Studies on the Kinetic Properties of Photocatalytic Degradation of Phenol in Water Using ZnO Nanopowder as a Photocatalyst

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ABSTRACT

Photocatalytic degradation of phenol was examined in slurry reactor with UV light irradiation using ZnO nanopowder as a photocatalyst. The effects of process parameters such as catalyst dosage, initial concentration of phenol, initial pH value of aqueous solutions and different anions on the degradation efficiencies of phenol were systematically investigated with high performance liquid chromatography (HPLC). The kinetic rate constants were evaluated by the changes in the phenol concentration and catalyst dosage. The degradation kinetics of phenol followed the pseudo first-order kinetics.

Keywords: photocatalytic degradation, ZnO nanopowder, slurry photoreactor, high performance liquid chromatography

1. INTRODUCTION

Phenolic compounds are the commonly encountered organic pollutants in the industrial effluents that have caused severe environmental problems. The use of these chemicals may result in widespread contamination of the aquatic ecosystems due to their persistent, toxic and carcinogenic properties [1]. A representative of this class of compounds is phenol. Phenol and their degradation products in the environment are major aquatic pollutants. Therefore, the concentration of phenol in drinking water has been limited only to be 1 μg L^{-1} by the World Health Organization (WHO). Since they are stable and soluble in water, their removal to reach safety levels in the range 0.1-1.0 mg/L is not easy.

In recent years, heterogeneous photocatalysis involving semiconductors mediated redox reaction has been proved to be one of the most effective methods to remove and detoxify organic pollutants in water. Many reviews in the recent past have evaluated the efficiency of TiO_2, which has an optimum band gap of 3.2 eV, in the oxidative degradation of numerous organic compounds and reduction of inorganic metal ions [2]. These processes are based on the generation of the strongly oxidizing hydroxyl radicals (HO•), which oxidize a wide range of organic pollutants that could be present in water and wastewater. As a contrast, ZnO, a kind of semiconductor which has the similar band gap as TiO_2, is not thoroughly investigated. However, the advantages of ZnO as a photocatalyst are that it can absorb the large fraction of solar spectrum and more light quanta than TiO_2 [3]. Otherwise, ZnO has more functions than TiO_2 [4]. Recently, some researchers have demonstrated that ZnO can be used in the acidic and alkaline conditions [5, 6]. On the other hand, nano-sized particles have their different physical and chemical properties from bulk materials. When used as catalysts, their catalytic activities could be expected to be enhanced not only because of their increased surface area but also because of the changes of their surface properties such as surface defects [7]. Therefore, in the present work, the suitability of ZnO nanopowder as a photocatalyst in degradation of phenol was investigated as compared with TiO_2 and the degradation kinetics of phenol in nano-ZnO suspension solution was examined with the changes of various parameters, such as initial concentration of phenol, amount of catalysts, initial pH of solution and anions.

The purpose of this study was to investigate the photocatalytic kinetics properties of phenol in the home-made slurry reactor using ZnO nanopowder as a photocatalyst under external UV light irradiation. Meanwhile, the photocatalytic activity of ZnO was compared with that of TiO_2 in the removal of phenol from wastewater. Effects of operating parameters such as the dosage of photocatalyst, the initial concentration of phenol and the initial pH of solution were quantitatively discussed. The parameters in the proposed simulation model were assessed using the experimental results by varying the operation conditions.

2. EXPERIMENTALS

2.1 Materials

Photocatalyst TiO_2 (particle sizes: 10 nm and specific area: 100-130 m^2/g) and ZnO (particle sizes: 40 nm and specific area: 10-25 m^2/g) were obtained from Alfa Aesar Com. Ltd., USA. Phenol (analytical reagent grade, purity ≥ 99%) was purchased from Sigma Aldrich Com. Ltd., German. All chemicals were analytical purities. Ultrapure water obtained by Millipore system was used for the preparation of solutions.

2.2 Photoreactor

Photocatalytic degradation experiments were carried out in a 200-mL Pyrex-glass cell (6 cm i.d. and 14 cm length) wrapped with aluminum foil to avoid the release of radiation. The light source assembly consisting of 13 W UV-lamp with a jacket quartz tube (3.2 cm i.d., 3.8 cm o.d. and 16 cm length) was put concentrically inside the glass cell filled with 100 mL of prepared dispersion containing phenol and catalyst at appropriate concentrations, respectively. The lamp radiated predominantly at 365 nm (3.4 eV) wavelength. Cool water was circulated in the Pyrex-glass container (8 cm i.d. and 14 cm length) outside the cell to control the solution temperature below 30 ^{o}C as excess temperature might deplete the dissolved oxygen in the solution. A magnetic stirrer was used to homogenize the slurry solution in the reactor.

2.3 Analysis

Prior to irradiation, the slurry solutions were magnetically stirred for about 10 min to obtain the equilibrium of adsorption and desorption. The pH of solutions was measured and adjusted by HCl (0.1 mol/L) and NaOH (0.1 mol/L). At the given interval time, 5-mL samples were withdrawn and filtered through a Millipore membrane, then centrifuged to remove any nano-sized catalyst particles before injections into HPLC system. The concentration of phenol was determined by HPLC (Shimadzu) with UV-Vis detector. The mobile phase was the mixture of methanol and water at the volumetric ratio of 80:20 and the detection UV wavelength was 274 nm. The degradation efficiency of phenol in the slurry photocatalytic system was calculated as following:

$$DRE = \frac{C_t}{C_0} \times 100\ \% \qquad (1)$$

where C_0 and C_t were the initial phenol concentration and the residual phenol concentration at t time (mg L^{-1}), respectively.

3. RESULTS AND DISCUSSIONS

3.1 Comparison the activities of catalysts

The photocatalytic activities of TiO_2 and ZnO nanopowder were compared at various dosages. The different dosages of catalysts for the degradation of phenol by two kinds of catalysts were plotted versus reaction time in Fig.1. Obviously, the efficiencies of ZnO nanopowder were superior to TiO_2 as catalysts. One possible explanation for the high photocatalytic activity of ZnO could be the higher production of hydrogen peroxide yielded on the catalyst surface compared with TiO_2 when illuminated [8]. Some studies have confirmed that ZnO exhibits a better efficiency than TiO_2 in photocatalytic degradation of some dyes, even in aqueous solution [9, 10]. The results in the present work were consistent to those studies.

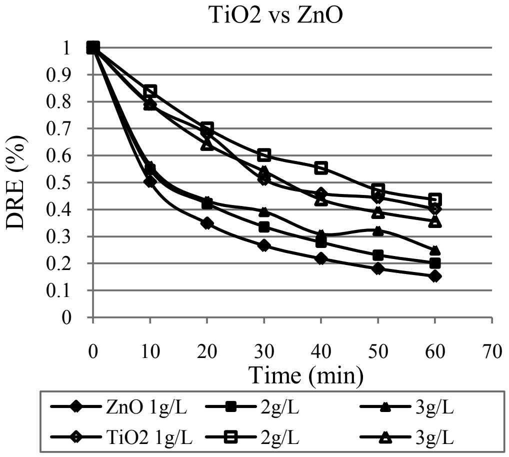

Fig.1. Performance comparisons of different catalytic systems.

3.2 Effect of pH

In heterogeneous mediate, the pH of the suspension solutions was altered to study the photocatalytic degradation occurring on the surfaces of semiconductor particles, because the pH could change the surface charge properties of the photocatalysts, resulting in the available surface sites for the adsorption potential and the photocatalytic activities [7]. The effects of pH on photocatalytic degradation efficiencies were investigated over the pH range of 4 to 8. The results in Fig.2 showed the degradation efficiency of phenol increased steadily with the slow increase of pH from 4 to 6, then decreased slightly at a higher pH value from 7 to 8.

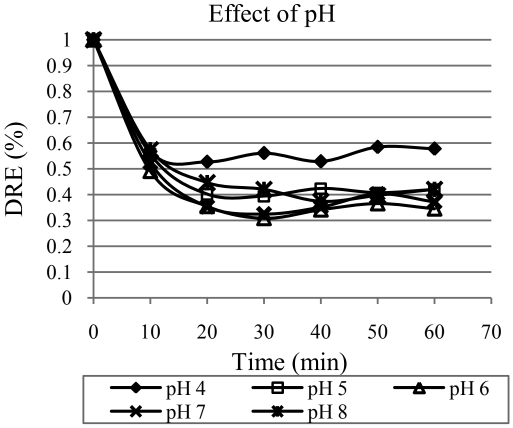

Fig.2. Effects of initial pH on the degradation efficiency of phenol.

Higher pH value could provide higher concentration hydroxyl ions to react with holes (h^+) to form hydroxyl radicals (OH•), subsequently to promote the photocatalytic efficiency of phenol. Meanwhile, it has been demonstrated the zero charge point in the ZnO particles ranges from 6 to 7. At the higher pH more than 8, the surface charge of ZnO particles could be slightly negative. Therefore, the reduction in the adsorption frequency might probably due to the electrostatic repulsion between the anions and the negatively charged surface, resulting to the decrease of the reactivity of photocatalysis of phenol occurring on the surface of ZnO nanopowder.

3.3 Effect of initial concentration of phenol

The effects on the photocatalytic degradation of phenol were investigated by varying the concentration of phenol from 5 mg L^{-1} to 40 mg L^{-1} at constant catalyst loading (1 g L^{-1}, pH 7). The results (in Fig.3.) obviously shown the degradation efficiencies decreased with the increase of initial concentrations of phenol. The negative effects could be explained that the equilibrium adsorption of phenol at the active sites on the catalyst surface decreased with the increase of phenol concentration; hence the competitive adsorption of O_2 and hydroxyl ions at the same time decreased, implying that a lower formation of O_2• and OH• radicals, the principle oxidants necessary for the high degradation efficiency. Meanwhile, according to the Beer-Lamber law, the path length of photons entering solutions decreases with the initial concentration increases, which causes lower photon adsorption on the catalyst particles, and consequently, a lower degradation efficiency [11].

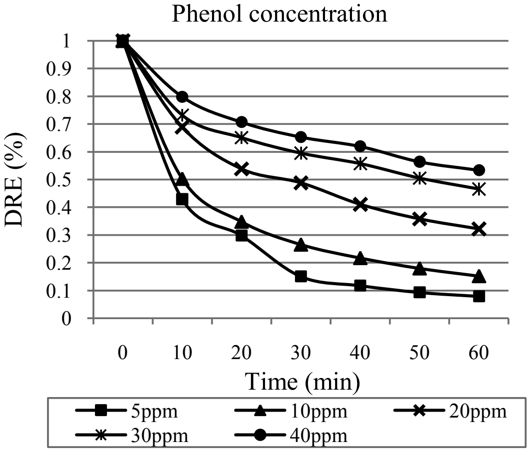

Fig.3. Effects of initial concentration of phenol on the degradation efficiency.

3.4 Effect of catalyst dosage

In the slurry photocatalytic processes, the amount of catalysts was an important parameter. So the effect of catalyst concentrations on the photodegradation efficiency of phenol was studied by changing the catalyst dosage from 0 to 3 g L^{-1} with a constant phenol concentration (5 mg L^{-1})., the degradation efficiencies of phenol, shown in Fig.4., were found to increase then decrease as ZnO dosage increased more than 0.5 g L^{-1}. The probable cause could be the aggregation of ZnO particles at higher concentrations to result in the decrease of active sites on the catalyst surface [12]. While, it is known there exists a practical limit of the scatter light (around 1 mg L^{-1}), above which the photon fluxes would be reduced within the suspension solution, hence, resulting to the decrease of the degradation efficiency [13, 14].

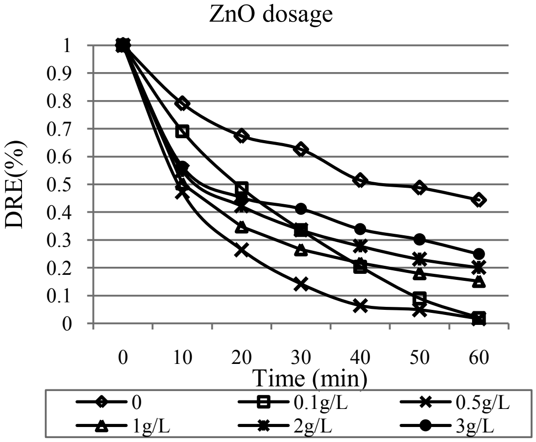

Fig.4. Effects of catalyst dosages on the degradation efficiency of phenol.

3.5 Effect of inorganic anions

Commonly, there are various inorganic anions in water, which have serious effects on the properties of water. They also can change the ionic strength of the solution, therefore, affect the catalytic activities of catalysts and the photocatalytic degradation efficiencies. The effects of chloride ion, carbonate ion, nitrate ion and sulphate ion were investigated using corresponding Na^+ as cation. The results (data not shown) illustrated the negative effects of all anions on the photocatalytic degradation efficiencies, which were in agreement with the earlier researches [11, 15-18]. The inhibition effects of anions could be explained that the anions as oxidants scavengers reacted with hydroxyl radical to form inorganic radical anions. Although, the radical anions possess their oxidization, they have lower oxidizing potentials, compared with hydroxyl radicals. Therefore, in the presence of anions in the slurry solutions, the photocatalytic degradation would be hindered.

3.6 Photocatalytic kinetics of phenol

Although many theoretical equations have been proposed for described the kinetics based on the mass balance, chemical kinetics and initial conditions, the heterogeneous photocatalytic degradation process in a slurry reaction system involves complicated mechanisms with hydroxyl radicals and organic solution adsorbed on catalyst surface. As documented in published researches[19, 20], the photocatalytic reaction equation can be expressed as the apparent first-order rate formula:

$$\ln \frac{C_t}{C_0} = -\kappa_{app}\, t \qquad (2)$$

where is C_0 is the initial concentration of organic solution, C_t is the residential concentration of organic solution at *t* time. The linearity dependence of ln (C_t/C_0) versus *t* can be used to obtain as the data of κ_{app}. By fitting the pseudo-first-order model, the values of κ_{app} were listed in Table 1.

Process parameter	Value	First-order reaction model	
		κ_{app} (min^{-1})	R^2
Initial concentration of phenol	5 ppm	0.041± 0.003	0.936
	10 ppm	0.029 ± 0.002	0.928
	20 ppm	0.018 ± 0.009	0.950
	30 ppm	0.011 ± 0.009	0.920
	40 ppm	0.010 ± 0.005	0.937
ZnO dosage	0 g/L	0.013 ± 0.001	0.967
	0.1 g/L	0.059 ± 0.002	0.911
	0.5 g/L	0.070 ± 0.001	0.991
	1 g/L	0.029 ± 0.005	0.928
	2 g/L	0.025 ± 0.003	0.938
	3 g/L	0.020 ± 0.004	0.916

Table 1 Apparent first-order reaction model parameters for the photodegradation of phenol

4. CONCLUSIONS

In the home-made slurry photocatalytic reactor, the catalyst dosage, the initial phenol concentration and pH value were examined and the optimal values were obtained in the suspension system with ZnO nanopowder as catalyst. Moreover, in all the photocatalytic experiments, the photodegradation kinetics for the destruction-removal of phenol in water could be well described by pseudo-first-order reaction model. The apparent first-order reaction constants (κ_{app}) thus obtained from the fittings of the model seemed to be proportional to ZnO dosage.

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