

Degradation of phenol by nanomaterial TiO₂ in wastewater

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Abstract

The degradation of 100 mg/L phenol solution under ultraviolet (UV) in the presence of TiO₂ and in the absence of it was analyzed with gas chromatography/mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC). After 12 h of degradation, the products under the two conditions were both derivatized by MSTFA and TMIS, and then analyzed by GC–MS. The results show the main intermediates are the same. They are hydroquinone, resorcinol, catechol, 1,2,3-benzenetriol, (E)-2-butenedioic acid, 2-hydroxy-propaldehyde, glycerol, 3-hydroxy-propyl acid, and hydroxy-acetic acid. The chromatogram given by HPLC indicates that the presence of TiO₂ is not in favor of the degradation when the concentration of phenol is 100 mg/L; its catalysis becomes evident when the concentration gets lower. Based on the intermediates, it can be proved that besides •OH, •H is also an important active free radical in the degradation.

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1. Introduction

In industry and daily life, phenolic compounds are widely used. As they have high stability, high toxicity and a carcinogenic character, they have caused considerable damage and threat to the ecosystem in water bodies and human health. How to eliminate phenolics in wastewater effectively has been in urgent demand. Traditional wastewater treatment techniques include activated carbon adsorption, chemical oxidation and biological digestion, in which photocatalytic degradation assisted by titanium dioxide under ultraviolet is one of the technologies studied widely. More research has been focused on the types and modification of the catalyst, the photocatalytic principles, the factors influencing photocatalytic rate and the reaction kinetics [1–12]. As for the reaction route, A Santos et al. summarized it into six schemes, in which the intermediates are mostly acids, phenolic compounds; there are no alcohols [13]. Andrzej Sobczyk et al. based on their many years of research, also provided a reaction route, in which the intermediates include phenolic compounds, alcohols, aldehydes, but they did not detect them by phenol direct degradation [14]. The key to speculate the reaction route is to detect the intermediates. There are at least 20

intermediates on the route from substrate to carbon dioxide during photodegradation of phenol [15]. But literature data show that many other intermediate compounds can be expected in the process of TiO₂ photocatalytic destruction of water aromatic pollutants, including phenols [16]. The most widely used method to detect them is extraction by organic solvent, after esterification or acetylation, followed by analysis by gas chromatography or gas chromatography/mass spectrometry (GC–MS) [14,17], but these methods have two weaknesses: (1) as the intermediates are mostly polar compounds, they can easily dissolve in water, the non- or low-polar solvents extract them from water hardly; while polar solvents are so easily dissolved in water that it is hard to part them from water. (2) Esterification only fits for derivatizing acids, while acetylation only for hydroxylated compounds. In addition to that, it is possible to detect intermediates by means of HPLC [18,19], using retention time to analyze them qualitatively. However, this method needs not only many calibration standards but also a lot of time because there are many unknown compounds in the intermediates, and some compounds have the same retention time. Accordingly, this method is not perfect.

The focus of this work is also to detect intermediates, using gas chromatography/mass spectrometry after derivatization by *N*-methyl-*N*-(tri-methylsilyl)trifluoroacetamide (MSTFA) and trimethyliodosilane (TMIS), this silane reagent can derivatize organic substances with active hydrogen. Before the

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derivatization, no extraction was carried out; the solution after illumination was dried by nitrogen in order not to lose any substance and intermediates such as alcohols, aldehydes, acids, etc. As these intermediates can be detected by phenol direct degradation, it is not necessary to start the degradation from diphenols [14]. The degradation in the presence of nanomaterial titanium dioxide (TiO_2) was compared with that in the absence of it. In this work, glycerol, hydroxyl acids, hydroxyl aldehyde, etc., also were detected as the main intermediate products. And it is also discovered that the presence of TiO_2 does not favor the degradation when the concentration of phenol is 100 mg/L.

Phenol was chosen as the studying object, for it is typical in phenolic compounds, moreover, it is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic compounds [20,21]. To detect the intermediates produced by phenol is useful for disclosing the photodegradation mechanism; it is also helpful for studying the degradation of its derivatives like chlorophenols, chlorinated pesticides, phenoxy herbicides, etc.

2. Materials and methods

Phenol and chloroform used in this experiment are analytical reagent grade. Acetic acid and methanol are chromatogram purity. TiO_2 is mixed crystal and particle size is 20–30 nm, provided by Hebei University Nanomaterial research center. MSTFA and TMIS were purchased from Sigma. The water used for the photocatalytic studies was doubly distilled in quartz water still.

Photocatalytic experiments were carried out in a cylindrical photoreactor with a lid, it was made from glass in which quartz content is no less than 95%, penetration is 69% at wavelength 253.7 nm. its height 55 mm, i.d. 85 mm and wall thickness 2 mm. During the experiment, the photoreactor contained 40 cm³ 100 mg/L of phenol solutions and 8.16 mg of TiO_2 , which was sonicated before illumination with a small amount of the phenol solution for 5 min. The reactor was placed within a dark box, A 20 W, length 480 mm, the dominant wavelength 253.7 nm ultraviolet lamp was 5 cm over the reactor. The reactor content was mixed by a magnetic stirrer at room temperature. 1 cm³ of the slurry was withdrawn respectively at the time of 0, 3, 12 h. After centrifugation, 25 μL was analyzed by HPLC (Shimadzu) using SPD-6AV detector, the wavelength of UV absorbance detector was 280 nm. The reaction products were separated on an ODS C₁₈ column using 1% acetic acid +35% methanol +64% water (v/v) as eluent.

GC–MS measurements were performed as follows. Primarily, after 12 h of illumination, 6 cm³ of the slurry was withdrawn from the reactor. After centrifugation, the pellucid solution was dried by nitrogen, derivatized by 50 μL MSTFA and 0.5 μL TMIS at 62 °C for 70 min. Then 1 μL was analyzed on the gas chromatography (Hewlett-Packard model 6890 series) coupled with mass spectrometry (VG70E-HF, Micromass corporation) in scan mode between 30 and 600 m/z . The analyzed products were separated on a HP-5 column using programmed tempera-

ture: started at 28 °C, holding for 2 min then to 280 °C, holding for 10 min at a rate of 6 °C/min, the column pressure was kept at 6.9×10^3 Pa. The carrier gas (Helium) was kept at a flow rate of 1.5 mL/min and a linear speed of 44 cm/s. The sample was injected in splitless mode. For MS analysis, ionization energy 70 eV and accelerated voltage 6 kV were applied; the resolving power was 1000.

A 40 cm³ of a 100 mg/L phenol solutions without TiO_2 was illuminated under the same conditions and analyzed with the same method, but did not need centrifugation. Simple extraction of the reaction products (by chloroform, without derivatization) from the solution after illumination for 3 and 12 h under the two conditions was also done and products were analyzed by GC–MS. Because the background produced by the derivatization is complex, 6 mL doubly distilled water was used to do blank test with the same method.

3. Results and discussion

The main task of the study was to detect the intermediate products; 100 mg/L phenol solution was used because the concentration of the intermediates was higher. A 15 mg/L phenol solution was also experimented under the same concentration of titanium dioxide, the degradation rate was obvious, but the concentration of the intermediates are also low, they may be lower than the detection limit, so 100 mg/L phenol solution was chosen. The amount of titanium dioxide, 8.16 mg, used in the study, was chosen experimentally. When the amount was added, the photoreaction rate was not increased obviously owing to light scattering on TiO_2 particles. Therefore, in order to omit any influence of the concentration of titanium dioxide, 8.16 mg TiO_2 was used.

After 3 h of degradation the color of the solution became light yellow; after 12 h, the color was yellow. Simple extractions of the reaction products in the presence of TiO_2 and in absence of it were both analyzed by GC–MS respectively, but there was no other peak except phenol in the total ion current graph. The pellucid solutions after illumination under the two conditions were analyzed by HPLC, the results revealed phenol was decreased, contrasting to the content of phenol by HPLC before illumination. The intermediates were eluted before phenol, as the ODS C₁₈ column is non-polar and the polarity of the detected intermediates was higher than the one of phenol. After derivatization by MSTFA and TMIS, the reaction products were analyzed by GC–MS; there were many peaks in the total ion current graph under the two conditions. The total ion current graphs were similar, see Fig. 1. These peaks were identified by MS, The results indicated the main intermediates are the same in the two cases. They are 2-hydroxy-propaldehyde, hydroxy-acetic acid, 3-hydroxy-propyl acid, glycerol, catechol, (E)-2-butenedioic acid, resorcinol, hydroquinone and 1,2,3-benzenetriol. The mass spectrum of some products after derivatization by MSTFA and TMIS is reported in Fig. 2. In the two ion current graphs, peak 8 is the sum of resorcinol and hydroquinone, since GC does not separate them and they are also very similar on the MS. There are also some high peaks in the total ion current graphs without number because they

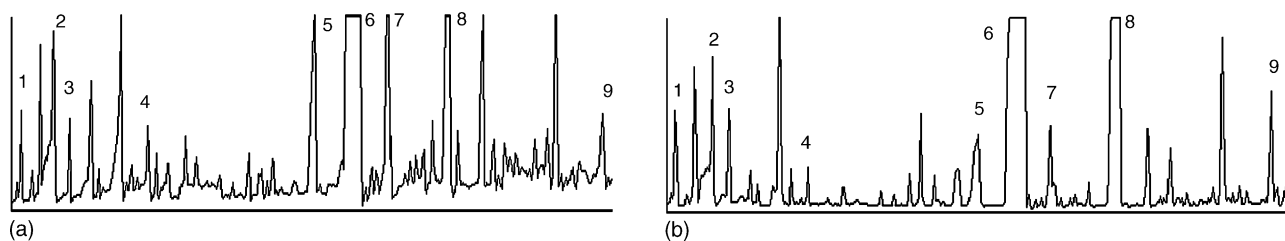


Fig. 1. Total ion current graph of intermediates after 12 h of ultraviolet illumination (a) in the presence TiO_2 and (b) in the absence of TiO_2 . The peaks in the graph corresponding to the organic compounds before derivatization are respectively: (1) phenol; (2) 2-hydroxy-propaldehyde; (3) hydroxy-acetic acid; (4) 3-hydroxy-propyl acid; (5) glycerol; (6) catechol; (7) (E)-2-butenedioic acid; (8) resorcinol and hydroquinone; (9) 1,2,3-benzenetriol.

are the peaks in the background. Some small peaks could not be analyzed qualitatively because the MS information was not sufficient.

In this experiment, hydroxyaldehyde, hydroxyacid, (E)-2-butenedioic acid, glycerol, etc., were detected. Benzoquinone, maleic acid, malonic acid, some low molecule weight organic acids such as oxalic acid and acetic acid were not detected [17,18,21]. About the mechanism of the photodegradation by TiO_2 , it has been reported [5,22] that $\bullet\text{OH}$ radicals attack the phenyl ring, yielding catechol, resorcinol and hydroquinone, then the phenyl rings in these compounds break up to give malonic acid, then short-chain organic acids such as maleic, oxalic, acetic, formic, and finally CO_2 . The production of $\bullet\text{OH}$ radicals takes place as follows: TiO_2 under the ultraviolet radiation gives rise to electron–hole pairs on the surface, which react with water molecules to give $\bullet\text{OH}$. During the process,

H^+ or H^\bullet is scavenged by oxygen to form HO_2^\bullet radicals, which finally convert to $\bullet\text{OH}$ radicals. Therefore, the principal reaction leading to organics decomposition would be the one with $\bullet\text{OH}$ radicals. But based on the intermediates detected in this experiment, it can be concluded that $\bullet\text{H}$ also takes part in the photodegradation. The reaction route can be described as follows, see Scheme 1. $\bullet\text{H}$ may be produced through three routes: (1) water molecules react with holes in the electron–hole pairs to produce $\bullet\text{OH}$ and H^+ , H^+ combines with the electron from the electron–hole pairs; (2) during the process of $\bullet\text{OH}$ attacking the aromatic ring, carbon–hydrogen bond break up, hydrogen is substituted for $\bullet\text{OH}$, and $\bullet\text{H}$ is produced; (3) as TiO_2 exists or not, the main intermediates detected are the same and UV only provides energy to break covalent bonds, $\bullet\text{H}$ may also be produced by the break of oxygen–hydrogen bond in water molecules and phenol molecules; or carbon–hydrogen in phenol molecular. For

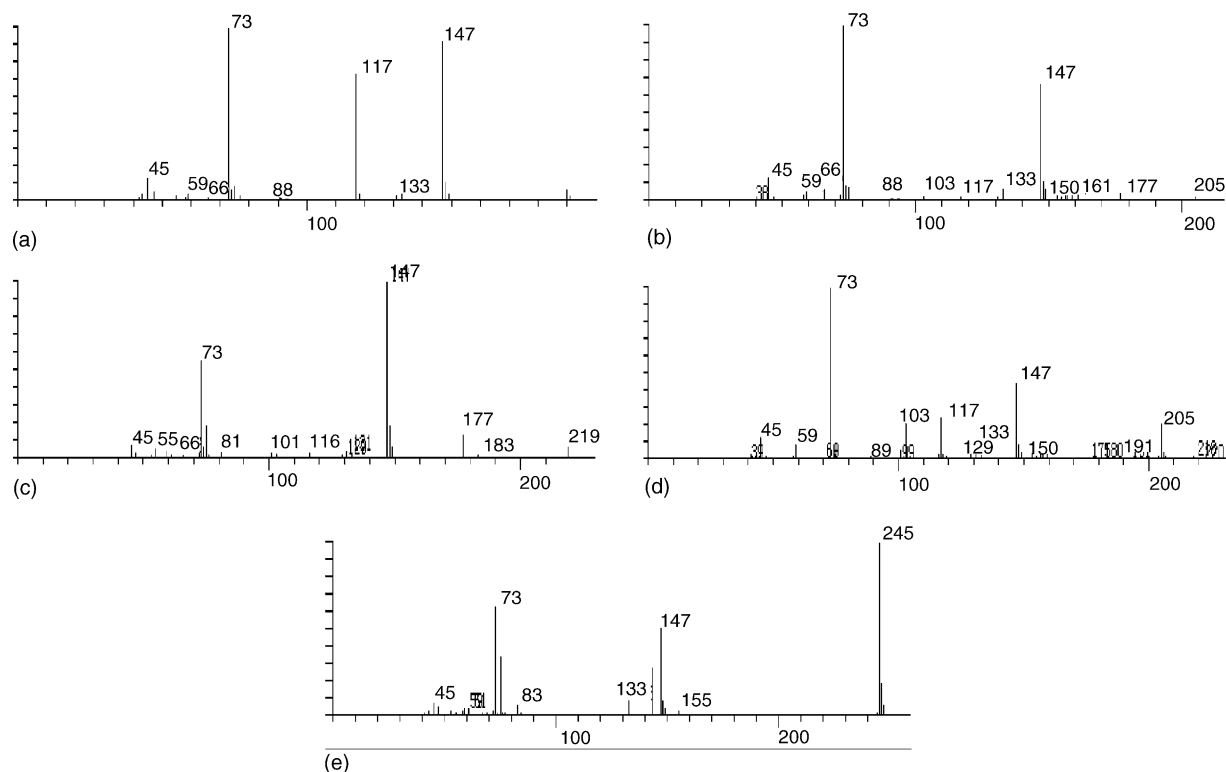
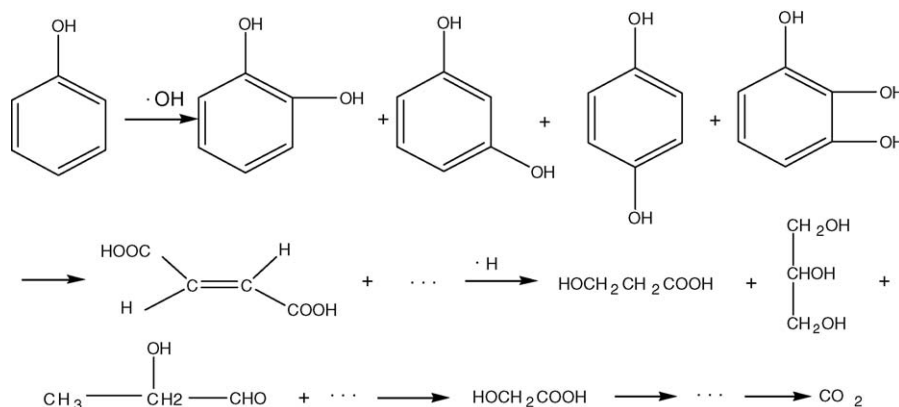


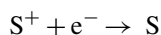
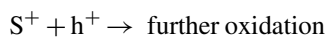
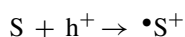
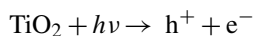
Fig. 2. The mass spectrum of some products after derivatization by MSTFA and TMIS: (a) 2-hydroxy-propaldehyde; (b) hydroxy-acetic acid; (c) 3-hydroxy-propyl acid; (d) glycerol; (e) (E)-2-butenedioic acid.



Scheme 1. Phenol photodegradation route.

UV, the energy of wavelength 253.7 nm is equal to 472 kJ/mol, which is higher than the bond energy of H–O (462.8 kJ/mol), C–H (413.0 kJ/mol), C–O (357.7 kJ/mol), so these bonds probably break upon UV irradiation.

HPLC was used to analyze the degradation efficiency. The degradation efficiency of the solution in the presence of TiO_2 is 16% and 76% when illuminated for 3 and 12 h, while the efficiency in the absence of TiO_2 is 40% and 81.6%, respectively. It can be seen that in the first 3 h, the concentration of phenol is higher; the degradation efficiency without TiO_2 is two times more than that in presence of TiO_2 . As the reaction follows, the phenol concentration becomes lower and lower, the degradation efficiency in the presence of TiO_2 becomes closer and closer to that without TiO_2 . After 12 h irradiation they are almost the same. TiO_2 decreases the reaction rate when the phenol concentration is higher; its catalysis becomes evident when the concentration is lower. Actually, the photocatalytic degradation rate of phenol in the presence of TiO_2 does not increase linearly with phenol concentration. On the contrary, the rate reaches a maximum around 5×10^{-4} M phenol and starts decreasing [23,24]. It is possible to account for such a trend upon consideration of the kinetics of the process taking place at the water–semiconductor interface. A substrate S can be oxidized upon reaction with holes or hydroxyl radicals on photocatalyst surface, but the oxidized intermediate can react with reducing species (e.g. electrons) yielding back S, which finally results in a decrease of the degradation rate of the substrate (phenol, but also other compounds) with increasing initial concentration [24–26]. A simplified scheme of the overall process is reported below (oxidizing and reducing species are generically indicated as h^+ and e^-):



4. Conclusion

The main intermediates of phenol degradation under ultraviolet illumination are the same, whether Nanomaterial TiO_2 presents or not. They include 2-hydroxy-propaldehyde, hydroxy-acetic acid, 3-hydroxy-propyl acid, glycerol, catechol, (E)-2-butenedioic acid, resorcinol, hydroquinone and 1,2,3-benzenetriol. The formation of glycerol, hydroxyaldehyde and hydroxyacid showed that besides $\cdot\text{OH}$, $\cdot\text{H}$ is also an important active free radical in the degradation. When the concentration of phenol is 100 mg/L, TiO_2 does not favor the degradation; as the concentration gets lower, its catalysis becomes obvious step by step.

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