*Research Article*

# Application of a Novel Semiconductor Catalyst, CT, in Degradation of Aromatic Pollutants in Wastewater: Phenol and Catechol

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Water-soluble phenol and phenolic compounds were generally removed via advanced oxidation processes. A novel semiconductor catalyst, CT, was the first-time employed in the present study to degrade phenol and catechol. The phenolic compounds (initial concentration of 88 mg $L^{-1}$) were completely mineralized by the CT catalytic nanoparticles (1%) within 15 days, under acidic condition and with the presence of mild UV radiation (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$). Under the same reaction condition, 1% $TiO_2$ (mixture of rutile and anatase, nanopowder, <100 nm) and $H_2O_2$ had lower removal efficiency (phenol: <42%; catechol: <60%), whereas the control (without addition of catalysts/$H_2O_2$) only showed <12% removal. The processes of phenol/catechol removal by CT followed pseudo-zero-order kinetics. The aromatic structures absorbed the UV energy and passed to an excited state, which the CT worked on. The pollutants were adsorbed on the CT's surface and oxidized via charge-transfer and hydroxyl radical generation by CT. Given low initial concentrations, a circumstance encountered in wastewater polishing, the current set-up should be an efficient and less energy- and chemical-consumptive treatment method.

## 1. Introduction

Phenol and phenolic substances, such as catechol and hydroquinone, are widely used as raw materials in petrochemical, chemical, and pharmaceutical industries [1]. They also occur in various common phenolated industrial effluents, with concentrations ranging between 35 and 8000 mg $L^{-1}$ [2]. These highly water-soluble and stable compounds are toxic, carcinogenic, mutagenic, and teratogenic [3] and potentially may lead to adverse effects in human and aquatic organisms [4]. Therefore, their concentrations in the industrial effluents are usually regulated. For example, in China, phenol at concentrations above 0.3 mg $L^{-1}$, respectively, is not allowed to be discharged to the natural water bodies, according to the Integrated Wastewater Discharge Standard [5].

Treatment processes for phenolic wastewater include physical, biological, and chemical methods. High concentration phenolic wastewaters refer to those with phenol more than 1000 mg $L^{-1}$, which are recycled via methods such as adsorption or solvent extraction [6–8]. Intermediate concentration phenolic wastewaters are those with phenol levels between 5 and 500 mg $L^{-1}$, which are treated by biological methods [9] or chemical oxidation [10]. Generally speaking, it is practically impossible to remove phenol and phenolic substances simply by using conventional biologic treatment [11]. Advanced oxidation processes (AOPs) have been widely

used for the treatments over the last few decades. Particularly, AOPs combining oxidants (e.g., ozone and $H_2O_2$), UV radiation, catalysts (e.g., $TiO_2$ and $V_2O_5$), and ultrasound have received most of the attention [12]. For example, Gurol and Vatistas [13] treated mixtures of phenol, p-cresol, 2, 3-xylenol, and catechol by ozone, UV light, and a combination of ozone and UV light (photolytic ozonation). They observed that the photolytic ozonation removed more than 95% of the total organic carbon (much higher than the <30% of the removal by ozonation and UV radiation alone). Li et al. [14] observed that phenol was oxidized rapidly by a $Ti/SnO_2$-Sb anode, and its concentration decreased from around 490 mg/L to 0 after the electrolysis for 5 hr. Ŭgurlu and Karaoğlu [15] reported that more than 90% phenol was degraded within 24 hr using $UV/H_2O_2$ and $UV/H_2O_2/TiO_2/$Sepiolite, much greater than by simply using UV or $H_2O_2$ alone.

Despite the progress in AOPs research, it seems that practical applications of these AOPs have some limitations such as consumption of large amounts of chemicals (e.g., ozone and $H_2O_2$) and energy (UV and electrochemical oxidation) [16]. In this regard, we attempted to employ a novel catalyst, charge transfer auto oxidation-reduction type semiconductor catalyst (CT catalyst), for the degradation of phenol and phenolic substances. This nanosized (around 70 nm) material/crystal was developed by one of the authors, Dr. Shoji Ichimura, via sintering of a mixture of MnO, CoO, and $TiO_2$ in Pt and Pd complex powder at 1350°C [17]. CT is a crystal with an 8-phased perovskite form inside a 6-phased spinel structure. The core of the crystal has the base composition form with arranged electron donor and acceptor pair and electron carrier chain and oxidation/reduction center, which allows electron chain reactions to take place and be mediated. It simply relies on thermal energy to vibrate the crystal and cause electron transfer [17], which is different from photocatalysts, function with the presence of UV radiation [18]. With enough thermal energy, electron donor in CT produces electron ($e^-$) and positive hole ($h^+$). $h^+$ moves to oxidation centre in CT to oxidize the pollutant in solution motivated by oxidation activator. The electron moves to the electron acceptor in CT by electron carrier and then reaches the reduction centre in CT to reduce substances like oxygen in water motivated by reduction activator. This catalyst has been widely used in tiles in Japan (>8000 buildings as an environmentally friendly material for odor removal), but not in any other applications such as water/wastewater treatment. Yet, according to CT's remarkable characteristic that it can function in the dark, CT should have enormous potential in pollutant removal/degradation, especially in circumstances when light is not easily accessible in pollutant-carrying media (e.g., particles, cloudy water, and colored water). However, such chemical- and energy-saving applications have not been attempted previously.

In this study, we conducted experiments to degrade phenol and catechol in water using CT catalytic nanoparticles. A mild UV radiation (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$), not sufficient to induce effective photocatalysis in pure $TiO_2$ catalyst [1], was provided. The hypothesis was that, following exposure to UV

radiation, aromatic compounds would absorb the UV energy and reach excited state [19], upon which the CT catalysts could react (causing electron transfers). This eventually might lead to decomposition of these compounds. Compared with $TiO_2$, we expected that CT might need low energy (mild UV radiation). Compared with $H_2O_2$, CT catalyst might be more efficient, because hydroxyl radicals released by $H_2O_2$ should be depleted with a short period of time, not be sufficient to support the mineralization of these phenolic compounds.

Overall, the objectives of this study were as follows: (1) to identify whether CT catalyst can be applied in treating/removing phenolic compound in water; (2) to determine kinetics of the catalysis process; and (3) to understand catalytic mechanisms of the CT catalysts. We hope that the data would provide fundamental information for a future design of reactors in phenolic wastewater treatment using CT catalyst.

## 2. Materials and Methods

The CT catalyst is invented by one of the authors, Dr. Shoji Ichimura, and is commercially available. CT in this study was provided by FIRAC International Co., Ltd. (Dr. Shoji Ichimura owned company) for free. Phenol, catechol, hydrogen peroxide (30% w/w), and $TiO_2$ (mixture of rutile and anatase, nanopowder, <100 nm) were of analytic grade (Sigma-Aldrich Chemical Co.). Phenol and catechol were chosen as the target pollutants, and the initial concentrations were chosen at 88 mg L$^{-1}$ (chemical oxygen demand (COD): 179 mg L$^{-1}$; total organic carbon (TOC): 54 mg L$^{-1}$) and 91.8 mg L$^{-1}$ (COD: 164 mg L$^{-1}$; TOC: 57 mg L$^{-1}$), respectively. The pH level of 3, simulating phenol-containing industrial wastewater, was adjusted using hydrochloride acid and sodium hydroxide solutions.

Four treatments, namely, pollutant + UV, pollutant + UV + 1% CT, pollutant + UV + 1% $TiO_2$, and pollutant + UV + $H_2O_2$ (60 $\mu$L $H_2O_2$ added into 200 mL phenolic solution), were applied to the solutions containing phenol and catechol. Each treatment has 2 replicates. The choice of the level of CT (1%) was based on our preliminary tests. $H_2O_2$ amount, as hydroxyl radical generator and scavenger, was chosen according to previous reports [20]. Flasks (250 mL) with the phenolic solutions were placed in a shaker, which located between two mercury UV lamps (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$). Positions of the flasks were rotated in order to prevent an uneven exposure of the UV radiation. The experiments were conducted at room temperature (20°C) and had lasted for 10–15 days until complete elimination of TOC in the flasks occurred in any treatment.

To further investigate mechanism of CT catalyst in degrading phenolic compounds, the role of CT and UV radiation in reacting with the phenol was compared. One treatment involved that a phenol solution (initial concentration of 76 mg L$^{-1}$) was exposed to UV radiation for 4 days followed by 1% CT treatment in the dark. The other treatment involved a reversed sequence of the treatments in which a solution (initial concentration of 76 mg L$^{-1}$) was subjected
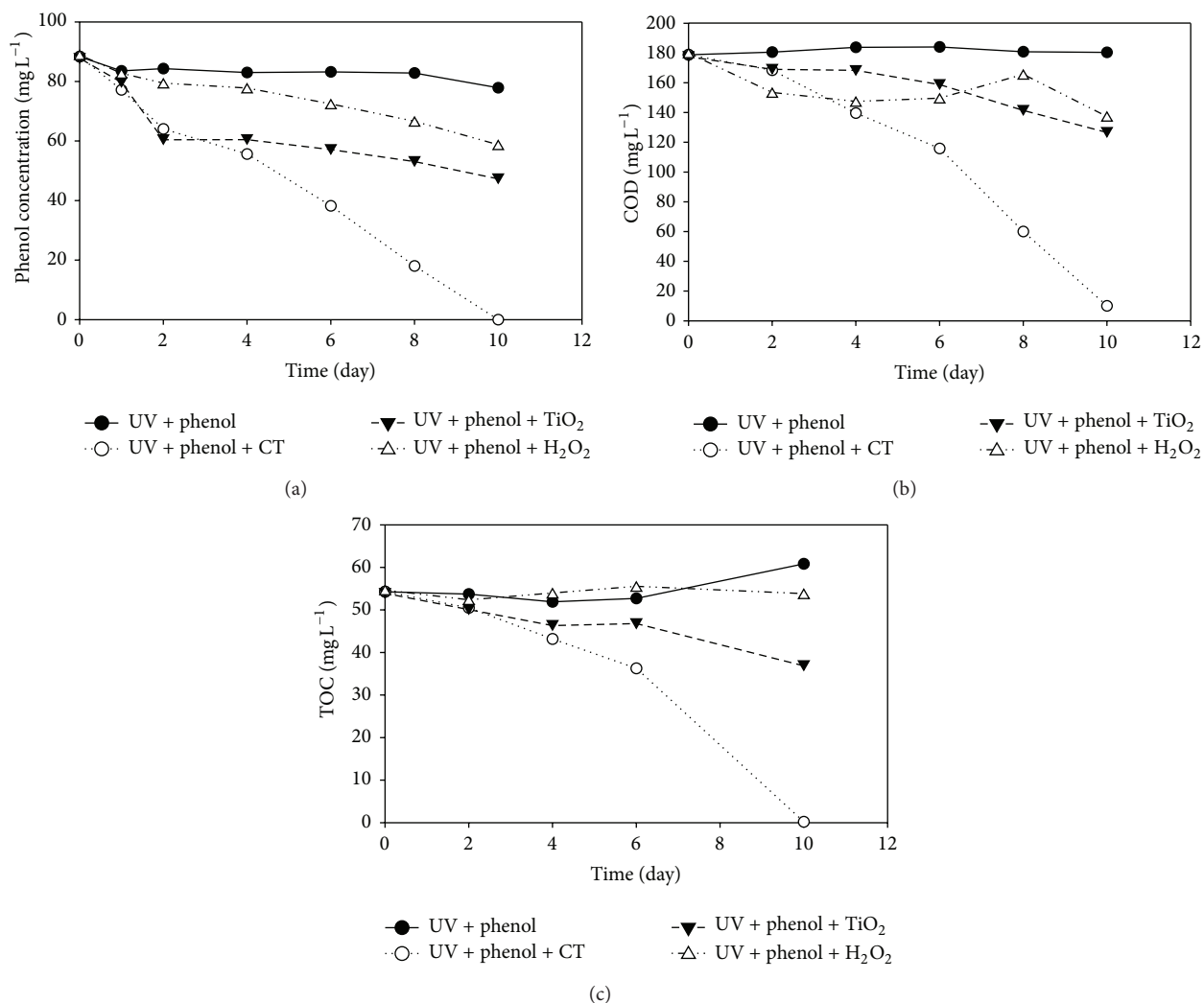
(a)

(b)

(c)

FIGURE 1: Time-dependent degradation of phenol by CT catalyst compared with $TiO_2$, $H_2O_2$ ((a) phenol concentration; (b) COD; (c) TOC).

to 1% CT treatment and then followed by the UV radiation. The comparison of the outcome allowed for an identification of difference between functions of UV radiation and CT catalyst.

During the experiments, the flasks were withdrawn from the shaker at predetermined time and the solutions were centrifuged at 3000 r/min for 30 min using a centrifuge (Allegra 6R). Concentrations of phenol, catechol, total organic carbon (TOC), chemical oxygen demand (COD), and pH were analyzed. Briefly, the phenol concentration was measured using the 4-aminoantipyrine method as described in Standards Methods [21], while that of catechol was measured according to Liu et al. [22]. Level of TOC was analyzed using a TOC analyzer (TOC-VCPH) based on the combustion-infrared method [23]. Level of COD was measured using open reflux method [21]. Level of pH was determined using a pH meter.

High performance liquid chromatography (HPLC, Agilent 1200), equipped with a ZORBAX column (Eclipse XDB-C18 ID = 4.6 mm, length = 150 mm) and a UV detector (used at working wavelength of 215 nm), was used to analyze

the intermediate compounds of catechol, hydroquinone, and benzoquinone from the treatments of UV + CT + phenol and UV + $TiO_2$ + phenol, respectively. A ratio of 1/3 (V/V) of methanol/5% orthophosphoric acid was used as the mobile phase at a flow rate of 1.0 mL min$^{-1}$. The injection volume was 10 $\mu$L, while the column temperature was set at 25°C. Before HPLC analysis, each sample was filtered through a 0.22 $\mu$m membrane filter (water phase filter, polyethersulfone).

## 3. Results and Discussion

*3.1. Removal of Phenolic Compounds by CT Catalyst.* Heterogeneous photocatalytic oxidation process generally is not suitable for high concentration phenolic wastewater. Instead, it is used as the pretreatment or the posttreatment combined with the biological treatment to achieve acceptable concentration efficiently and economically feasible [16, 24] (Table 1).

Time-dependent degradation of phenol and catechol was shown in Figures 1 and 2, respectively. Phenol was completely removed in the treatment of phenol + UV + 1% CT

TABLE 1: Summary of phenol treatment processes.

| Processes | Phenol level in wastewater | Capacity | Stage of development | Capital cost | Operating cost | Performance | Complete destruction of phenol | Residue generation | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Physical | High ($>500\ mg\,L^{-1}$) | High | | High | High | For phenol recovery, >99% | No | Recovered/condensed phenol for further treatment; adsorbate must be processed for regeneration; spent adsorbates needs treatment/disposal | [25] |
| Liquid-liquid extraction, carbon adsorption, resin adsorption, and so forth | | | Well developed | | | | | | |
| Liquid membrane | | | Developed | | | | No | Recovered/condensed phenol for further treatment | [25] |
| Biological | Intermediate ($<500\ mg\,L^{-1}$) | High | Developed | High | Low | For final treatment, >99% | No | Sludge needs further treatment/disposal | [25] |
| Chemical | | | | | | | | | |
| Wet air oxidation | High | High | Well developed | High | High | Pretreatment for bio-treatment, high temperature/pressure technology | No | Some | [25] |
| Supercritical water oxidation | High | High | Developed | High | High | Up to 100%, high temperature/pressure technology | Yes | Not likely | [25, 26] |
| Ozonation | Low-intermediate | High | Developed | High | High | >99% | No | Off gasses needs further treatment | [25] |
| Oxidation by chlorine dioxide, hydrogen peroxide and potassium permanganate | Intermediate | Low | Developed | Low | High | Up to 100%, generally require facilities for oxidants generation on site, | Yes | Likely | [26, 27] |
| Electrolysis | Intermediate | High | Not fully developed | Low | High | Up to 100%, requires high energy input | No | Possible | [26] |
| Ultrasound | Intermediate | Low | Not fully developed | Low | High | Up to 100%, requires high energy input | Yes | Not likely | [26] |
| Homogeneous photocatalysis | Low ($<5\ mg\,L^{-1}$) | Low | Not fully developed | Low | High | Up to 100%, requires input of UV energy, $H_2O_2$, $Fe^{2+}$, $O_3$, and so forth | Yes | Not likely | [26] |
| Heterogeneous photocatalysis | Low ($<5\ mg\,L^{-1}$) | Low | Not fully developed | Low | High | Up to 100%, requires high UV radiation intensity (>100 W) | Yes | Not likely | [26] |
| Catalysis by CT | Low ($<5\ mg\,L^{-1}$) | Low | Laboratory feasible | Low | Low | Up to 100%, requires LOW UV radiation intensity (<30 W) | Yes | No | This study |

(a)

(b)

(c)
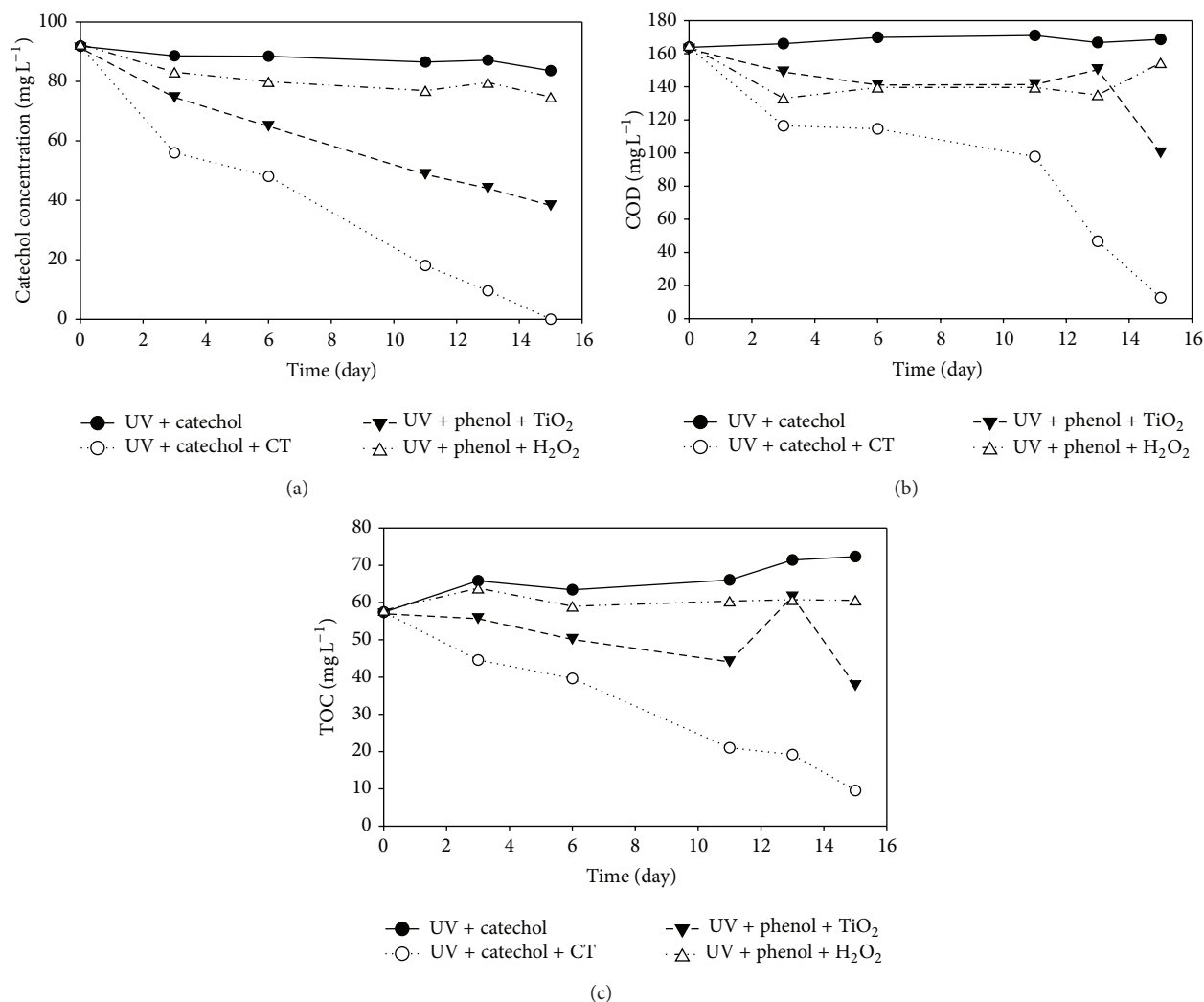
FIGURE 2: Time-dependent degradation of catechol by CT catalyst compared with TiO$_2$, H$_2$O$_2$ ((a) catechol concentration; (b) COD; (c) TOC).

after 10 days (Figure 1(a)), with residues of COD (10.0 mg L$^{-1}$) and TOC (0.206 mg L$^{-1}$) (Figures 1(b) and 1(c)). In contrast, the control (phenol + UV) only had a slight degradation (<12% phenol reduction), while TiO$_2$ and H$_2$O$_2$ showed similar phenol removal efficiencies (34–41% phenol reduction) (Figure 1). Pattern of the removal of catechol was similar to that of phenol (Figure 2), but a longer reaction time was required for a complete removal by CT (15 d). Additionally, TiO$_2$ was more potent than H$_2$O$_2$ in treating catechol (Figure 2(a)) that up to 57.8% of the catechol removal occurred in the treatment by TiO$_2$, much higher than the treatment by H$_2$O$_2$ (19.3%) and the control (8.9%).

The processes of phenol/catechol removal followed pseudo-zero-order kinetics (Figure 3), whereas correlation coefficients for the pseudo-first-order kinetic model were generally low. This suggested that mass transfer was not a rate controlling process in the experiments [23]. However, the result was different from previous studies that phenol removal mostly followed pseudo-first-order kinetics [16, 28–30]. Further investigation is needed in order to understand

more of the mechanisms. UV+TiO$_2$ for phenol and catechol and UV + H$_2$O$_2$ for phenol and catechol follow pseudo-first-order kinetics, and the calculated rate constant $k$ values were 0.03 × 10$^{-3}$/min, 0.04 × 10$^{-3}$/min, 0.03 × 10$^{-3}$/min, and 0.01 × 10$^{-3}$/min, respectively. But UV + CT follows pseudo-zero-order kinetic calculated rate constant $k$ values (for phenol and catechol) were 5.28 × 10$^{-3}$ mol L$^{-1}$ min$^{-1}$ and 4.59 × 10$^{-3}$ mol L$^{-1}$ min$^{-1}$, according to slopes of the regression models (Figure 3) (slope = $k$/initial concentration of phenol/catechol).

The result demonstrated that CT catalyst could be used for a complete removal of phenolic compounds in wastewater, with the presence of mild UV radiation (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$). Compared with previous reports on phenol degradation, such as employing sono-/photo-Fenton reactions [11], immobilized TiO$_2$ photodegradation [31], or electrochemical oxidation [28], the present treatment using CT catalyst had notably advantage of (1) less energy consumption and (2) no chemical consumption. Further comparison of the UV
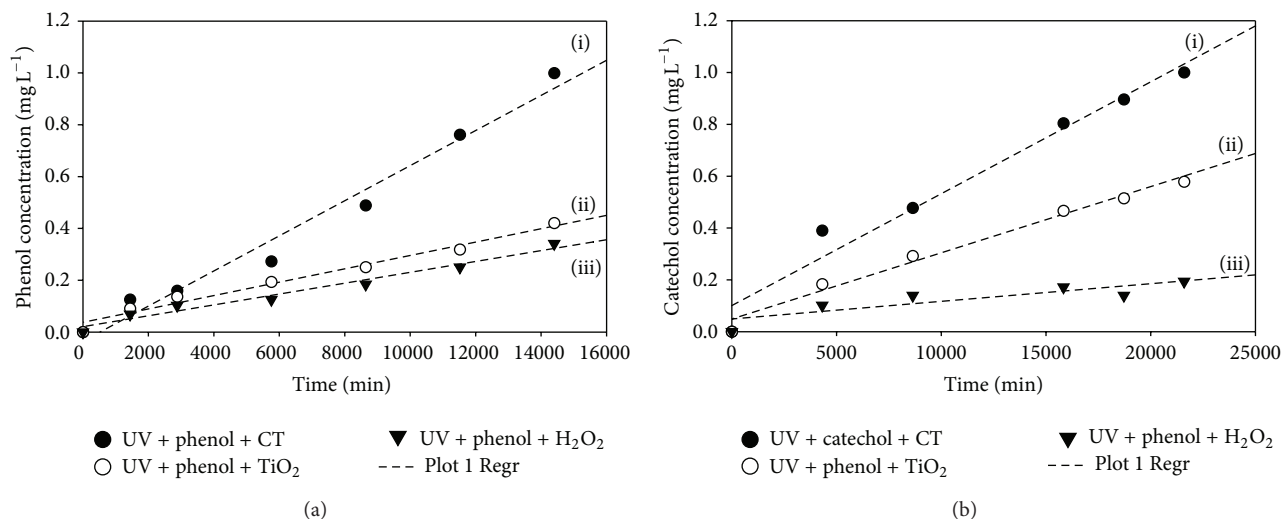
FIGURE 3: Degradation kinetics of (a) phenol: (i) $y = 7*10^{-5}x - 0.0288$, $r^2 = 0.9761$; (ii) $y = 3*10^{-5}x + 0.0349$, $r^2 = 0.9767$; (iii) $y = 2*10^{-5}x + 0.0628$, $r^2 = 0.9902$; and (b) catechol: (i) $y = 4*10^{-5}x + 0.0951$, $r^2 = 0.9686$; (ii) $y = 3*10^{-5}x + 0.0426$, $r^2 = 0.9831$; (iii) $y = 7*10^{-6}x + 0.0432$, $r^2 = 0.7685$.

TABLE 2: Comparison of UV intensity adopted by varied studies in photodegradation of phenol.

| Treatment | Reaction condition | Performance | Study |
|---|---|---|---|
| UV + $H_2O_2$ + $TiO_2$ supported on sepiolite | UV intensity 17 w; pH 5.5; solid/liquid 0.5 g $L^{-1}$; $H_2O_2$: 30 ml $L^{-1}$ | $k = 0.87 \times 10^{-3}$/min, within 24-25 h, conversion >90% | Uğurlu and Karaoğlu 2011 [15] |
| UV + $TiO_2$/perlite | UV intensity 250 w, pH 10.7; initial phenol concentration 0.5 mmol $L^{-1}$; $TiO_2$/perlite dosage, 6 g $L^{-1}$; reaction temperature 27°C | Experimental conversion (%): 97.3 | Jafarzadeh et al. 2011 [1] |
| Sono-photo-Fenton | UV intensity 250 w, emitting radiation between 300–420 nm; pH 3; $Fe^{2+}$ 20 mg $L^{-1}$, $H_2O_2$ 700 mg $L^{-1}$, room temperature | 93% phenol reduction, 84.6% COD reduction within 60 min, $k = 0.1186$/min | Babuponnusami and Muthukumar 2011 [11] |
| UV/$H_2O_2$ | UV intensity 5000 w output; $H_2O_2$ concentration: 7.08 mmol $L^{-1}$ | Within 50 min, 50 mg $L^{-1}$ phenol degraded into 10 mg $L^{-1}$ | Huang and Shu [33] |
| UV/$TiO_2$ supported on fiberglass cloth | a UV/Vis mercury lamp: 6 Kw, 330 W$m^{-2}$ initial phenol Concentration: 25 mg $L^{-1}$ | 80% phenol reduction within 15 h | Mozia et al. 2012 [32] |
| UV/CT | UV intensity 15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$; pH 3, initial phenol concentration 88 mg $L^{-1}$ (0.936 mmol $L^{-1}$), 1% CT nanoparticles; room temperature | Within 10 day, 100% degradation, $k = 5.28 \times 10^{-3}$ mol $L^{-1}$ min$^{-1}$ | This study |

intensity among varied photodegradation of phenol (Table 2) demonstrated that CT catalyst required low UV radiation (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$). This suggested that the present set-up using CT catalysis could be applied in removing wastewater containing low levels of phenol. Although it took CT 10 and 15 days to mineralize phenol and catechol (both with the initial concentration of 88 mg $L^{-1}$), respectively, CT/UV followed zero-order kinetics, suggesting the reaction rate constant was not

a function of phenol concentration. If CT/UV is applied for posttreatment, with much lower concentrations (<5 mg $L^{-1}$) of phenol or catechol, less removal time is expected. Nevertheless, our follow-up experiments verified our hypothesis (unpublished). The band gap energy of $TiO_2$ is up to 3.2 eV. Usually $TiO_2$ absorbs light with the wavelength less than 385 nm. Previous reports by other researchers showed that the UV intensity is a critical parameter in order to allow $TiO_2$ to function efficiently [16, 32]. Compared with $TiO_2$/UV,
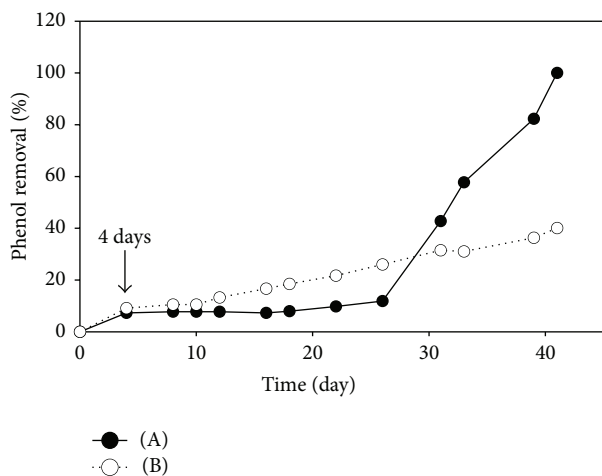
FIGURE 4: Sequential degradation of phenol: (A) four days of UV radiation followed by 1% CT treatment in the dark; (B) four days of 1% CT in the dark followed by UV radiation.

CT has the advantage that it works better under mild UV intensity. Further investigation will be needed for treating water with higher phenol level; the pollutants treatment efficiency also needs to be improved and optimized.

The result of the treatments of UV + $H_2O_2$ and UV + $TiO_2$ was expected. For the former treatment, the one-time spiking of $H_2O_2$ limited a continuous supply of hydroxyl radicals, leading to an incomplete mineralization of the phenolic compounds. For example, we observed that the solution in the treatment of phenol + UV + $H_2O_2$ turned from colorless at the start of the experiment to dark brown at the end (10 days). For the latter, due to the low UV intensity provided, $TiO_2$ did not absorb enough photon energy to form sufficient holes ($h^+$) and hydroxyl radicals [34], which are the most important species for oxidation organic compounds [31]. As a result, low levels of phenolic compounds were decomposed.

*3.2. Mechanism of CT Catalyst in Degrading Phenolic Compounds.* Although complete removal of phenol was achieved with the copresence of CT and UV (Figure 1), sequential degradations of phenol (treatment by UV followed by CT (A) and treatment by CT followed by UV (B)) showed much lower efficiency (Figure 4). For example, both treatments (A and B) at 4 days showed <10% phenol removal (Figure 4), whereas the treatment with the copresence of CT and UV at 4 days removed 26.8% phenol (Figure 1(a)). It took 40 days for a complete removal of phenol in treatment A (Figure 4), but 10 days in the copresence of CT and UV (Figure 1(a)). This indicated that the copresence of CT and UV had a synergistic effect in degrading phenol.

Moreover, remarkable difference was observed between treatments A and B (Figure 4). At 26 days, treatment A started to show a remarkable increasing removal percentage (>6%/day), and eventually at 40 days phenol was completely removed (100%). In contrast, the increase in the removal percentage of treatment B was not significant (<40%) during the whole treatment period (40 days). This proved that CT and UV did not play an equal role in phenol degradation. For

treatment B, the slight decrease in phenol in the treatment B (by CT and then UV) most likely was due to residue CT catalyst in the filtrate after filtration. However, for treatment A, it is more probable that the phenolic compounds absorbed the UV energy and passed to the higher state of energy (excited state) first, and then in the dark the unstable excited-state phenolic compounds underwent charge transfer processes mediated by the CT catalyst. In particular, under acidic condition, electron donor of CT generated holes, which moved towards the oxidation center, and pulled electrons out from the phenolic compounds, and therefore the phenolic compounds were oxidized. The reduction center of the CT accepted those electrons and sent them to electron acceptors, such as oxygen in the water. In this regard, whether the pseudo-zero-order kinetic model derived from the present kinetic study reflected a rate limiting influence by the charge transfer process remained to be investigated. Another explanation can be that hydroxyl radicals were generated from CT in the solution [35] that the phenolic compounds adsorbed on the surface of CT were oxidized and mineralized. However, concentration of the hydroxyl radicals was not measured in the present study, but should be examined in the future. The contrast of the result of treatments A and B partially supported our hypothesis on the functions of UV and CT and the associated mechanism, which indicates that CT has the potential for degrading organics in the dark condition, although uncertainties remained to be clarified in our future work.

Probable pathway of phenol degradation in water was established according to previous studies, that is, phenol–catechol or hydroquinone/benzoquinone–maleic acid–acrylic acid/succinic–malonic acid–acetic acid–$CO_2$ + $H_2O$ [14, 36–38], and the identified and quantified intermediates in the present phenol degradations (UV + CT and UV + $TiO_2$) were shown in Figure 5. Furthermore, levels of TOC calculated based on the carbon concentrations in the intermediates (Figure 5) were also compared with the corresponding measured TOC concentrations using a TOC analyzer (Figures 1(c) and 2(c)) (Table 3). For the treatment of UV + CT, it seems that the three measured compounds (catechol, hydroquinone, and benzoquinone) were the predominant intermediates, accounting for more than 95% of the measured TOC (Figure 5(a)). Concentrations of catechol and hydroquinone reached the maxima (catechol: 0.826 mg $L^{-1}$; hydroquinone: 4.43 mg $L^{-1}$) at 2 d, while that of benzoquinone only peaked at 6 days (1.02 mg $L^{-1}$). At 10 days, a complete mineralization occurred, in which all intermediates were transformed into the end products ($CO_2$ and $H_2O$). However, varied acids as intermediates between benzoquinone and the end products were not detectable. Based on mass balance, these compounds accounted for <5% of the TOC (Table 3). Similarly, acids were not detected in the treatment of UV + $TiO_2$, accounting for <10% of the TOC (Table 3), whereas only catechol and hydroquinone were identified and quantifiable (Figure 5(b)). The difference between these two treatments was expected as the UV intensity was low and $TiO_2$ could not generate adequate energy and radicals for the degradation.
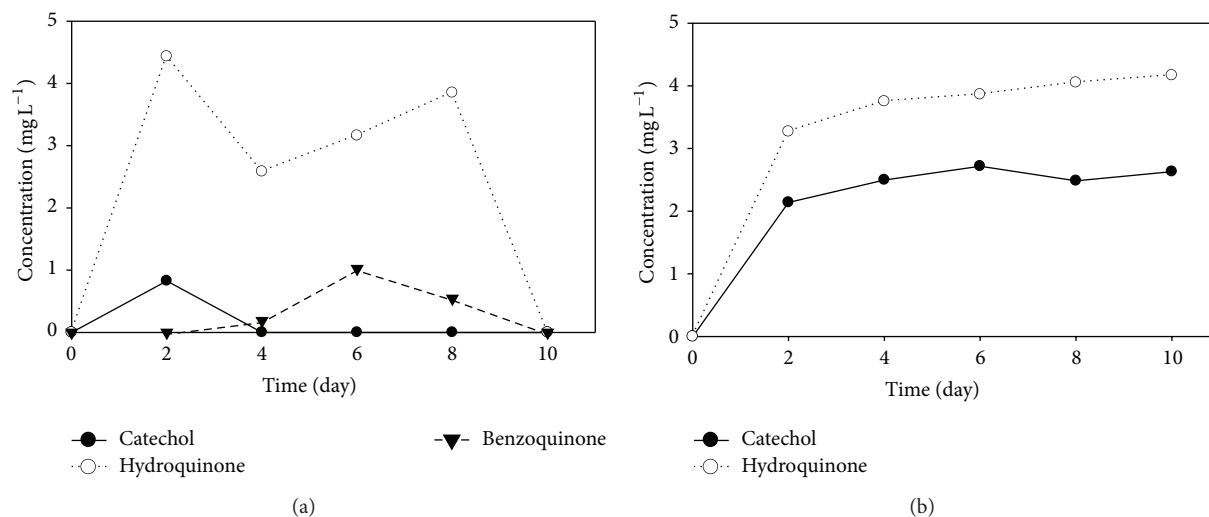
FIGURE 5: Degradation intermediates of phenol from the treatment of (a) UV + CT and (b) UV + TiO$_2$.

TABLE 3: Levels of TOC calculated from carbon contents in phenol and its intermediates compared with TOC concentrations measured by a TOC analyzer.

| TOC (mg L$^{-1}$) | Time (day) | | | | |
|---|---|---|---|---|---|
| | 0 | 2 | 4 | 6 | 10 |
| UV + CT | | | | | |
| Phenol | 67.4 | 49.0 | 42.6 | 29.3 | ND |
| Catechol | ND | 0.541 | ND | ND | ND |
| Hydroquinone | ND | 2.90 | 1.69 | 2.07 | ND |
| Benzoquinone | ND | ND | 0.125 | 0.683 | ND |
| Total calculated value | **67.4** | **52.4** | **44.4** | **32.0** | **ND** |
| Measured value | 54.3 | 50.5 | 43.2 | 36.3 | 0.206 |
| UV + TiO$_2$ | | | | | |
| Phenol | 67.4 | 46.7 | 46.7 | 44.2 | 36.7 |
| Catechol | ND | 1.40 | 1.63 | 1.78 | 1.72 |
| Hydroquinone | ND | 2.14 | 2.45 | 2.53 | 2.73 |
| Total calculated value | **67.4** | **50.3** | **50.8** | **48.5** | **41.1** |
| Measured value | 54.3 | 50.5 | 46.7 | 47.1 | 37.3 |

ND: undetectable; method detection limits (MDLs) of phenol, catechol, hydroquinone and benzoquinone were 0.0158, 0.0240, 0.0124 and 0.0190 mg C L$^{-1}$, respectively.

## 4. Conclusions

This is the first report on employing CT catalyst, a novel charge transfer auto oxidation-reduction type of semiconductor, in degrading aromatic compounds in water. Phenolic compounds (initial concentrations, phenol: 88 mg L$^{-1}$ and catechol: 91.8 mg L$^{-1}$) were completely mineralized by the CT catalytic nanoparticles (1%) within 15 days, under acidic condition and with the presence of mild UV radiation (15 w, the emitted wavelength is 254 nm and the light intensity <26 $\mu$w/cm$^2$). The reaction condition allowed CT to be applied in pollutant removal in wastewater that light transfer was quite often a challenge if photocatalysis was attempted. Phenol elimination followed pseudo-zero-order kinetics with a rate constant of 5.28 × 10$^{-3}$ mol L$^{-1}$ min$^{-1}$ under the present treatment condition. It seems that, given low initial phenol concentration, a circumstance encountered in wastewater polishing, the current set-up should be more efficient and less energy-/chemical-consumptive.

A probable mechanism of the CT's functions related to a synergistic performing between UV radiation and the CT. In particular, the aromatic structures in phenol absorbed the UV energy and passed to an excited state. The CT worked on these excited compounds by absorbing pollutants on the surface, oxidizing the pollutants via charge transfer, and producing hydroxyl radicals and eventually completely transformed all the pollutants to CO$_2$ and H$_2$O. Analysis of the degradation intermediates of phenol showed that the reaction in the CT's treatment followed general pathway observed by other researchers. In the practical application, CT can be separated from the effluent through nanofiltration.

## Conflict of Interests

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

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