

Photoelectrocatalytic Degradation of Phenol Using a TiO_2/Ni Thin-film Electrode

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Abstract—As a new type of photoelectrode, TiO_2/Ni thin-film electrode was prepared by dip-coating technique. The structural and surface morphology of electrode was examined by X-ray diffraction (XRD) and scanning electron microscope (SEM). Effects of initial phenol concentration, pH value, number of film layers, voltage of electrical bias applied, variation of inorganic salt type and types of dissolved gas on the photoelectrocatalytic (PEC) degradation of phenol using ultraviolet (UV) illuminated TiO_2/Ni thin-film electrode were investigated. The mechanism of PEC degradation of phenol was also studied by analyzing reaction intermediates.

Key words: Phenol, Photoelectrocatalytic, Degradation, TiO_2/Ni Thin-film Electrode, Mechanism

INTRODUCTION

Since the first study on photocatalytic oxidation for treating organic contaminants in wastewater was carried out by Carey in 1976 [Carey et al., 1976], photocatalytic oxidation using large band gap semiconductor particles (such as TiO_2 , ZnO , WO_3) as a method of purifying water has been developed extensively. Numerous research reports have shown that most kinds of refractory organic pollutants could be degraded, such as surfactants, detergents, dyes, pesticides, and herbicides, etc. [Park et al., 2001; Ollis et al., 1991; Tang et al., 1995; Vulliet et al., 2002]. Among the various available semiconductor photocatalysts, TiO_2 has attracted the most attention due to its ready availability, non-toxic nature, photochemical inertness and effective catalytic activity.

However, there are some inherent problems in using the TiO_2 particle suspensions for toxic water remediation such as the difficulty of separating and recovering the photocatalyst particles from aqueous phase, and the low quantum yield (less than 10% in general [Choi et al., 1994]) mainly resulting from high degree of recombination between photogenerated charge carriers [Morison, 1984]. To solve these problems, many efforts and attempts have been made by researchers. One improvement is to immobilize TiO_2 film on a solid carrier such as sand, resins, glass media and metallic substrates by coating, precipitating, soaking, or spinning methods. The immobilized TiO_2 photocatalytic oxidation processes made the TiO_2 separation from water phase much easier, but they did not achieve any improvement in quantum efficiency. Then on the basis of immobilized TiO_2 photocatalytic oxidation, researchers developed photoelectrocatalytic (PEC) oxidation by applying a positive potential bias to TiO_2 film [Vinodgopal et al., 1993; Janet et al., 1997; Candal et al., 1998; Li et al., 2002]. The externally applied anodic bias can withdraw the excited electrons to a counter-electrode and results in a decrease in the recombination rate of photogenerated electrons and holes.

In this study, a TiO_2/Ni thin-film electrode as a new type electrode was produced by dip-coating technique, and phenol was em-

ployed as a target chemical for PEC oxidation under UV irradiation. Our purpose here was to investigate the influence of various parameters (such as pH value of solution, initial phenol concentration, quantity of catalyst, voltage of electrical bias applied, etc.) on degradation of phenol. The pathway and mechanism of PEC degradation of phenol was further illustrated.

EXPERIMENTAL

1. Preparation of Photoelectrodes (TiO_2/Ni)

The TiO_2 sols were synthesized according to the sol-gel methods [Yu and Zhao, 2001]. The photoelectrodes utilized rectangle

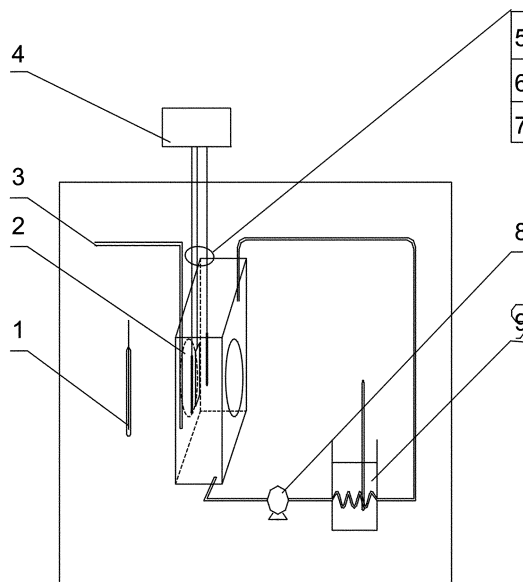


Fig. 1. Schematic diagram for the reactor system for the photoelectrocatalytic reaction.

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|---------------------------------------|---|
| 1. 300 W medium pressure mercury lamp | 5. Working electrode (TiO_2/Ni) |
| 2. PEC reactor | 6. Counter electrode (Pt foil) |
| 3. Bubbled gas | 7. Reference electrode (SCE) |
| 4. Potentiostat | 8. Gear pump |
| | 9. Water bath |

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plates of raw foamed nickel (10 cm×5 cm, 2.0 mm thick, porosity 95%) as supported materials. The upper 5mm of foamed nickel plate was tapped off before coating in order to provide a place for ohmic contact. Titania film was deposited by dip-coating technique using a withdrawal speed of 2 mm s⁻¹. Then the film was fired in the muffle furnace with a temperature ramping rate of 20 °C min⁻¹. At 520 °C, the film was allowed to dwell for 1h and then was cooled until it attained room temperature. The mass of titania deposited was determined by weighing the foamed nickel before and after the titania coating.

2. Photoelectrocatalytic (PEC) Reactions

The PEC degradation reaction of phenol was carried out in the reactor system as shown in Fig. 1. The main components are the glass reactor, an ultraviolet light source and a potentiostat. The reactor and the UV lamp were placed in a black box in order to avoid extraneous illumination. The rectangular reactor (125 mm×80 mm×125 mm) with an effective volume of 1,000 mL, was placed 9 cm in front of the UV lamp. A plastic cap was placed on the reactor in order to seal it and install three electrodes. The PEC reaction employed a potentiostat connected with a TiO₂/Ni working electrode, a platinum foil counter electrode, and a saturated calomel reference electrode (SCE) (Therefore, all potentials are referred to SCE). A collimated light beam from a 300 W medium pressure mercury lamp with a maximum UV irradiation peak at 365 nm was used for excitation of the photoelectrode. The temperature of the solution was maintained at 20±2 °C. Test solution was recirculated through the system at a flow rate of 80 mL min⁻¹ by using a gear pump and gas (such as air, oxygen or nitrogen) was bubbled through the solution during the PEC reaction at a rate of 20 L h⁻¹.

3. Characterization and Analysis

3-1. Characterization of Photocatalysts

The crystalline phases of the electrode samples were identified by X-ray diffraction (XRD) measurement with a Rigaku D/MAX 2550 pc X-ray diffractometer with CuK_α irradiation at 40 kV. The microstructure of the samples was observed with a Hitachi S-570 scanning electron microscope (SEM).

3-2. Chemical Analysis

Analysis of phenol and oxidation products was carried out with high performance liquid chromatography (HPLC, Shimadzu LC-10ATV_p). The concentration of carboxylic acid was determined by ion chromatograph (792 Basic IC, Metrohm, Switzerland). Samples were withdrawn from the reactor at specified time intervals.

RESULTS AND DISCUSSION

1. Characterization of TiO₂/Ni Photoelectrode

From a visual observation, the raw foamed nickel was silver in color, the TiO₂/Ni electrode was light gray. Their morphologies were examined by SEM and are shown in Fig. 2 and Fig. 3. It was found that the raw foamed nickel has a three-dimensional grid structure with pentagon casement outspreading toward space. This structure could offer large surface area. In addition, foamed nickel has good electric conductivity. Therefore, foamed nickel is a suitable material for preparing TiO₂-coated photoelectrode. From Fig. 3, we found the spherical TiO₂ particles were distributed on the surface of foamed nickel homogeneously. The particle size was in the range of 150-200 nm. The XRD patterns of the electrode samples are shown in

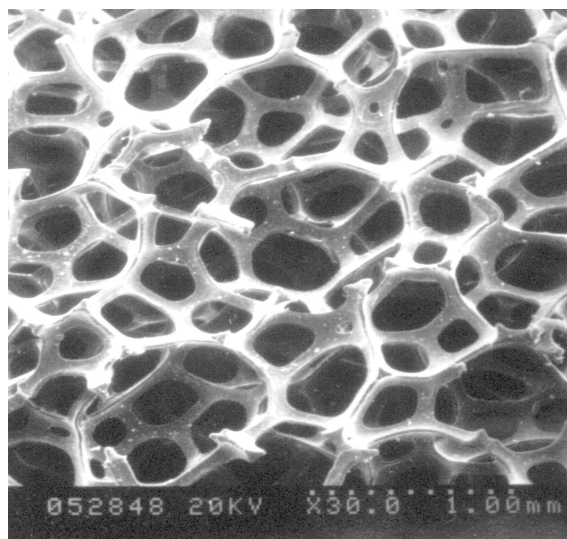


Fig. 2. SEM micrograph of foamed nickel (magnifies to 30).



Fig. 3. SEM micrograph of TiO₂/Ni sample (magnifies to 15000).

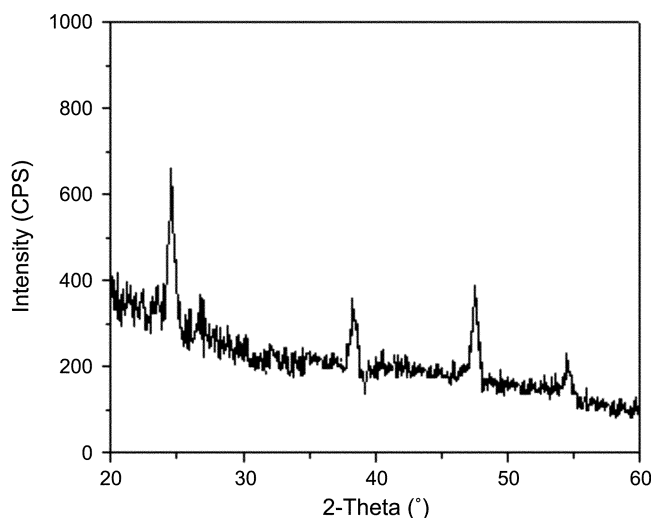


Fig. 4. X-ray diffraction pattern of TiO₂/Ni sample.

Fig. 4. The result of the XRD indicated that the TiO_2 was in the anatase form. The photocatalytic activity of anatase is often considered to be higher than that of rutile because the former has a larger band gap [Tanaka et al., 1991; Schlafani and Hermann, 1996; Bickley et al., 1991].

2. Photoelectrocatalytic (PEC) Reactions

2-1. Comparison of Photocatalytic (PC) and Photoelectrocatalytic (PEC) Degradation

The PEC oxidation may follow different reaction mechanism from the PC oxidation, so it is important to compare the rates of PEC oxidation and PC oxidation. The experimental results, shown in Fig. 5, demonstrated that the removal rate of phenol in the PEC

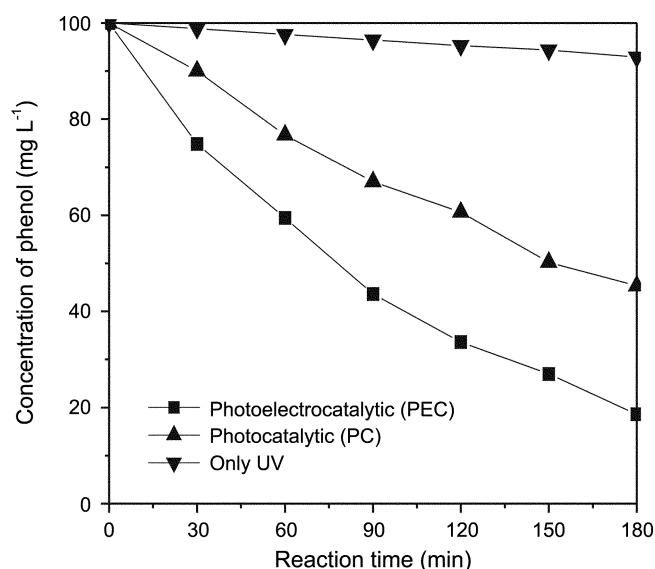


Fig. 5. Comparison of PEC and PC degradation of phenol. Operation conditions: pH 7.0, initial phenol concentration $100 \text{ mg} \cdot \text{L}^{-1}$, number of film layers 9, External bias 0.6 V vs. SCE, bubbled gas air.

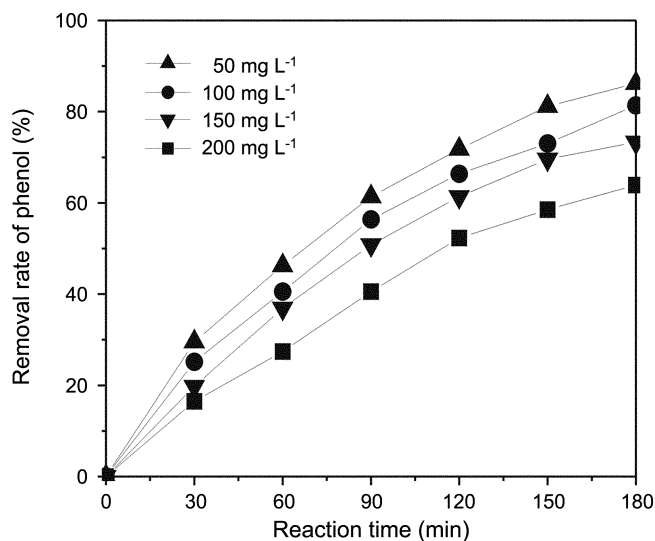


Fig. 6. Effect of initial phenol concentration on phenol degradation. Operation conditions: pH 7.0, number of film layers 9, External bias 0.6 V vs. SCE, bubbled gas air.

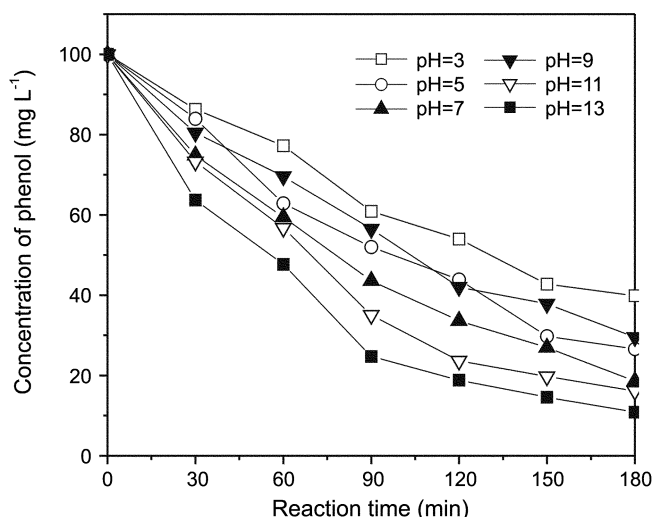


Fig. 7. Effect of different pH value on PEC degradation of phenol. Operation conditions: initial phenol concentration $100 \text{ mg} \cdot \text{L}^{-1}$, number of film layers 9, External bias 0.6 V vs. SCE, bubbled gas air.

oxidation was more than that in the PC oxidation and direct photolysis.

2-2. Effect of Initial Phenol Concentration.

Fig. 6 shows the effects of initial phenol concentration on degradation. The amount of the PEC degradation of phenol increased but the removal rate decreased with the increase of initial phenol concentration. This phenomenon was related with the number of the catalyst surface adsorption positions. Since the PEC oxidation took place on the catalyst surface, not in the bulk of the solution [Kim and Anderson, 1994], the accumulation of the adsorbate (phenol or the intermediates) on the surface of the electrode may result in a decline of degradation rate.

2-3. Effect of Initial pH Value

The initial pH values of solutions were adjusted with sulphuric acid and sodium hydroxide solution. As the experimental results show in Fig. 7, the phenol degradation shows its maximum at pH 7 when pH values were lower than 11. The dependence of the degradation rate of organics with pH was explained as a consequence of pH-mediated changes in the adsorption of organics on the surface of TiO_2 . It is reported that the isoelectric point of titanium dioxide anatase is pH 6.4. And at the isoelectric point, the surface charges are neutral so that it is easy to adsorb the active species such as elemental oxygen [Li et al., 2001]. Another explanation is that the reduction potential of the TiO_2 valence band changes enough with pH to affect the rate of degradation of phenol [Lu, 1996]. However, when pH was over 11, a rapid increase of removal rate was observed in our experiment. The reason may be that under the strong alkaline condition phenol would lose protons, and then being easier to be oxidized. Meanwhile, in alkaline medium, there were large quantities of hydroxyl radicals with strong oxidizing ability [Leng et al., 2000].

2-4. Effect of Film Layers

As shown in Fig. 8, the amount of the PEC degradation of phenol increased with the increase of layers of TiO_2 film. The decrease in effectiveness noted with 11 layers of film may be due to its relative

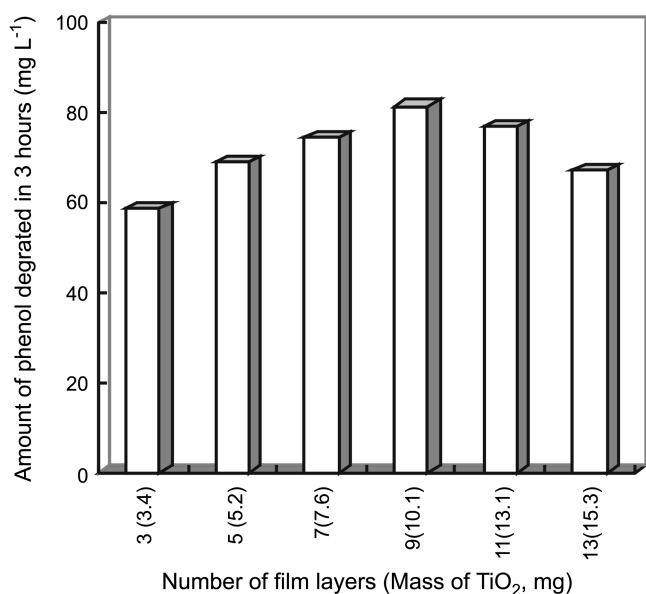


Fig. 8. Effect of number of TiO₂ layers on PEC degradation of phenol. Operation conditions: pH 7.0, initial phenol concentration 100 mg·L⁻¹, external bias 0.6 V vs. SCE, bubbled gas air.

high resistance. And if the film is too thick, light cannot reach the bulk of the catalysts; therefore, part of the TiO₂ could not be activated. These observations suggested that there might be optimum layers of TiO₂ film for an effective PEC reaction, and that was about 9 layers.

2-5. Effect of Applied Potentials

The PEC reactions were performed with different electrical bias. The test lasted 3 hr (the experimental results are shown in Fig. 9). The results indicated that the amount of phenol degraded under a negative bias (versus SCE) did not exceed the amount degraded when no bias (0 V versus SCE) was applied. However, when posi-

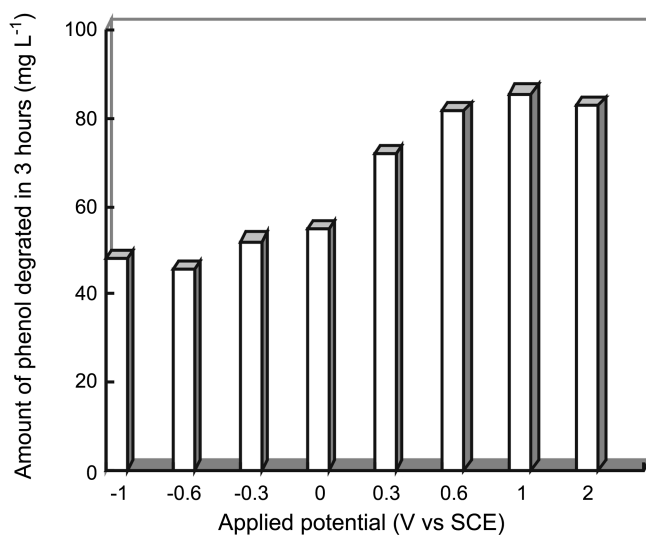


Fig. 9. Effect of different applied potentials (V vs. SCE) on degradation of phenol. Operation conditions: pH 7.0, initial phenol concentration 100 mg·L⁻¹, number of film layers 9, bubbled gas air.

tive potentials were applied across a photoelectrode, the amount of phenol degraded increased with the increase of potential. We believe this to be due mostly to a decrease in the electron-hole recombination rate. The application of positive potential across the foamed nickel supported TiO₂ photoelectrode could produce a potential gradient inside the film that forced the photogenerated holes and electrons to move in opposite directions. Subsequently, the concentration of photogenerated holes (or hydroxyl radicals formed by subsequent oxidation of water) on the surface increased. Consequently, the amount of phenol degraded increased with the increase of the potential. Most of the photogenerated electrons were removed either by the electric field or by reaction with dissolved oxygen; further increasing the applied potential beyond 1.0 V did not enhance the phenol degradation.

2-6. Effect of Dissolved Gas

If nitrogen was bubbled through the solution instead of oxygen, the efficiency decreased only by about 10%, as illustrated in Fig. 10. It means the PEC system can also be used under anaerobic conditions, unlike the PC reaction. Because in PEC reaction efficient charge separation of the photogenerated electrons and holes can be achieved by applying an anodic bias potential to the TiO₂/Ni thin-film photoelectrode, so oxygen is not necessary to scavenge the photogenerated electrons.

2-7. Effect of Dissolved Inorganic Ions

After NaNO₃, NaSO₄, NaCl and NaClO₄ were added, the amounts of phenol degraded were 83.7, 74.8, 85.6 and 79.1 respectively. Compared with no inorganic ion addition, there were no evident differences in the amount of the phenol degraded as shown in Fig. 11. So the effect of dissolved inorganic ions was not important when a positive potential was applied to the electrode. The amounts of degradation of phenol decreased slightly while SO₄²⁻ or ClO₄⁻ was supplemented. The reason is that SO₄²⁻ or ClO₄⁻ could compete either for the photogenerated holes or for the hydroxyl radicals generated by these holes. In addition, adsorption of them on TiO₂ could displace surface hydroxyl groups, consequently decreasing the num-

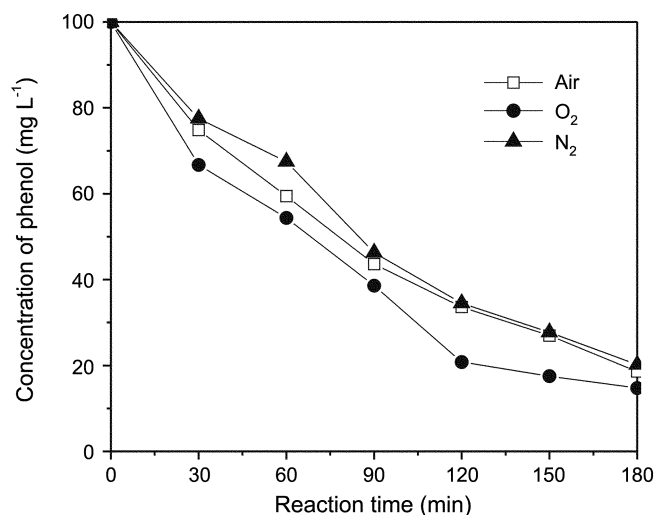


Fig. 10. Effect of different types of dissolved gas on phenol degradation. Operation conditions: pH 7.0, initial phenol concentration 100 mg·L⁻¹, number of film layers 9, external bias 0.6 V vs. SCE.

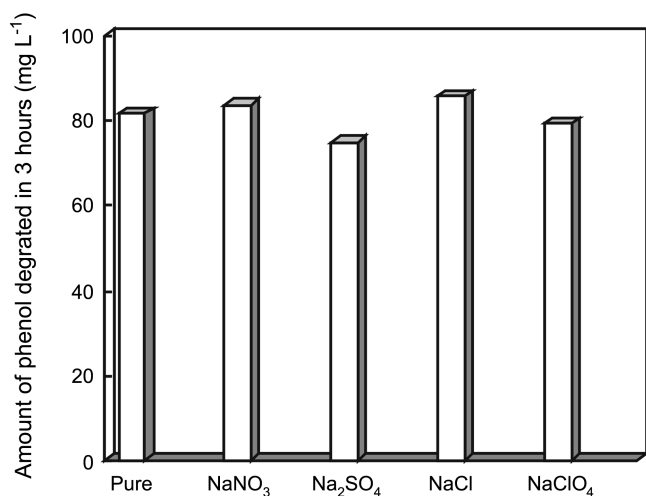


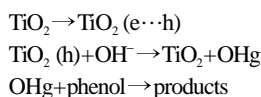
Fig. 11. Effect of 0.01 M inorganic ions on phenol degradation. Operation conditions: pH 7.0, initial phenol concentration 100 mg·L⁻¹, number of film layers 9, external bias 0.6 V vs. SCE, bubbled gas air.

ber of such groups available to produce hydroxyl radicals.

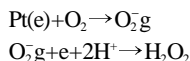
3. Mechanism of Photoelectrocatalytic (PEC) Reaction

The major PEC reactions that initiate redox process in the electrode components can be summarized as follows:

At photoanode:



At dark cathode:



where e and h are electron and hole, respectively [Vinodgopal et al., 1996]. They are formed within the semiconductor particle after

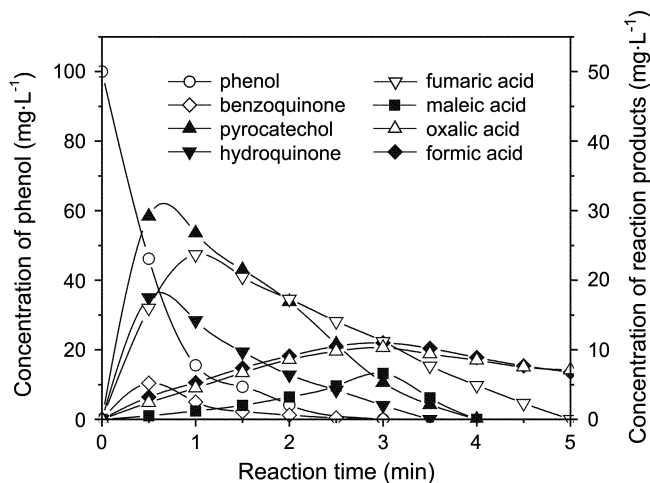
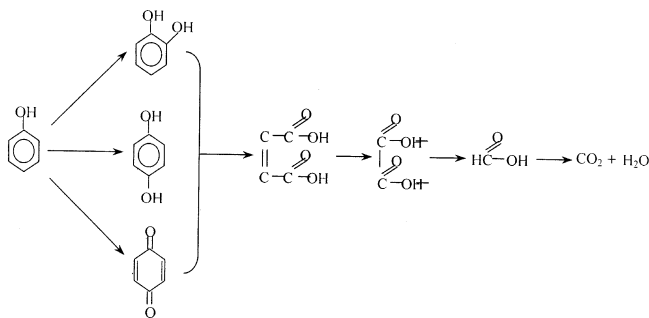


Fig. 12. Phenol and reaction products concentration during the PEC degradation of phenol. Operation conditions: pH 7.0, initial phenol concentration 100 mg·L⁻¹, number of film layers 9, external bias 1.0 V vs. SCE, bubbled gas oxygen.

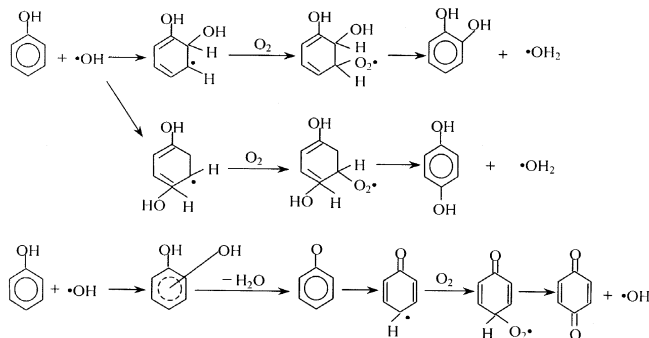
band gap excitation.

The phenol was degraded mainly through the oxidizing reaction induced by hydroxyl radical, which was produced in the PEC reaction shown in above stated equations. The intermediates of the PEC reaction have now been analyzed to probe the reaction pathways. The main products detected were pyrocatechol, hydroquinone, benzoquinone, fumaric acid, maleic acid, oxalic acid and formic acid detected with HPLC and IC. Fig. 12 shows that the concentrations of phenol and intermediates varied with the reaction time.

In general, the degradation of phenol follows the pathway below: (1) oxidation of phenol to other hydroxylated or oxygenated compounds, especially quinonic compounds (cyclic intermediates), (2) the ring opening reaction to form organic acids, and (3) mineralization of organic acids to carbon dioxide. However, Fig. 12 indicates that the degradation was not simple following the sequences (1)-(2)-(3). The first and second stages proceeded almost simultaneously. And the third stage was going on relatively slowly. The entire PEC degradation pathway of phenol could be expressed as follows:



The dihydroxyl compounds generated in the first stage such as pyrocatechol, hydroquinone and benzoquinone support the mechanism of hydroxyl radical attacking benzene ring. The detailed process of generation may be proposed to follow as:



CONCLUSIONS

This study demonstrated that Titania coatings on foamed nickel provided suitable materials for constructing PEC reactors for phenol wastewater treatment. And the advantages of combining photocatalysis with electrochemistry, by applying positive potentials (versus SCE) across the photoelectrode, have been confirmed. Influence of various parameters on degradation of phenol was investigated in detail. And it was found that the pH value of the solution, initial phenol concentration, number of film layers and voltage of electrical bias applied obviously has an influence on the degrada-

tion of phenol. Meanwhile, types of dissolved gas and inorganic ions did not significantly affect the degradation of phenol. It means the PEC process could maintain its high reaction efficiency under adverse conditions, such as in the absence of oxygen or in the presence of interfering ions. In addition, insight into the pathway of phenol degradation has also been gained from our PEC experiments. The result showed that the stages of oxidation of phenol to other hydroxylated or oxygenated compounds and ring opening reaction to form organic acids proceeded almost simultaneously, and the stage of mineralization of organic acids was going on relatively slowly.

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