

Research Article

Photocatalytic Degradation of Phenol Using a Nanocatalyst: The Mechanism and Kinetics

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The study of photocatalytic degradation of phenol was exploited with nano-ZnO as immobilized photocatalysts in a laboratory scale photocatalytic reactor. The photocatalytic degradation mechanism and kinetics of phenol in water were studied using the solid-phase microextraction (SPME) technique. Based on optimized headspace SPME conditions, phenol in water was first extracted by the fibre, which was subsequently inserted into an aqueous system with immobilized photocatalysts (nano-ZnO) exposed to an irradiation source (i.e., ultraviolet A (UVA) lamps). After different irradiation times (5–80 min), four main intermediates of photocatalytic degradation generated on the fibre were determined by GC-MS.

1. Introduction

Phenolic compounds were a constant concern from the environmental point of view with regard to their toxicity, bioaccumulation, and persistency in the environment. Among this class of compounds, the representative was phenol which was widely used as a raw material in the petrochemical industries and oil refineries. Phenol and its degradation products were major aquatic pollutants in the environment. Polychlorinated phenol could occur as a result of the chlorination of phenol. Therefore, the increasing presence of phenol represented significant hazardous environmental toxicity. The World Health Organization (WHO) has limited phenol concentration in drinking water to 1 µg/L [1]. However, traditional water treatment techniques including active carbon adsorption, chemical oxidation, and biological digestion had difficulty in the removal of phenol to the safe levels.

Over the last two decades, application of advanced oxidation process (AOP) to degrade organic pollutants in wastewater is a relatively new process. Among AOP, heterogeneous photocatalysis using various semiconductor nanoparticles has been shown to be potentially advantageous and useful for the degradation of wastewater pollutants. Several advantages of this process are: (1) complete mineralization of organic

pollutants to CO₂, water, and mineral acids, (2) no waste-solid disposal problem, and (3) only mild temperature and pressure conditions are necessary. In photocatalysis, water and hydroxide ions react with the electron holes to form hydroxyl radicals, proven to be the primary oxidant in the photocatalytic oxidation of organics [2]. These hydroxyl radicals have an oxidation potential higher than that of ozone or hydrogen peroxide, second only to fluorine [3]. Repeated hydroxyl radical attacks can eventually lead to complete oxidation of the organic contaminants. Even if complete oxidation is not achieved, it is desirable that pollutants are at least degraded into less hazardous hydrocarbons that are easier to remediate with a secondary treatment or disposed of completely. Thus, it is essential to understand the mechanism and kinetics involved in these processes to assess the feasibility and efficiency of the degrading organic compounds.

There were many methods for analyzing phenol in water, which encompassed various pretreatment techniques coupled with analytic instruments, such as solid-phase extraction (SPE) or liquid-liquid extraction (LLE) with gas chromatograph-flame ionization detector (GC-FID) [4] and electronic capture detector (ECD), solid-phase extraction (SPE) [5–7] or solid-phase microextraction (SPME) [8–11] with capillary electrophoresis [12, 13], or high performance

liquid phase (HPLC) [14, 15]. Due to the inherent advantages of SPME, it had been recently validated and proposed as the extraction technique for the analysis of phenol in water and sewage sludge [16, 17]. On the other hand, SPME technique has been used for identifying, quantifying, and following the evolution of intermediates of degradation by various processes including photolysis [18–20], photocatalysis, and ultrasound [21].

The aim in this study was to investigate the photocatalytic degradation mechanism of phenol using SPME technique directly in the home-made photocatalytic reactor. Qualitative and quantitative analyses were carried out by using SPME after the study of the influence of several extraction parameters: fibre coating, extraction time, pH value, salinity effect, and presence of catalysts.

2. Experimental Data

2.1. Chemicals and Instruments. Phenol was obtained from Sigma-Aldrich Pte. Ltd. (MO, USA) and prepared to 1000 $\mu\text{g}/\text{mL}$ of stock solution. The solvent of the stock solution was chromatographically pure methanol. The working solutions for SPME experiments were diluted by deionized water. All the remaining solvents and reagents used were purchased from Merck. Deionized water was used in all experiments and analytical determinations.

2.2. HS-SPME and In-Situ Photocatalytic Degradation Procedures. The following HS-SPME procedure was proposed: 20 μL of the stock solution of phenol in methanol was diluted into 10 mL with deionized water placed in 20 mL sample vials, and preheated for 5 min at the extraction temperature $35 \pm 2^\circ\text{C}$. The SPME fibre (85 μm , polyacrylate, Supelco-Bellefonte, PA, USA) was then exposed to the headspace above the samples and HS-SPME was executed with moderate stirring for 60 min. The fibre was thermally desorbed in the injection port of GC-MS at 250°C for 5 min in case of extraction carryover.

Then the fibre was transferred to a home-made reactor (illustrated in Figure 1) for photocatalytic degradation experiments. In the apparatus, two UVA lamps (Philip mL-18 W) as irradiation source were horizontally assembled above the reaction vial adhered with immobilized photocatalysts. In the present work, nano-ZnO powder (metal base, APS 40–100 nm, S.A. 10–25 m^2/g , Alfa-Aesar, MA, USA) used as photocatalyst was immobilized on the supporting substrate of commercial aluminum foils by modified screen-printing technique, reported by Ito et al. [22]. The internal temperature of the photocatalytic simulator was controlled at 35°C . For the in-situ photocatalytic degradation experiments, after HS-SPME the fibre carried with phenol was subjected to UV irradiation for the desired time.

2.3. GC-MS Determination. Analyses were carried out by Shimadzu GCMS-QP2010 Plus system. Experimental GC parameters were as follows: the chromatographic column was a DB-5MS (30 m \times 0.32 mm I.D. coated with a 0.25 μm film). The GC oven temperature program was: 40°C holding for

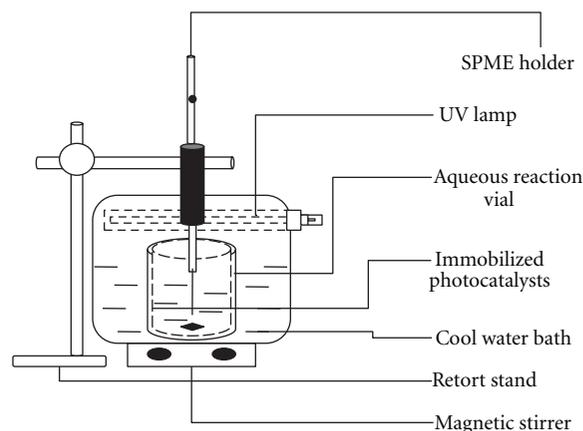


FIGURE 1: The sketch of home-made photocatalytic reactor with immobilized catalysts.

5 min, $15^\circ\text{C}/\text{min}$ rate to 150°C holding for 3 min, $20^\circ\text{C}/\text{min}$ rate to the final temperature of 250°C holding for 5 min (total analysis time 29 min). Helium was employed as a carrier gas, with a constant flow of 1.5 mL/min. The injector was operated at 250°C in the splitless mode (1 min). MS monitoring conditions were set as follows: transfer line temperature, 250°C ; detector voltage, 1.5 kV; ion source temperature, 200°C ; dwell time, 0.1–0.3 s; and the total number of ions per group between 2 and 4. Electron impact ionisation in the positive mode and SIM (Selected Ion Monitoring) acquisition mode were used. The quantification ions (mass/charge ratio) was 94 and the qualification ions were 64, 65 for phenol.

3. Results and Discussions

3.1. SPME Conditions. In SPME, the extraction efficiency could be affected by several parameters, for example, the properties of the fibre coating, the extraction temperature and the extraction time, the addition of salts or organic solvents to the sample, pH modification, agitation of the sample, and the sample volume. Matrix effects and the introduction of a derivatization step could also affect the extraction of analytes in SPME. Therefore, it was necessary for SPME procedure to be optimized.

The experiments on the SPME optimization were conducted in 20 mL glass vials (from Agilent Technologies, Germany) and 20 mm crimp seals with PTFE coated septa (from Supelco).

The extraction of phenol was performed with the constant concentration of 10 mL of water spiked with 50 μL of a standard solution. The sample solution was extracted with stirring at a desired temperature. And a probe was inserted into the solution for the precise control of temperature. The sample solution was preheated for 5 min before extraction. Then the fibre was placed in the headspace of sample solutions for designed time. After extraction, the fibre extracted with phenol was immediately inserted into the GC injector for subsequent analysis. Each analysis was carried out in triplicate ($N = 3$).

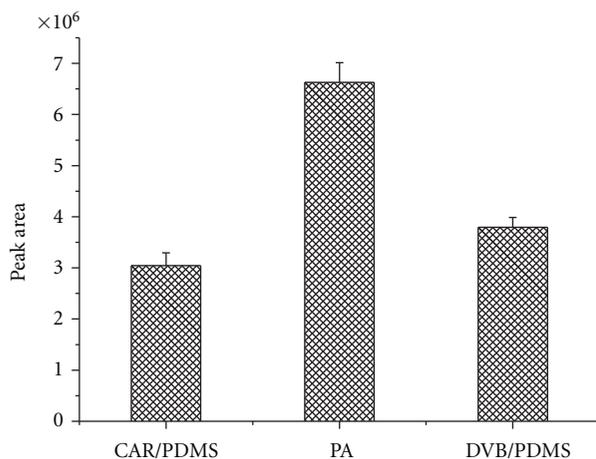


FIGURE 2: Fiber coating.

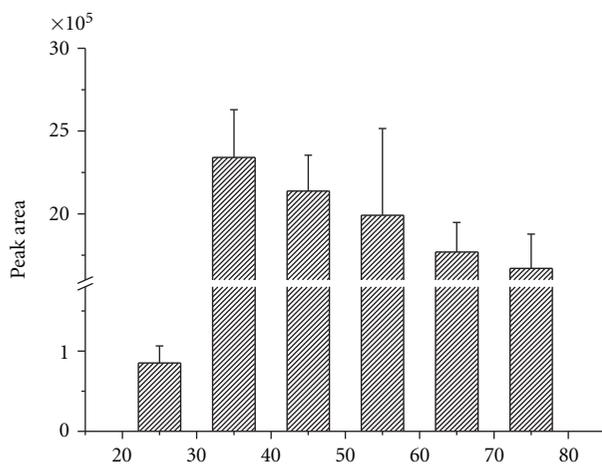


FIGURE 3: Extraction temperature (°C).

The choice of suitable fibre coating was most important for achieving good selectivity for the target analyte. In the study, three fibres with different coatings were investigated. As could be expected, the best performance was obtained with PA coating which was the most polar of all the fibres (Figure 2). The principle of “like dissolves like” could be applied to the fibre selection. All subsequent experiments were performed with PA fibre coating.

During the extraction, the temperature also played an important role, especially for the headspace extraction mode. For analytes, thermal variations could significantly impact the extraction efficiency or the system equilibrium time. In the study, the extraction temperature was investigated in the range of 25 to 75 °C. The profile of extraction performance versus extraction temperature was obtained in Figure 3. The extraction efficiency of phenol increased with the increasing of temperature and got to the maximum at 35 °C, then gradually decreased. Accordingly, the temperature of the extraction was selected at 35 °C.

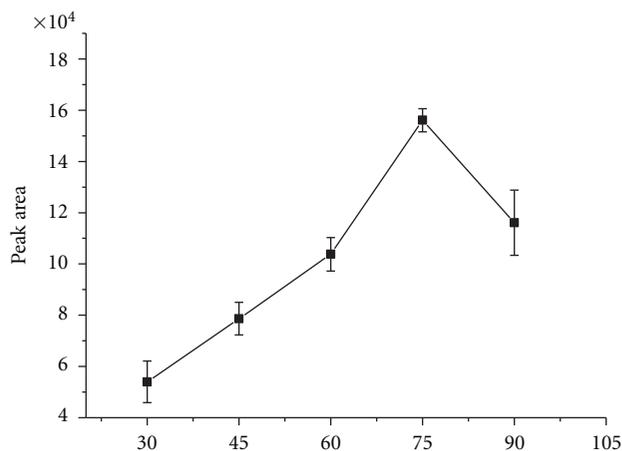


FIGURE 4: Extraction time (min).

On the other hand, the extraction time might affect the partition coefficient of analytes between water and fibre coating, so it was necessary to study its effect on the performance of the analysis. Figure 4 showed the effect of the extraction time on the extraction efficiency. According to the results, the maximum extraction efficiency was obtained at 75 min.

3.2. Validation of “In-Situ” Photocatalysis of Phenol. In previous publications [19, 23], it was demonstrated that SPME fibres were very good supports for photodegradation studies. Those preliminary studies were considered extremely successful, not only because the SPME fibre was shown to work as a photoreaction support, but also because of the possibility of the photoproducts formed in such experiments being detected.

In the present study, a series of preliminary experiments including blanks, dark tests, and thermal tests was also carried out, demonstrating that few losses of analytes through volatilization and/or thermal degradation occurred. Therefore, the clear differences observed when comparing phenol peak areas obtained in GC-MS with standard SPME (just extraction and desorption) and “in-situ” SPME photocatalysis (extraction, “in-situ” irradiation, and desorption) were due to UV exposure and ZnO as immobilized catalyst.

Detailed analysis of chromatograms selected through representative ions for phenol confirmed the conclusions made from the RIC chromatograms and Figure 5 showed the results.

3.3. Kinetics by “In-Situ” Photocatalysis under UV Irradiation. To study the influence of irradiation time on the extent of photocatalytic degradation, the standard solution of phenol was first extracted and then the fibre was subjected to UV light for the designed time: from 0 to 80 min (7 points, shown in Figure 6). Average area changes for phenol after UV exposure were evaluated. The amount of the initial compound remaining after 30 min UV light irradiation was under 20%. When the maximum irradiation time (80 min) was used, less than 5% phenol was detected.

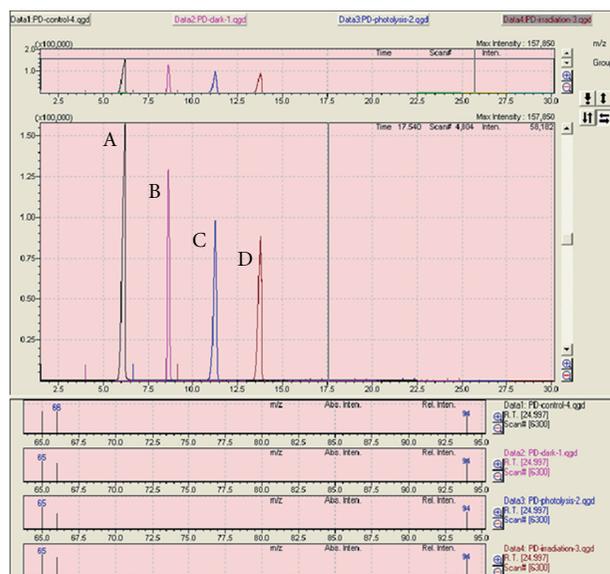


FIGURE 5: A: standard; B: dark experiment; C: photolysis; D: photocatalysis.

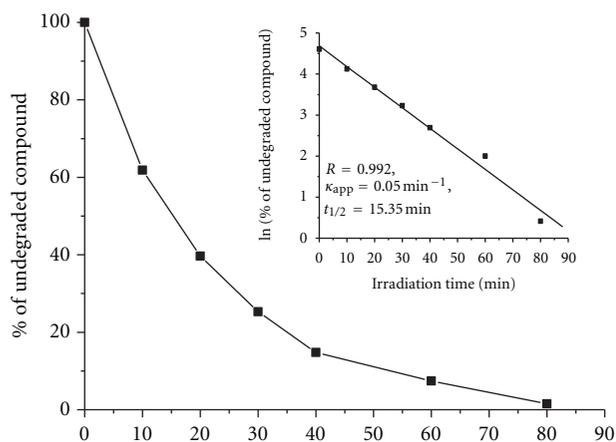


FIGURE 6: Irradiation time (min).

The kinetic curve of the photocatalytic degradation of phenol was also illustrated in Figure 6. The observed exponential decay suggested first order or pseudo-first-order kinetic models with high reaction rates being the main decomposition mechanism observed.

3.4. Analysis of New Intermediates. The “in-situ” SPME photocatalysis approach was then exploited to monitor the photocatalytic degradation behavior of phenol and to determine the photocatalytic products occurring at different irradiation times. Four photoproducts were clearly determined in the experiments: hydroquinone, catechol, benzoquinone, and acetic acid. And on the basis of qualitative and quantitative analysis by GC-MS, Figure 7 illuminated the trends of the

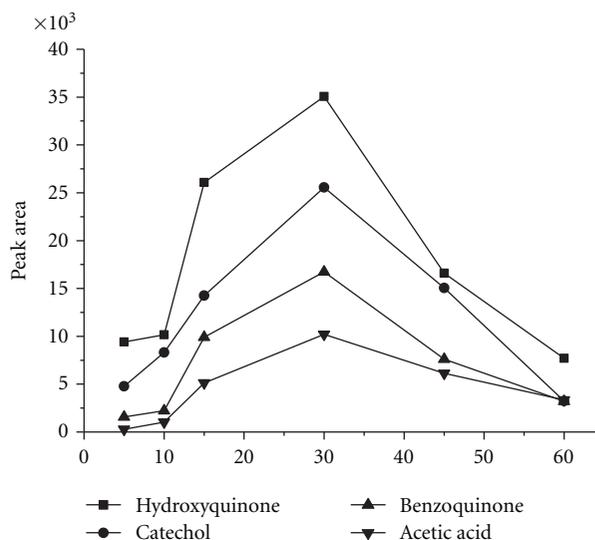


FIGURE 7: Irradiation time (min).

amount of four intermediates produced in the photocatalytic degradation. According to the substitution rules, hydroxyl radicals attacked the phenol molecule with higher probability in 2 and 4 position versus OH group of the aromatic ring. Therefore, the higher amount of hydroquinone (if compared to catechol) was on account of much lower reaction rate constant for this compound. The concentrations of catechol and hydroquinone increased at the beginning of illumination, then the changes were smaller. The slow changes of the concentrations were on account of simultaneous formation (from phenol) and decomposition of the compounds. Based on the obtained results, a probable mechanism of phenol oxidation under the experimental conditions arrayed could be depicted; see Figure 8.

4. Conclusions

Headspace solid-phase microextraction and “in-situ” photocatalysis allowed the establishment of pathways in the degradation of AOPs without manipulation of the sample. The kinetic behavior of phenol degraded on SPME fibre was observed similar in aqueous solution. Both approaches were suitable for studying the photocatalytic degradation kinetics of persistent organic pollutants in water and for analyzing photocatalytic products which were in-situ generated on the fibre or extracted from the matrix with minimum sample manipulation.

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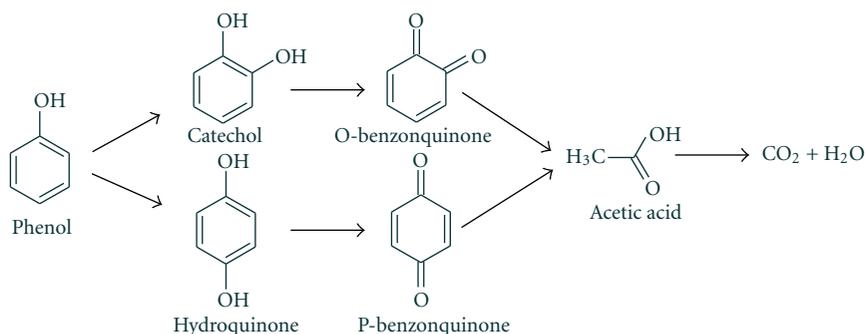


FIGURE 8: Proposed photocatalytic degradation pathways of phenol under the UV irradiation.

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