Research Article

Phenol Removal by a Novel Non-Photo-Dependent Semiconductor Catalyst in a Pilot-Scaled Study: Effects of Initial Phenol Concentration, Light, and Catalyst Loading

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A novel non-photo-dependent semiconductor catalyst (CT) was employed to degrade phenol in the present pilot-scaled study. Effect of operational parameters such as phenol initial concentration, light area, and catalyst loading on phenol degradation, was compared between CT catalyst and the conventional photocatalyst titanium dioxide. CT catalyst excelled titanium dioxide in treating and mineralizing low-level phenol, under both mild UV radiation and thunder conditions of nonphoton. The result suggested that CT catalyst could be applied in circumstances when light is not easily accessible in pollutant-carrying media (e.g., particles, cloudy water, and colored water).

1. Introduction

Heterogeneous photocatalytic oxidation (HPO) can degrade refractory organics through combination of semiconductor photocatalyst (TiO\(_2\) and ZnO), in the presence of energy-provided light source (UV) and oxidant (oxygen or air). This process largely depends on in situ generation of hydroxyl radicals under ambient conditions [1]. Among different semiconducting materials, titanium dioxide, a widely used photocatalyst for oxidizing degradation of organics in the wastewater [2–5], is always preferred for its strong oxidizing ability, bulk nontoxicity, ready availability, and long-term stability [6–8]. Anatase is the crystalline phase of TiO\(_2\) with the highest photocatalytic activity [9]. Generally speaking in heterogeneous photocatalysis, oxidation reaction takes place on the surface of catalyst, and the degradation rates of organics relate mainly to some important parameters including substrate concentration, light intensity, catalyst loading, and the solution pH [10, 11]. Also, photocatalytic oxidation of phenol was usually investigated in a slurry reactor because of the easy handling, less limitation on mass transfer, and more efficiency than a reactor using immobilized catalysts [12].

A novel catalyst, charge transfer autooxidation-reduction-type semiconductor catalyst (CT catalyst), was developed by two Japanese scientists [13]. Our previous bench-scaled research revealed that the CT catalyst could be used for removal of low concentration phenolics under mild UV radiation and total mineralization can be realized, better than the conventional photocatalyst TiO\(_2\) [14]. In general, CT catalyst has two significant advantages: (1) low energy consumption; (2) nonchemical consumption [14].

In the present pilot-scaled study, we aimed to investigate influencing factors, including pollutant initial concentration, lighting area, and catalyst loading, on phenol degradation using CT catalyst. Upon data analysis, optimal operational parameters for application of CT catalyst in wastewater treatment were determined.

2. Materials and Methods

Phenol (analytic grade), chosen as the target pollutant, and TiO\(_2\) (mixture of rutile and anatase nanopowder, <100 nm, 99.5% trace metals basis) as the photocatalyst were purchased...
from Sigma-Aldrich Chemical Co. CT catalyst was purchased from BOIS Ltd. The phenol solutions were adjusted to pH 3 using hydrochloride acid and sodium hydroxide solutions, simulating the pH level in phenol-containing industrial wastewaters.

The experiments were carried out in a 5 L glass immersion photochemical reactor. The main body of reactor was cylindrical with the radius of 10.5 cm bearing the structure of double jackets. The outer layer of the reactor with running water was for cooling and the inner layer was the reaction space containing 3 L phenol solution. The axis position of reactor was equipped with a stirrer, controlled at 180 rpm to realize a complete mixing of the solution. A low-pressure UV mercury lamp was set in a quartz tube immersed in the solution. The main emission wavelength of the UV lamp was 254 nm UV-C. Levels of the light intensity were approximately 3400 μW/cm² outside of the quartz tube and 335 μW/cm² near the inner wall of the inner reaction cylinder, respectively. Initial concentrations of phenol were 5.0, 20.0, 50.0, and 100.0 mg L⁻¹, respectively. Lengths of the UV lamp were used in the study, including 3.0, 6.0, 8.0, 8.8, and 18.5 cm, respectively. To study the effect of catalyst loading, the phenol solution was first exposed to UV irradiation for 2 h and then the rest of the reactions took place in the dark. The catalyst loading was set at 0.03%, 0.1%, 0.2%, 0.5%, 1%, 2%, and 3%, respectively. In the experiment with thunder condition of nonphoton, 0.1% of the catalyst loading level for both CT and TiO₂ was adopted.

Samples were collected from the reactor during the treatments and filtered through 0.45 μm mixed cellulose ester (MCE) membrane before chemical analyses. Concentrations of phenol and hydroquinone were analyzed using a spectrophotometer at 270 nm and 289 nm, respectively [15]. The relationships between absorbance readings
and concentrations of phenol or hydroquinone were shown in Figure 1.

3. Results and Discussions

3.1. Effect of Phenol Initial Concentration on Phenol Degradation by CT Catalyst and TiO$_2$. Phenol degradation upon UV radiation (18.5 cm UV lamp) with and without the presence of 1% CT was compared (Figure 2). It shows that UV radiation alone (without the presence of CT) had ignorable effect on phenol removal, while 1% CT achieved an 87% removal in 6 h.

Contribution of phenol initial concentration in phenol degradation was shown in Figure 3. It seems that, under the condition of UV radiation with the lamp length of 18.5 cm, degradation rate by CT catalyst was maintained at a constant level of 0.017 min$^{-1}$, regardless of different phenol initial concentrations (5–100 mg L$^{-1}$). The result demonstrated that phenol photocatalytic degradation by CT was independent of the phenol initial concentration. This is consistent with the pseudo-zero-order kinetics of phenol photocatalytic degradation by CT derived in our previous bench-scaled study [14]. In comparison, the UV light intensity employed in this pilot-scaled experiment (approximately 3400 $\mu$W/cm$^2$ near
the light tube) was much higher than that in the previous bench-scaled experiment (<26 μW/cm²) [14]. This probably led to a higher rate constant $K$ (0.017 min⁻¹) obtained in this study than the previous value ($K_{\text{bench-scale}}$: $5.28 \times 10^{-3}$ min⁻¹) [14]. The result suggested that, within the range of initial phenol concentration we set in the present study, reaction sites on the surface of the CT catalyst were not fully occupied by the phenol molecules/activated molecules. A possible process is that the UV radiation activated the aromatic structure of the phenol molecules and subsequently these activated molecules lost their stability due to an electron change on the surface of CT and eventually were decomposed due to nonaromatic substances. The process is different from that of TiO$_2$ mediated phenol degradations; phenol initial concentration played important role in the reactions, most likely due to light availability and therefore hydroxyl radical generation for the oxidation of the phenol molecules [16]. In addition, the produced intermediates may lead to deactivation of active sites on the surface of TiO$_2$ [17, 18]. For example, Silva and Faria reported that photocatalytic oxidation followed pseudo-first-order kinetic model ($[\text{PhOH}] = [\text{PhOH}]_0 e^{-K_{\text{app}}t}$; $K_{\text{app}}$ was the apparent first-order kinetic constant) [12]. Hong et al. also reported that phenol photocatalytic degradation rate by TiO$_2$ decreased as phenol initial concentration increased from 50 to 400 mg L⁻¹ [19].

3.2. Effect of UV Light on Phenol Degradation by CT Catalyst and TiO$_2$. Figure 4 showed that phenol photocatalytic degradation rate increased with the increase of UV tube length under the condition of phenol initial concentration of 5 mg L⁻¹ with 1% CT, and the pseudo-zero-order kinetic rate constants were 0.0036, 0.0066, 0.0104, 0.0114, and 0.0139 min⁻¹, respectively. This phenomenon was expected because the increase of UV tube length results in increase of lighting area and then of UV energy. Figure 5 demonstrated that there was a good linear relationship between UV tube length and phenol photocatalytic degradation rate by
3.3. Effect of Catalyst Loading on Phenol Degradation. After 2 h of UV irradiation, different CT loading degraded phenol and the photocatalytic rates were higher than the corresponding phenol reduction rates in the thunder condition of nonphoton (Figure 6). Phenol photocatalytic degradation rates increased as CT loading increased from 0.03% to 0.5%, resulting from an increment of the active sites available for phenol absorption and degradation. However, the rates reduced as CT loading further increased from 0.5% to 3%. This may be because of a screen effect due to the redundant dispersion of UV radiation and aggregation of the catalyst particles with consequent decrease in the active sites available to catalytic reaction [1]. Therefore, there was photocatalytic degradation rate peak ($14.815 \times 10^{-3}$ min$^{-1}$) at 0.5% CT, whereas different CT catalyst loadings had the similar phenol removal rates without the presence of photon ($1.612 \times 10^{-2}$ min$^{-1}$).

The optimal TiO$_2$ loadings in degrading phenol were reported by the other researchers. TiO$_2$ concentrations in the suspension varied from 0.1 to 1.5 g L$^{-1}$. $K_{app}$ increased with the mass of catalyst up to amount of 1.0 g L$^{-1}$ but decreased at 1.5 g L$^{-1}$ [12]. The present study obtained a similar TiO$_2$ loading level; 1% was the optimum with a maximum $K_{app}$ ($31.54 \times 10^{-3}$ min$^{-1}$) (Figure 7). However, different from CT, phenol degradation by titanium in the thunder condition peak ($1.932 \times 10^{-3}$ min$^{-1}$) occurred upon 0.1% loading of TiO$_2$. 

CT ($y = 0.0014x - 0.001, R^2 = 0.9853$), which verified the photo-induced nature of the aromatic compounds [12].

For TiO$_2$, Jafarzadeh et al. reported that photodegradation rate of phenol increased with the increasing medium-pressure mercury UV lamps power from 125 w to 250 w [20]. Chiou et al. reported that the rate constants of different UV power (20, 100, and 400 w) were different (8.3 $\times$ $10^{-3}$, 0.012, and 0.031 min$^{-1}$, resp.) [21]. There was a good linear relationship between the apparent rate constant and light intensity, because of the increasing amount of hydroxyl radicals.
Phenol photocatalytic degradation rate by TiO$_2$ was faster than that by CT (Figure 8), probably due to the fact that UV intensity (approximately 3400 $\mu$W/cm$^2$ near the light tube) was sufficient to excite the valence electrons of TiO$_2$. In contrast, CT should have higher potential in phenol removal under conditions when light is not easily accessible in pollutant-carrying media (e.g., particles, cloudy water, and colored water).

### 3.4 Phenol Degradation by CT and TiO$_2$ in the Thunder Condition of Nonphoton

In the dark after a brief UV exposure, both CT and TiO$_2$ removed phenol, and the efficiencies at 47 h were 77% and 60%, respectively (Figure 8(a)). Production of the intermediate hydroquinone was observed in the treatments (Figure 8(b)). For CT catalyst, concentration of hydroquinone increased with the decrease in phenol. In contrast, hydroquinone was not detected in the treatments by TiO$_2$. This verified that CT catalyst could function in the dark via charge transfer to destabilize phenol, a similar result to that observed in the bench-scaled experiments [14]. For TiO$_2$, it is possible that phenol molecules were simply absorbed on the surface, blocking further degradation. This phenomenon was observed previously when using TiO$_2$ for degrading methylene blue, and, with the increasing initial concentration of methylene blue, the removal efficiency decreased [22]. Liu et al. also reported that nano-TiO$_2$ had good absorption ability and the absorption rate was above 97% [23]. After all, it is not unexpected that, at TiO$_2$, positively charged, absorbed phenol molecules at pH 3.0 and 0.1% TiO$_2$ showed the best absorption ability.
4. Conclusions

(1) Phenol photocatalytic degradation by CT catalyst was independent of phenol initial concentration, following a pseudo-zero-order kinetic model. In contrast, phenol photodegradation by TiO₂ followed a pseudo-first-order kinetic model, and the removal rate decreased with the increase in phenol initial concentration.

(2) The increase in the length of the UV lamp led to an increase in radiation area and energy and therefore enhanced phenol degradation in both treatments by CT catalyst and TiO₂.

(3) For photocatalysis, the optimal loadings for CT catalyst and TiO₂ treatments were 0.5% and 1%, respectively.

(4) For phenol removal under thunder condition of nonphoton, CT catalyst mediated the degradation, leading to the formation of hydroquinone, whereas the main function of TiO₂ in the process seemed to be absorption.

Overall, CT catalyst excelled the conventional photocatalyst TiO₂ in polishing low concentration of phenol under either mild UV radiation or thunder condition of nonphoton and eventually realized mineralization. CT catalyst should have enormous potential in phenol removal in wastewater, especially in circumstances when light is not easily accessible in pollutant-carrying media (e.g., particles, cloudy water, and colored water).

Conflict of Interests

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

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