as pH and doses of Cu(II), HCO₃⁻, and H₂O₂, influenced the rate of phenol degradation by affecting the generation and consumption of reactive oxidants as well as their speciation. The Cu(II)/HCO₃⁻/H₂O₂ system can be used to treat water and

wastewater after addressing such issues as the immobilization and long-term stability of the catalyst, environmental impacts of released copper ions, and economic feasibility.

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Supplementary Data

TABLE S1. SUMMARY OF EXPERIMENTAL CONDITIONS

No	Cu(II) (mM)	Co(II) (mM)	HCO ₃ ⁻ (mM)	H ₂ O ₂ (mM)	Organic compounds (mM)	Oxidant scavengers (mM)	pH	Figure
1	0.1	-	50	10	0.1 (Phenol)	-	10.0	Fig. 1 (a, b)
2	-	0.1	50	10	0.1 (Phenol)	-	10.0	Fig. 1 (c, d)
3	0.001, 0.005, 0.01, 0.02, 0.05, 0.1	-	50	10	0.1 (Phenol)	-	10.0	Fig. 2
4	0.1	-	1, 5, 10, 20, 50, 100	10	0.1 (Phenol)	-	10.0	Fig. 2
5	0.1	-	10	1, 5, 10, 20, 50, 100	0.1 (Phenol)	-	10.0	Fig. 2
6	0.1	-	50	10	0.1 (Phenol)	-	7.0, 8.0, 9.0, 10.0, 11.0, 12.0	Fig. 3 (a, b)
7	0.1	-	50	10	50 mg/L (RB5)	-	7.0, 8.0, 9.0, 10.0, 11.0, 12.0	Fig. 3 (c)
8	0.1	-	50	10	0.1 (Benzoic acid, Phenol, Bisphenol A, 4-Chlorophenol)	-	10.0	Fig. 4
9	0.1	-	50	10	0.1 (Phenol)	50, 200, 1000 (<i>tert</i> -Butanol, Methanol)	10.0	Fig. 5
10	0.1	-	(CO ₂ aeration)	10	0.1 (Phenol)	-	10.0	Fig. 6

FIG. S1 REMOVAL OF COD DURING THE PHENOL DEGRADATION BY THE Cu(II)/HCO₃⁻/H₂O₂ SYSTEM ([PHENOL]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [HCO₃⁻]₀ = 50 mM; [H₂O₂]₀ = 10 mM; pH = 10.0)

FIG. S2 H₂O₂ USE EFFICIENCY FOR PHENOL DEGRADATION BY THE Cu(II)/HCO₃⁻/H₂O₂ AND Co(II)/HCO₃⁻/H₂O₂ SYSTEMS (CALCULATED FROM THE DATA OF FIGURE 1)

FIG. S3 SPECIATION OF Cu(II) IN THE ABSENCE (a) AND PRESENCE (b) OF HCO₃⁻, CALCULATED BY MINEQL+ 4.6. ([Cu(II)]₀ = 0.1 mM; [HCO₃⁻]₀ = 50 mM)

FIG. S4 SPECIATION OF Cu(II) IN THE PRESENCE OF HCO_3^- WITH DIFFERENT CONCENTRATIONS, CALCULATED BY MINEQL+ 4.6 ([Cu(II)]₀ = 0.1 mM)