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Degradation of Reactive Brilliant Red KE-3B in aqueous solution by mesoporous ZnO

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ABSTRACT

The photocatalytic degradation of Reactive Brilliant Red KE-3B using mesoporous ZnO as photocatalyst in aqueous solution had been investigated under UV irradiation. The average particle size and specific surface area of the mesoporous ZnO were 40.3 nm and 20.7 m^2/g, respectively. The effects of catalyst loading, solution pH, initial dye concentration and anions (SO_4^{2-}, NO_3^-, Cl^- and CO_3^{2-}) on the photocatalytic degradation of the model compound were investigated. Under the optimum conditions, approximately 98.9% decolorization efficiency within 45 min and 83.7% total organic carbon removal efficiency within 3 h were achieved, which were higher than that by the commercial ZnO. In addition, the degradation intermediates were analyzed by a gas chromatography coupled with mass spectrometry system and the probable pathways for the formation of the intermediates were proposed.

Keywords: ZnO; Photocatalysis; Photocatalytic degradation; Reactive Brilliant Red KE-3B

1. Introduction

Large amounts of colored dye wastewaters released into the environment mainly by dyestuff and textile industry lead to severe surface water and groundwater contamination [1,2]. Conventional methods such as physical methods, chemical methods, or their combinations are used for decolorization of these dyes [3]. Nevertheless, these methods are usually nondestructive, inefficient and costly and easily result in secondary pollution. Thus, it is necessary to develop treatment methods that are more effective in eliminating dyes from wastewaters.

Advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment, which are characterized by the generation of highly oxidative hydroxyl radicals in the homogeneous or heterogeneous phase [4,5]. Among AOPs, cheaply available nontoxic semiconductors (TiO_2, ZnO) are the most extensively used photocatalyst due to their high photocatalytic activity [6,7]. It is well known that TiO_2 is universally considered as the most active photocatalyst, while ZnO is found to be a suitable alternative to TiO_2 because its photodegradation mechanism has been proven to be similar to that of TiO_2 [8]. The biggest advantage of ZnO compared with TiO_2 is that it absorbs a larger fraction of the UV spectrum and more light quanta [9]. In addition, it has been reported that ZnO shows better activity than that of TiO_2 in the photodegradation of some dyes in aqueous solutions [10].

Mesoporous materials with high surface areas have been widely used in photocatalysis for the degradation of organic pollutants, which can achieve high photocatalytic activity since the mesoporous channels facilitate fast intraparticle molecular transfer [11]. Moreover, the large surface area of the mesoporous materials may enhance the light harvesting and the adsorption for reactant molecules [12]. The Reactive

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Brilliant Red KE-3B is extensively used in dyeing the textile fabrics. Zhang et al. have investigated the degradation of this dye by ozone and found that the dye additives/impurities in commercial dyes affected the microbial activity as well as the biodegradability [13]. To the best of our knowledge, few studies have been made to investigate the degradation of this dye by using mesoporous ZnO as photocatalyst [13]. Accordingly, in hopes of shedding some light on the mechanistic details of photodegradation of KE-3B dye in the ZnO/UV process, the photocatalytic reaction intermediates were analyzed and a possible degradation pathway of the reactive dye was proposed in this study. Additionally, the effects of parameters such as catalyst loading, solution pH, initial dye concentration, and anions (SO_4^{2-}, NO_3^-, Cl^- and CO_3^{2-}) on the decolorization were also investigated.

2. Experimental

2.1. Reagents

The mesoporous ZnO photocatalyst was prepared by using polystyrene microemulsion as templates and the detailed synthesizing procedure was similar to elsewhere [14]. The average particle size and specific surface area of the synthesized mesoporous ZnO were 40.3 nm and 20.7 m^2/g, respectively. The commercial ZnO was obtained from a Merck China Ltd. (specific surface area < 5 m^2/g). The dye of Reactive Brilliant Red KE-3B was purchased from the Eighth Dye Chemical Factory of Shanghai (Shanghai, China) and used directly without further purification. All other chemicals were of reagent grade and used as received.

2.2. Procedure and analysis

All experiments were carried out in a photoreaction apparatus as reported in our previous study [15]. A 300-W high-pressure mercury lamp with the strongest emission at 365 nm was used as the light source (Shanghai Jiguang Company, China). The temperature of the reactions was controlled at room temperature by circulating water. The pH value of the solution was controlled by adding 0.5 M HCl or NaOH solution. In all experiments, 500 ml of the dye solution containing appropriate quantity of ZnO suspensions was used. The suspension was sonicated for 10 min and stirred for 45 min in the dark in order to reach the adsorption–desorption equilibrium. At specific time intervals, 5 ml of the sample was withdrawn and centrifuged to separate the catalyst before analysis.

For the determination of the dye concentration, ultraviolet and visible absorption spectroscopy (UV–vis, Model T60, Beijing Purkinje General Instrument Company, China) was used at λ_{max} of 519 nm. The total organic carbon (TOC) of the dye before and after decolorization was also measured by using a TOC analyzer (Apollo 9000, Terkmar Dohrmann, USA).

The degradation products were identified using a gas chromatography coupled with mass spectrometry system (GC/MS). The samples collected at different time intervals during the degradation process were acidified and extracted with dichloromethane. The extracts were dehydrated using anhydrous sodium sulfate. Afterward, the dehydrated solution was concentrated to 1 ml. The GC system (TRACE GC, Thermo Fishier) was equipped with a TR-35MS capillary chromatographic column (30 m × 0.25 mm, 0.25 μm) and coupled to a MS system (DSQII, Finnigan). The injection was conducted on a splitless mode, and the injector temperature was 300℃ with helium served as the carrier gas at the flow rate of 1.0 $ml\,min^{-1}$. The extracted samples were analyzed under the following temperature gradient: the initial column temperature was held constant at 50℃ for 5 min, increased at 10 $℃\,min^{-1}$ to 100℃ and kept constant for 2 min, then ramped at 8 $℃\,min^{-1}$ to 250℃ and maintained constant for 5 min, further increased at 20 $℃\,min^{-1}$ to 280℃ and retained constant for 5 min, and finally raised at 25 $℃\,min^{-1}$ to 300℃ and stayed constant for 5 min.

3. Results and discussion

3.1. Degradation

3.1.1. Photocatalytic oxidation

Fig. 1 shows the UV–vis spectrum obtained for the Reactive Brilliant Red KE-3B solution during the decolorization process taken along time in a typical experiment. Regarding the dye spectrum, it is characterized by one band in the ultraviolet region located at 371 nm and by one band in the visible region (519 and 538 nm), with a maximum located at 519 nm. The absorbance peaks in the ultraviolet region can be assigned to the naphthalene rings [16]. The two absorption maximums in the visible region (519 and 538 nm) can be attributed to the whole conjugated structure, which is caused by the π–π* transition of electrons in the azo-group connecting phenyl and naphthyl [17]. By comparing the original spectrum ($t = 0$ min) with that achieved within 45 min of decolorization, it is evident that the treated dye sample is almost colorless and does not show significant absorbance in the visible region, indicating that color removal is practically complete. The disappearance of the absorbance peak at 519 nm reflects, unequivocally, the breakdown in the chromophoric group. However,

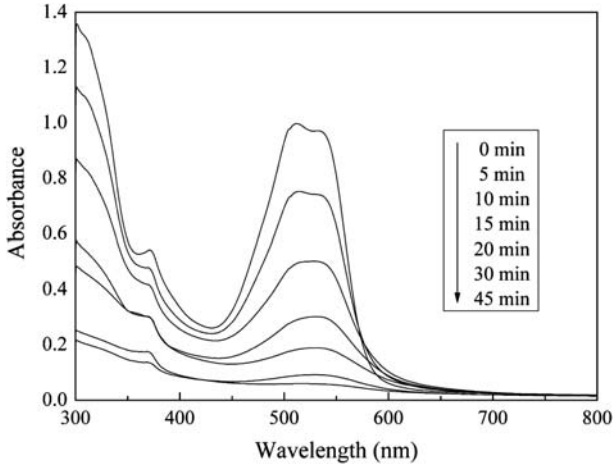

Fig. 1. Variation of UV–vis absorbance spectrum of Reactive Brilliant Red KE-3B at different reaction times under UV irradiation. Experimental conditions: [ZnO] = 0.5 g/l, pH 6.0, [dye] = 50 mg/l.

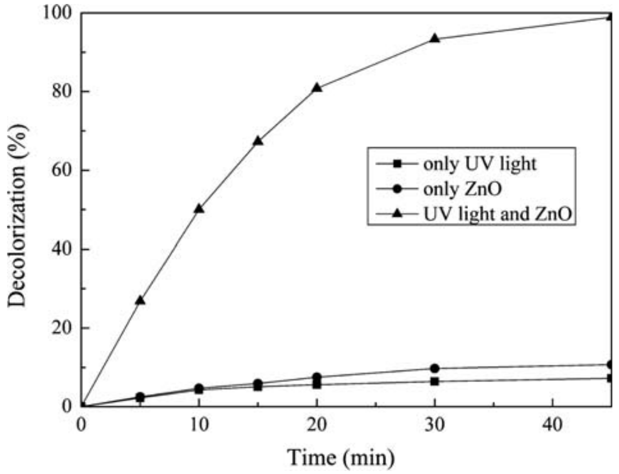

Fig. 2. Effect of UV light and ZnO on photocatalytic degradation of Reactive Brilliant Red KE-3B. Experimental conditions: [ZnO] = 0.5 g/l, pH 6.0, [dye] = 50 mg/l.

the spectrum in the ultraviolet region shows that the dye is not completely mineralized, even though the absorption intensity is reduced within the ultraviolet range. The slower decrease of the intensities of the bands at 371 nm, with respect to that of the azo bond, can be attributed to the formation of intermediates, resulting from the decolorization of the azo dye, which still contain benzene ring and naphthalene-type rings [18].

In order to observe the effect of the mesoporous ZnO and UV light, the dye was photochemically degraded for about 45 min under different conditions and the results were presented in Fig. 2. It can be seen that about 10.7% decrease in dye concentration is observed after 45 min of magnetic stirring in the dark, which is attributed to the adsorption of dye molecule on the ZnO surface. Fig. 2 also indicates that without the addition of catalyst, the decolorization of the dye is only achieved 7.2% even in the presence of UV light for about 45 min. However, with the addition of a small amount of ZnO into the solution, approximately 98.9% of the color removal can be obtained, which clearly indicates that both catalyst and irradiation are necessary for the destruction of this dye.

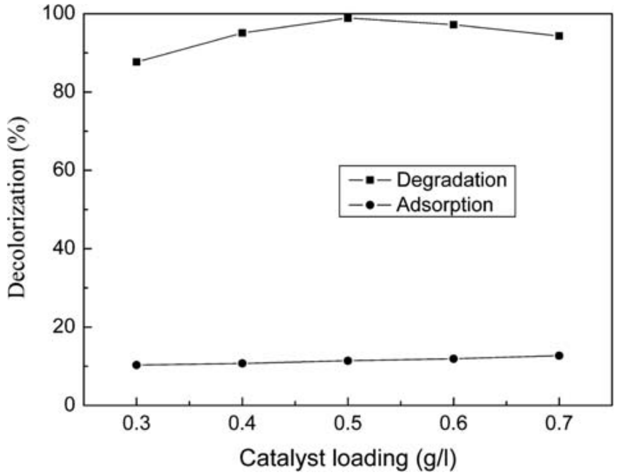

Fig. 3. Effect of catalyst loading on the photocatalytic degradation of Reactive Brilliant Red KE-3B. Experimental conditions: pH 6.0, [dye] = 50 mg/l, time = 45 min.

3.1.2. *Effect of catalyst loading*

In order to avoid the use of excess catalyst, it is necessary to find out the optimum loading for efficient removal of the dye. To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 0.3 to 0.7 g/l and the results were shown in Fig. 3. It can be seen from Fig. 3 that the amount of the adsorption of dye molecules increased with the increase of catalyst loading. But the decolorization efficiency did not show the same trend. As the concentration of the catalyst increases from 0.3 to 0.5 g/l, the dye removal increases sharply from 87.7% to 98.9% after 45 min irradiation. Higher reaction rates at a higher amount of catalyst loading may be explained in terms of complete utilization of incident photons striking on the catalyst surface and/or availability of active sites at the surface (i.e. higher adsorption of incident light can lead to the formation of high photoactivated volume in suspension thereby increasing the decolourization efficiency of the system) [19]. Nevertheless, it should be pointed out that the decolourization efficiency decreases to 94.3% with further increasing the ZnO loading to 0.7 g/l. These observations can be rationalized in terms of availability of active sites on ZnO surface and the penetration of photo-activating light into the suspension. Firstly, high catalyst concentration may lead to the aggregation of ZnO particles, which consequently causes a decrease in the number of surface active sites and reduces the catalytic activity [20]. Secondly, high catalyst concentration increases in opacity of the suspension and light scattering and thus results in decrease in the passage of irradiation through the sample [21]. On the basis of these results, 0.5 g/l is selected as the optimum loading for the subsequent experiments.

3.1.3. Effect of initial pH

The influence of the initial pH of the dye solution was studied in the pH range 4–10 since it influences the surface charge properties of ZnO (zero point charge = 8.9). So at lower pH the surface of the catalyst is positively charged but at higher pH it becomes negatively charged. As shown in Fig. 4, the amount of the adsorption of dye molecules decreased with the increase of pH but the decolorization efficiency did not show the same trend. The decolorization efficiency in the first stage increases rapidly with the increasing pH from 4.0 to 7.0, but at pH 8.0 there is a slight decrease of the decolorization rate. Thereafter, the decolorization efficiency increases with the increasing pH from 8.0 to 10.0, and a maximum is seen near pH 7.0. This is because, at higher pH the catalyst surface is negatively charged by means of adsorbed OH^- ions which favor the formation of $^{\bullet}OH$ radicals, the principal oxidant. On the other hand, at lower pH the anionic dye molecule is negatively charged, which favors adsorption on the catalyst surface. Consequently, pH affects process performance by influencing dye adsorption and $^{\bullet}OH$ radical creation on catalyst surface in a conflicting manner [22], which creates extreme points seen in Fig. 4. Moreover, the significant decrease in decolorization efficiency at pH 4.0 is attributed to the solubility of ZnO in acidic media. Because the difference between the decolorization efficiency at pH 7.0 and at pH 6.0 (the natural solution pH of the dye) is very small, the pH 6.0 is chosen as a moderate and optimum pH, and the experiments are performed under this pH value.

3.1.4. Effect of initial dye concentration

It is important both from a mechanistic and an application point of view to study the dependence of dye concentration on the photocatalytic reaction rate. As the oxidation proceeds, less and less of the surface of the catalyst particle is covered as the pollutant is decomposed. The effect of initial dye concentration was investigated by varying the initial concentration from 30 to 100 mg/l. As shown in Fig. 5, the decolorization efficiency decreases with the increase in the initial dye concentration. As the dye concentration increases, the equilibrium adsorption of dye at the active sites on the catalyst surface increases but the intensity of light and irradiation time are constant. Therefore, the path length of photons entering the solution decreases and consequently the $OH^{\bullet}$ radicals formed on the surface of ZnO decreases and thus results in the decrease of decolorization efficiency [23].

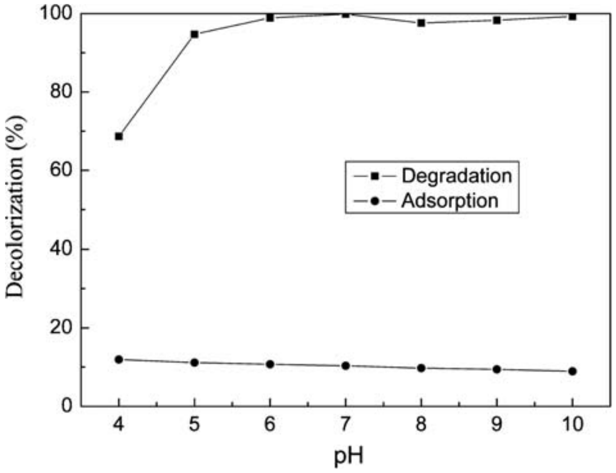

Fig. 4. Effect of initial pH on the photocatalytic degradation of Reactive Brilliant Red KE-3B. Experimental conditions: [dye] = 50 mg/l, [ZnO] = 0.5 g/l, time = 45 min.

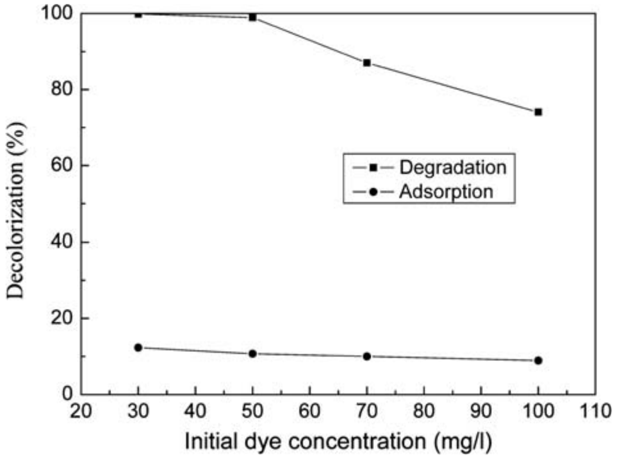

Fig. 5. Effect of initial dye concentration on the photocatalytic degradation of Reactive Brilliant Red KE-3B. Experimental conditions: pH 6.0, [ZnO] = 0.5 g/l, time = 45 min.

3.1.5. Effect of anions

The existence of inorganic anions such as SO_4^{2-}, NO_3^-, Cl^- and CO_3^{2-} is considerably common in wastewaters and also in natural water, of which great influence on photocatalytic decolorization and degradation of pollutants cannot be neglected. Therefore, 50 mM corresponding sodium salts were separately added into the 50 mg/l Reactive Brilliant Red KE-3B solution, and then the photocatalytic experiments were carried out under predetermined conditions. Fig. 6 shows the effect of anions on the decolorization efficiency. The results indicate that the existence of SO_4^{2-} and NO_3^- can increase the dye removal, whereas the decolorization efficiency is significantly reduced in the presence of Cl^- or CO_3^{2-}.

The enhancement in decolorization efficiency by SO_4^{2-} may be linked to the direct or indirect formation of $SO_4^{\bullet -}$ (Eqs. (1) and (2)). Previous literature has shown that this *in situ*-generated radical can sufficiently act as strong oxidizing agent or initiate the formation of hydroxyl radical [24].

$$SO_4^{2-} + h_{VB}^+ \rightarrow SO_4^{\bullet -} \tag{1}$$

$$SO_4^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \tag{2}$$

It can be seen from Fig. 6 that the presence of NO_3^- can slightly accelerate the photocatalytic degradation of the dye, which is mainly due to the direct or indirect formation of ${}^{\bullet}OH$ (Eqs. (3)–(5)) [25].

$$NO_3^- + hv \rightarrow NO_2^- + O \tag{3}$$

$$NO_3^- + H_2O + hv \rightarrow {}^{\bullet}OH + NO_2^- + OH^- \tag{4}$$

$$H_2O + O \rightarrow 2{}^{\bullet}OH \tag{5}$$

The observed decrease in the decolorization efficiency in the presence of Cl^- can be explained by competitive adsorption or by the hole-scavenging properties of chloride ions (Eqs. (6) and (7)) [26]. As is well known, $Cl^{\bullet}$ is less reactive than ${}^{\bullet}OH$ and h_{VB}^+ and therefore the presence of Cl^- hinders the photocatalytic degradation of the dye.

$$Cl^- + h_{VB}^+ \rightarrow Cl^{\bullet} \tag{6}$$

$$Cl^- + {}^{\bullet}OH \rightarrow Cl^{\bullet} + OH^- \tag{7}$$

Addition of sodium carbonate can evidently decrease the photocatalytic degradation of the dye, which can be attributed to the hydroxyl radical scavenger properties of carbonate ions (Eqs. (8) and (9)) [27]. The generated carbonate radicals have a lower oxidation potential than hydroxyl radicals. Thus, the rate of photocatalytic degradation was inhibited and exhibited the lower removal efficiency. It should be noted that the solution gets stronger color in the first 5 min, showing negative removal efficiency. Wang et al. inferred that this phenomenon was connected with the formation of polymeric materials, which might be formed by the combination of dye intermediates with aromatic radicals or with inorganic radicals [17]. Further investigation is imperative for detailed explanation.

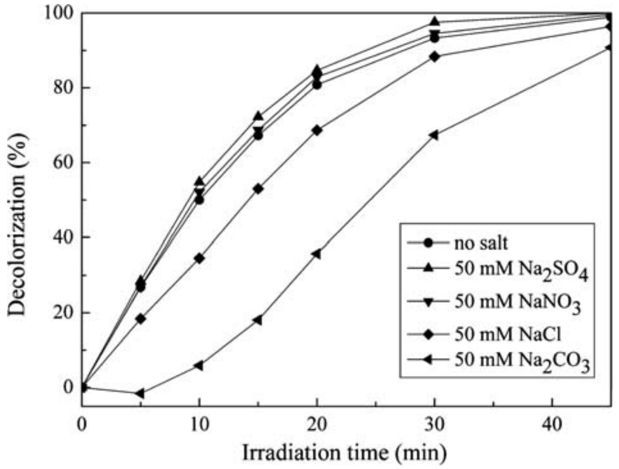

Fig. 6. Effect of inorganic anions on the removal of Reactive Brilliant Red KE-3B. Experimental conditions: [dye] = 50 mg/l, [ZnO] = 0.5 g/l, pH 6.0.

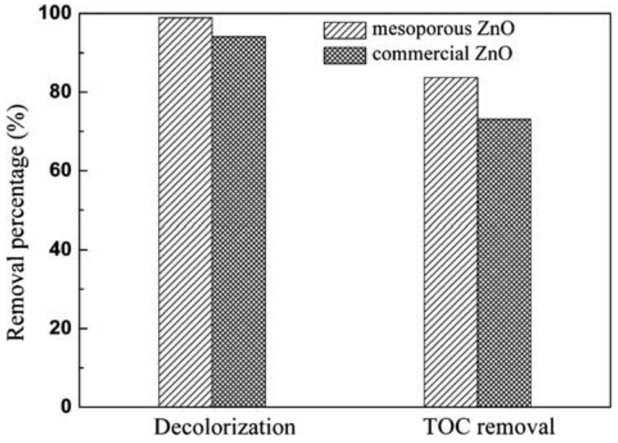

Fig. 7. Decolorization and TOC removal efficiencies of Reactive Brilliant Red KE-3B by mesoporous ZnO and commercial ZnO. Experimental conditions: [dye] = 50 mg/l, [ZnO] = 0.5 g/l, pH 6.0.

$$^{\bullet}\mathrm{OH} + \mathrm{CO}_3^{2-} \rightarrow \mathrm{OH}^- + \mathrm{CO}_3^{\bullet -} \quad (8)$$

$$^{\bullet}\mathrm{OH} + \mathrm{HCO}_3^{-} \rightarrow \mathrm{H_2O} + \mathrm{CO}_3^{\bullet -} \quad (9)$$

3.2. Comparison of the photocatalytic activity

To evaluate the photocatalytic activity of the synthesized mesoporous ZnO, the decolorization and TOC removal experiments using mesoporous ZnO and commercial ZnO as catalyst were carried out. As shown in Fig. 7, the decolorization efficiency of the dye by the mesoporous ZnO is higher than that by the commercial ZnO after 45 min of reaction time. After 3 h of reaction time, the TOC removal efficiency of the dye by mesoporous ZnO and commercial ZnO is 83.7% and 73.1%, respectively. It is evident that the synthesized mesoporous ZnO is more efficient for the mineralization and decomposition of the model compound as compared with the commercial ZnO powders. Similar results were reported earlier for the degradation of organic compound by mesoporous materials [11]. The good performance for the degradation of the dye by the mesoporous ZnO is attributed to its larger specific surface area, which can absorb more dye molecules and consequently enhance its photocatalytic activities. Moreover, measuring of TOC loss also indicated that mineralization was not complete within 3 h.

3.3. Degradation pathway of Reactive Brilliant Red KE-3B

The samples of Reactive Brilliant Red KE-3B oxidized at different intervals were collected to determine the intermediate compounds by GC/MS. As shown in Fig. 8, the degradation products obtained at 30 min showed the formation of isocyanatobenzene (D_1, m/z = 119), hydroquinone (D_2, m/z = 110), aniline (D_3, m/z = 93), phthalic acid (D_4, m/z = 104).

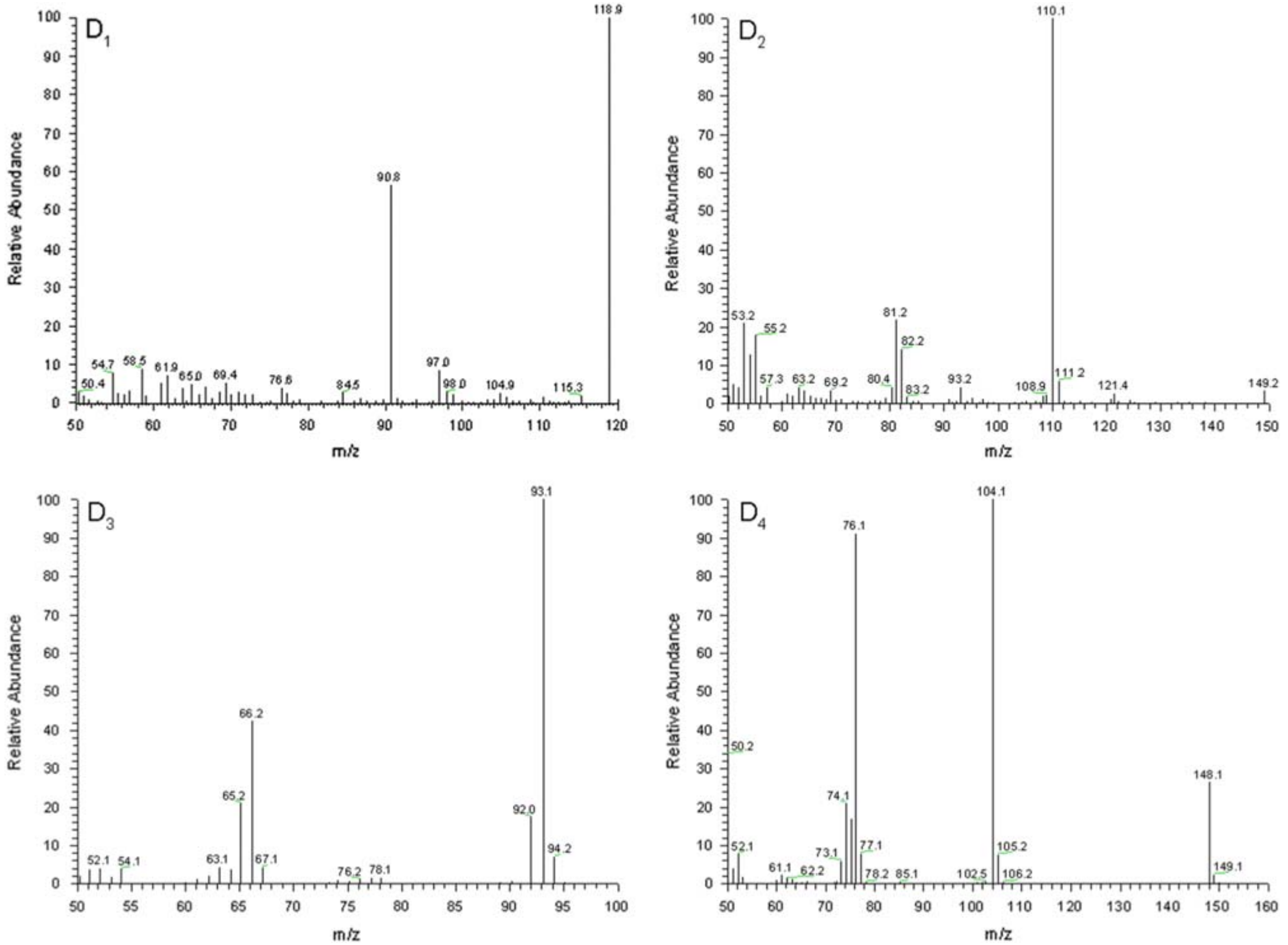

Fig. 8. GC–MS spectra of the identified compounds within 30 min degradation.

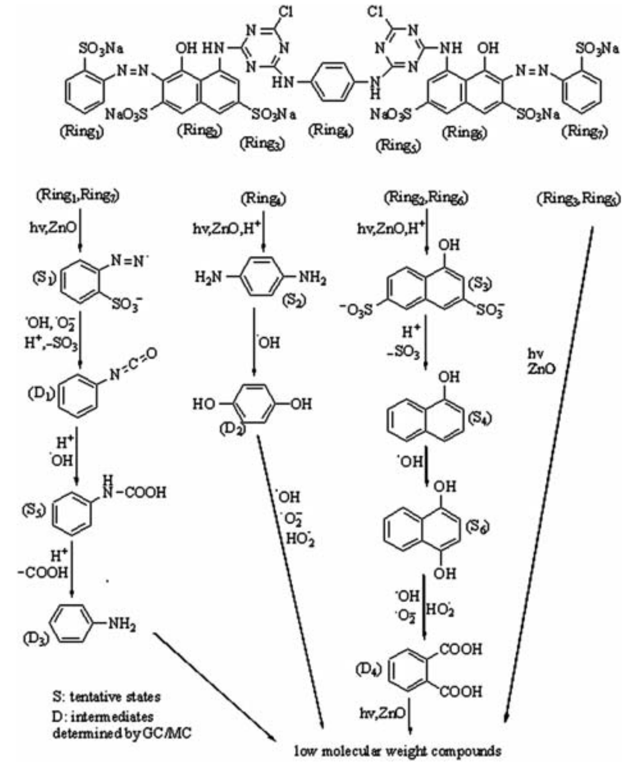

Fig. 9. Proposed pathways of the photocatalytic degradation of Reactive Brilliant Red KE-3B.

A tentative degradation pathway based on the GC/MS identification is proposed in Fig. 9. We theorize that the initial Reactive Brilliant Red KE-3B and the intermediates are degraded by direct oxidation, hydrolysis, and free radical attack. The C–N bonds are initially broken down to form compounds S_1, S_2 and S_3. Then the C–S bonds of compounds S_1 (oxidized by active radicals at the same time) and S_3 are cleaved to yield the corresponding compounds D_1 and S_4. Compound D_1 can be hydrolyzed in aqueous solution to form S_5, which then could be decarboxylated to yield compound D_3. Compound S_2 can be attacked by active radicals yielding D_2. Compound S_4 can be oxidized by active radicals yielding compound S_6 and generating D_4 by the breakdown of the aromatic ring. The compounds D_2, D_3, and D_4 are further oxidized to yield low molecular weight compounds.

4. Conclusion

Reactive Brilliant Red KE-3B can be easily degraded by mesoporous ZnO-assisted process in aqueous dispersions under UV irradiation. The operational parameters such as the ZnO loading, solution pH, dye concentration, and inorganic anions exhibit significant influence on the decolorization efficiency. For degradation of 50 mg/l of Reactive Brilliant Red KE-3B, the most suitable operation conditions are: catalyst loading 0.5 g/l, pH value 6.0. The presence of SO_4^{2-} and NO_3^- can enhance the decolorization efficiency, while the addition of Cl^- and especially CO_3^{2-} ions exhibits an inhibitory effect on the dye decolorization. Under the optimum conditions, the decolorization and TOC removal efficiencies are achieved 98.9% (45 min) and 83.7% (3 h), respectively, which is higher than that by the commercial ZnO. In addition, the volatile intermediate products are identified through GC/MS analysis and the possible degradation pathways are proposed.

Acknowledgments

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