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Photocatalytic degradation of C.I. Direct Red 23 in aqueous solutions under UV irradiation using SrTiO₃/CeO₂ composite as the catalyst

Shuang Song^a, Lejin Xu^a, Zhiqiao He^{a,*}, Haiping Ying^a, Jianmeng Chen^a, Xiuzhen Xiao^b, Bing Yan^{b,**}

^a College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, People's Republic of China ^b Department of Chemistry, Tongji University, Shanghai 200092, People's Republic of China

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Abstract

The photocatalytic degradation of C.I. Direct Red 23 (4BS) in aqueous solutions under UV irradiation was investigated with $SrTiO_3/CeO_2$ composite as the catalyst. The $SrTiO_3/CeO_2$ powders had more photocatalytic activity for decolorization of 4BS than that of pure $SrTiO_3$ powder under UV irradiation. The effects of catalytic dose, pH value, initial concentration of dye, irradiation intensity as well as scavenger KI were ascertained, and the optimum conditions for maximum degradation were determined. Under the irradiation of a 250 W mercury lamp, the best catalytic dose was 1.5 g/L and the best pH was 12.0. Light intensity exhibited a significant positive effect on the efficiency of decolorization, whereas the initial dye concentration showed a significant negative effect. Under the conditions of a catalytic dose of 1.5 g/L, pH of 12.0, initial dye concentration of 100 mg/L, light intensity of 250 W, and air flow rate of 0.15 m³/h, complete decolorization, as determined by UV-visible analysis, was achieved in 60 min, corresponding to a reduction in chemical oxygen demand (COD) of 69% after a 240 min reaction. A tentative degradation pathway based on the sensitization mechanism of photocatalysis is proposed.

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Keywords: Photocatalytic; UV irradiation; SrTiO₃/CeO₂ composite; Azo dye; Degradation pathway

1. Introduction

Azo dyes, characterized by nitrogen-to-nitrogen double bonds (N=N), constitute over 50% of all textile dyes and have been widely used in many industries, such as the production of textiles, paint, ink and cosmetics [1]. The effluent from these industries contains substantial amounts of such dyes, which causes coloration of water and poses a threat to aquatic life [2]. Due to the complex aromatic structure and the stability of these dyes, conventional biological treatment methods and activated sludge processes are ineffective for decolorization [3]. Common treatment processes such as flocculation, reverse osmosis and adsorption transfer the pollutants to other media, causing secondary pollution, and chemical oxidation methods are not cost-effective [4–6].

In recent years, advanced oxidation processes (AOPs) have been developed to deal with the problem of the destruction of dyes in aqueous systems. Within AOPs, photocatalyst-based degradation methods represent a very interesting branch of research and there has been continuous development. TiO_2 [7] and ZnO [8] are used as effective, inexpensive and non-toxic semiconductor photocatalysts for the degradation of a wide range of organic chemicals and synthetic dyes. Unfortunately, the use of TiO₂-based catalysts has been limited by the inevitable reduction of the overall active surface area associated with catalyst immobilization, leading to significant loss of performances [9]. Moreover, the band gap of TiO₂ is large ($E_g = 3.2 \text{ eV}$) and the separation of TiO₂ from effluent after degradation of the dye is difficult due to its small particle size [10]. Therefore, there is a need to find novel materials with high performance for use in heterogeneous photocatalysis.

The family of perovskite-type oxides generally formulated as ABO_3 (A is a rare earth metal with large ionic radius or alkali earth metals; B is a transition metal with a small ionic radius) has been found to have photocatalytic activity [11]. Recently,

^{*} Corresponding author. Tel.: +86 571 88320726; fax: +86 571 88320276.

^{**} Corresponding author. Tel.: +86 21 65984663; fax: +86 21 65982287. E-mail addresses: zqhe@zjut.edu.cn (Z. He), byan@tongji.edu.cn (B. Yan).

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perovskite (calcium titanium oxide, CaTiO₃) has been studied extensively as a promising photocatalyst due to its narrow band gap (often less than 3.0 eV), which can be excited easily under visible light or UV light irradiation [12]. Among alkaline earth metals, titanates belong to the typical ABO₃ compounds that have extensive applications in various functional ceramics. In these compounds, the alkaline earth metals behave only as the balance ions in the A site and the titanate framework plays the main role in the structure and properties with Ti in the B sites. The activity of perovskite is improved by partial replacement of the B-site metal with ions of different valency, such as Ce [13]. To the best of our knowledge, the confirmation and optimization of the efficiency of the perovskite catalyst and the degradation pathway for the photodegradation of azo dyes have received little attention in the literature.

In this study, the SrTiO₃/CeO₂ composite system, as reported earlier [14], was used as the catalyst in the photodegradation of water-soluble C.I. Direct Red 23 (known also as Fast Scarlet 4BS, and abbreviated here as 4BS). Experiments were conducted to investigate the effects of various process variables on the process performance, which was assessed in terms of decolorization and removal of chemical oxygen demand (COD).

2. Experimental

2.1. Reagents

C.I. Direct Red 23 (molecular mass 813.73 g/mol) was supplied by Zhejiang Runtu Co., Ltd., China: the purity is 99% without further purification and the solubility is 30 g/L in water at 80 °C. For preparation of the SrTiO₃/CeO₂ catalyst, strontium carbonate, ceria (cerium oxide, CeO₂) and tetrabutyl titanate were obtained from Shanghai, China. Details of the synthesis and characterization of the SrTiO₃/CeO₂ catalyst are given in our previous work [14]. The SrTiO₃ catalyst was purchased from Beijing Research Institute of Chemical Engineering and Metallurgy, China. Double-distilled water was used to prepare experimental solutions.

2.2. Photoreactor and experimental procedure

The UV irradiation experiments were carried out in a cylindrical Pyrex glass reactor, which has been described in detail elsewhere [14]. During the reaction, air was purged into the reactor at a rate of 0.15 m^3 /h and the temperature was maintained constant at $25(\pm 1)$ °C.

An aqueous solution of 1000 mL containing 4BS at different concentrations was used. Phosphate buffers with an ionic strength of 0.0667 mol/L were prepared in deionized water by the mixture of calculated amounts of sodium hydroxide solution and phosphoric acid solution. A 100 mg/L stock dye solution was prepared by dissolving 100 mg of 4BS in 1000 mL of phosphate buffer, and stored at 4 °C. Dye solutions of various strengths were made from the stock by appropriate dilutions with phosphate buffers. As the reaction progressed, samples were taken periodically for the measurement of color value, COD and pH. For analysis by gas chromatography/mass spectrometry (GC/MS), 10-mL samples were removed from the reactor at 1, 2 and 12 h. The samples then were adjusted to pH 2.0 using HCl; the samples used to detect urea were not pH adjusted. Before injecting into the GC/MS, the samples were centrifuged and then passed through 0.45 μ m membrane filter.

2.3. Sample analysis

Analytical analysis of 4BS in aqueous solution was performed using an ultraviolet/visible spectrophotometer (UV-9200, Beijing, China) coupled with a photoelectric detector at 500 nm.

For identification of intermediate products of 4BS photocatalytic degradation, the samples taken after complete decolorization were analyzed by GC/MS. The GC (Varian cp3800 system) was equipped with a WCOT fused silica series column ($30 \text{ m} \times 0.25 \text{ mm}$) and $0.25 \mu \text{m}$ film thicknesses, and interfaced directly to the MS (Varian Saturn 2000 mass spectrophotometer). The GC column was operated at $80 \,^{\circ}\text{C}$ for 2 min and then increased to $250 \,^{\circ}\text{C}$ at a rate of $15 \,^{\circ}\text{C/min}$. The other experimental conditions were: EI impact ionization 70 eV, helium as the carrier gas, injection temperature $280 \,^{\circ}\text{C}$, source temperature $80 \,^{\circ}\text{C}$.

The pH of the solution, adjusted using different buffer solutions, was measured with a pHs-25 instrument (Rex Analytical Instrument Co. Ltd., Shanghai, China). The extent of mineralization of the dye was examined by measuring the COD at regular intervals using the standard acid dichromate method [15].

3. Results and discussion

3.1. Comparison of photocatalytic activity between SrTiO₃/CeO₂ and SrTiO₃

The adsorption experiments were performed using dye solutions at pH 12.0 and an initial dye concentration of 100 mg/L. A 1000 mL sample of aqueous dye solution was mixed with 1.5 g of catalysts at 25 °C. After 90 min of magnetic stirring in the dark, no apparent decrease of color was observed using SrTiO₃/CeO₂ and SrTiO₃ as the catalysts. To study the effect of the nature of the catalyst, experiments were carried out at an airflow rate of 0.15 m³/h, a temperature of 25 °C, an initial dye concentration of 100 mg/L, pH 12.0 with a catalyst loading of 1.5 g/L under 250 W UV irradiation. The activity of the photocatalysts SrTiO₃/CeO₂ and SrTiO₃ was compared by evaluating the photocatalytic decolorization efficiency and COD removal of 4BS. As shown in Fig. 1, SrTiO₃ showed 77% decolorization whereas SrTiO₃/CeO₂ showed 97% decolorization after 45 min reaction. The COD removal using the SrTiO₃/CeO₂ catalyst was higher than that using the SrTiO₃ catalyst. It is obvious that the photocatalytic activity of SrTiO₃ was lower than that of SrTiO₃/CeO₂. When a photon of UV light strikes the catalyst surface, the conduction band electrons and the valence band holes are formed and then migrate to the surface of the catalyst where reactive oxygen species such as OH^{\bullet} , HOO^{\bullet} , $O_2^{\bullet-}$ radicals which lead to

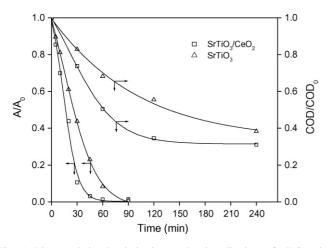


Fig. 1. Photocatalytic decolorization and mineralization of 4BS using $SrTiO_3/CeO_2$ and $SrTiO_3$ as catalysts: airflow rate 0.15 m³/h; temperature 25 °C; catalytic dose 1.5 g/L; pH 12.0; initial dye concentration 100 mg/L; and UV power 250 W.

the degradation of the dye are generated. Alternatively, the electrons in the conduction band can be picked up by the adsorbed dye molecules, thus decreasing the formation of reactive oxygen species [1]. The enhancing effect of Ce^{4+} may be explained by its ability to present high ultraviolet absorption ability in CeO_2 or oxysalts, just like TiO₂ or titanates.

3.2. Effect of catalytic dose

Experiments were performed to study the variations in the rate of decolorization at different concentrations of catalyst, ranging from 0.5 to 2.0 g/L, at pH 12.0. It was observed that the photocatalytic decolorization efficiency of 4BS increased with an increasing amount of the photocatalyst, and reached the highest value when the concentration of SrTiO₃/CeO₂ was 1.5 g/L and finally decreased, as shown in Fig. 2a. This phenomenon is similar to that found in the study of other photocatalysts, such as TiO₂ and ZnO [7,16]. The enhancement of the removal rate may be due to the increase in the availability of active sites, which increases the number of dye molecules adsorbed, and the increase in the density of particles in the area of illumination. At higher catalyst loading, the percentage of decolorization decreases because of the deactivation of activated molecules by agglomeration, the decreased radiation penetration and the increased radiation scattering. The best amount of SrTiO₃/CeO₂ must be added in order to avoid unnecessary excess catalyst and to ensure total absorption of light photons for efficient photodecolorization.

3.3. Effect of pH

The effect of pH from 2.0 to 12.0 on the decolorization at constant air flux, a temperature of 25 °C with 1.5 g of perovskite

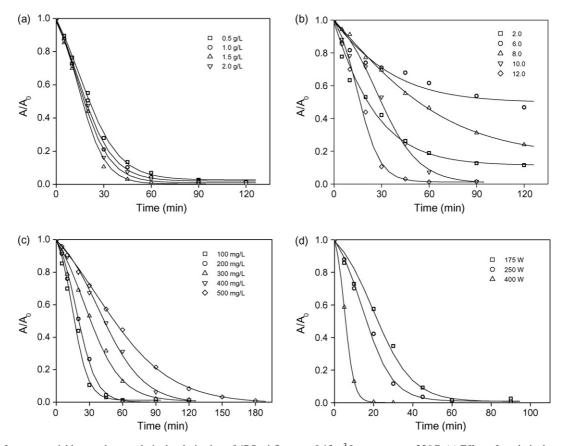


Fig. 2. Effect of process variables on photocatalytic decolorization of 4BS: airflow rate 0.15 m^3 /h; temperature $25 \degree$ C. (a) Effect of catalytic dose: pH 12.0; initial dye concentration 100 mg/L; UV power 250 W. (b) Effect of pH: catalytic dose 1.5 g/L; initial dye concentration 100 mg/L; UV power 250 W. (c) Effect of initial dye concentration: catalytic dose 1.5 g/L; pH 12.0; UV power 250 W. (d) Effect of light intensity: catalytic dose 1.5 g/L; pH 12.0; initial dye concentration 100 mg/L.

under 250 W UV irradiation for 90 min is illustrated in Fig. 2b. The worst results were obtained at pH 6.0, and acidic and alkaline pHs were favored. The photocatalytic removal of color was observed to be faster at alkaline pH than at acidic pH. The best pH was 12.0. Similar results are reported in the literature for RL and 3BL dyes [7].

The interpretation of pH effects on the efficiency of the dye photocatalytic degradation process is very difficult because of its multiple factors. The relevant reactions at the semiconductor surface causing the degradation of 4BS can be expressed as follows [17,18]:

Photocatalyst + $h\nu \rightarrow e^- + h^+$ (1)

 $h^+ + H_2 O \rightarrow \bullet OH + H^+ \tag{2}$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH$$
 (3)

$$O_2 + e^- \to O_2^{\bullet^-} \tag{4}$$

$$O_2^{\bullet-} + H^+ \to HOO^{\bullet}$$
 (5)

$$HOO^{\bullet} + HOO^{\bullet} \rightarrow O_2 + H_2O_2 \tag{6}$$

 $H_2O_2 + O_2 \rightarrow \bullet OH + OH^- + O_2 \tag{7}$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \tag{8}$$

First, pH changes could influence the adsorption of dye molecules onto the SrTiO₃/CeO₂ surface, an important step for the photocatalytic oxidation to take place. Second, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. Since air is bubbled continuously throughout the experiment in our system, oxygen will act primarily as an electron scavenger to reduce the recombination of excited electrons and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at alkaline pH [19]. It has been stated that in alkaline solution (pH > 10.0), since OH radicals are generated more easily by oxidizing more hydroxide ions available on the catalyst surface, the efficiency of the process is enhanced [20]. Although it should be noted that in alkaline solution there is a Coulombic repulsion between the negatively charged surface of the photocatalyst and the hydroxide anions. This fact could prevent the formation of OH radicals and thus decrease the extent of photo-oxidation but very high pH has been found favorable even when anionic azo dyes should hamper adsorption onto the negatively charged surface [21]. At low pH, reduction by electrons in the conducting band may play a very important role in the degradation of dyes due to the reductive cleavage of azo bonds. Third, the SrTiO3/CeO2 particles tend to agglomerate under acidic conditions, and the surface area available for adsorption of dye and photon adsorption would be reduced [22]. Hence, pH plays an important role in the reaction mechanisms that can contribute to dye degradation; namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band [23].

3.4. Effect of initial concentration of dye

The effect of the initial concentration of dye on the rate of decolorization was studied by varying the initial dye concentration from 100 to 500 mg/L at pH 12.0, with a constant intensity of 250 W and a catalyst loading of 1.5 g/L, as shown in Fig. 2c. These figures are in agreement with the results of studies by Neppolian et al. [24] and Toor et al. [25] who have shown that photodegradation of textile dye Reactive Red 2 and Direct Yellow 12 dye decreases with increasing initial concentration. The rate of decolorization relates to the probability of formation of OH radicals on the surface of the catalyst and to the probability of OH radicals reacting with dye molecules. As the initial concentration increases, the active sites of SrTiO₃/CeO₂ are covered by dye ions and the path-length of photons entering the solution decreases. In low concentrations, however, the reverse effect is observed; consequently, the number of OH radicals formed on the surface of SrTiO₃/CeO₂ increases, the relative number of OH radicals attacking the compound increases, and thus the photodegradation efficiency increases. Another possible cause for such results is the UV-screening effect of the dye itself. At a high concentration of dye, a significant amount of UV light may be absorbed by the dye molecules rather than the SrTiO₃/CeO₂ particles, and that reduces the efficiency of the catalytic reaction because the concentrations of $^{\bullet}$ OH and O₂ $^{\bullet-}$ decrease [23,25].

3.5. Effect of light intensity

The effect of UV radiation power on the decolorization of 4BS is shown in Fig. 2d. Our observations show clearly that the increase of radiation intensity from 175 to 400 W increases the extent of decolorization from 65% to 99% after 30 min with 1.5 g/L of SrTiO₃/CeO₂ and aeration at pH 12.0. The UV radiation intensity determines the amount of photons absorbed by the catalyst. In the UV/TiO₂ process, at increased light intensity electron-hole pair separation competes with recombination, causing less effect on the reaction rate [23]. Compared with the UV/TiO₂ process, the decolorization rate increased with increasing UV power in photocatalytic degradation of 4BS using SrTiO₃/CeO₂. With the increase of the UV power, the catalyst absorbs more photons, producing more electron-hole pairs in the catalyst surface, and this increases the concentration of hydroxyl radicals and consequently increases the removal rate.

3.6. The effect of KI

Iodide ion is a scavenger that reacts with positive holes and surficial hydroxyl radicals, reducing the number of oxidizing species available on the catalyst surface for reaction with dyes [26]. The dye solution (100 mg/L) mixed with scavenger KI (0–50 mmol/L) was irradiated for 60 min with 1.5 g/L SrTiO₃/CeO₂ and UV power of 250 W at pH 12.0. Fig. 3 shows the change of photocatalytic decolorization of 4BS with increasing KI concentration. Obviously, with the increase of the KI concentration, the rate of decolorization decreases. Since iodide ion scavenged the positive holes and surficial hydroxyl radicals S. Song et al. / Journal of Hazardous Materials 152 (2008) 1301-1308

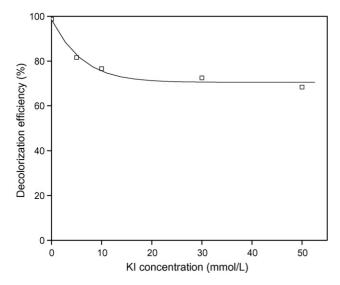


Fig. 3. Effect of scavenger KI on photocatalytic decolorization of 4BS: air flow rate $0.15 \text{ m}^3/\text{h}$; temperature $25 \,^{\circ}\text{C}$; catalytic dose 1.5 g/L; pH 12.0; initial dye concentration 100 mg/L; UV power 250 W; irradiation time 60 min.

on catalysts surface reduced the number of reactive species available for photodegradation the adsorbed 4BS. In addition, iodide ion competed the adsorptive sites on the SrTiO₃/CeO₂ surface with 4BS, resulting in efficiency decrease of photodegradation [27].

BODE COD reduction C

Fig. 4. Effect of SrTiO₃/CeO₂ reuse on photocatalytic decolorization (after 90 min irradiation) and COD reduction (after 240 min irradiation) of 4BS at air flow rate $0.15 \text{ m}^3/\text{h}$; temperature $25 \,^{\circ}\text{C}$; catalytic dose 1.5 g/L; pH 12.0; initial dye concentration 100 mg/L; and UV power 250 W. Run 1, fresh SrTiO₃/CeO₂; Run 2, first reuse; Run 3, second reuse; Run 4, third reuse.

3.7. Reuse of the photocatalyst

To evaluate reused photocatalyst efficiency, a series of experiments were performed using 1.5 g/L catalyst and UV power of 250 W at pH 12.0. As seen in Fig. 4, although photocat-

Table 1 Intermediate compounds identified by GC/MS

Symbol	Compounds	Structural formula	Sampling time (h)		
			1.0	2.0	12.0
D ₁	Urea	H ₂ N _C NH ₂ II O		\checkmark	\checkmark
D ₂	(4-Hydroxynaphthalene-2-sulfonato-kO)sodium	OH SO ₃ Na		\checkmark	
D ₃	1-Naphthol	OH		\checkmark	
D ₄	Phenol	ОН	\checkmark	\checkmark	
D ₅	Hydroquinone	но-Он	\checkmark	\checkmark	
D ₆	N-(4-hydroxyphenyl) acetamide	HO-NHCOCH 3	\checkmark		
D ₇	Phthalic acid	СООН		\checkmark	\checkmark
D ₈	Maleic acid	СООН		\checkmark	\checkmark
D9	Acetic acid	CH ₃ COOH		\checkmark	\checkmark

alytic efficiency marginally deteriorated on repeated use, it still remained sufficiently high both in terms of color and COD conversion. The recorded catalyst deactivation could be explained, to a certain degree at least, by the deposition of photo-insensitive hydroxides on the photocatalyst surface, which would block its active sites, and the presence of adsorbed species, which would change the dimension of the catalyst particles. The regeneration of the catalyst can be done in a very simple way. After finishing the reaction, the solution was kept standing for 12 h and then the supernatant was decanted. Then the catalyst was thoroughly rinsed with distilled water and dried at $110 \,^\circ$ C for 24 h.

3.8. Photocatalytic mineralization of 4BS

The intermediates of some organic compounds could be longlived and even more toxic to aquatic life than the original dye, as reported by many researchers [28], and complete destruction of such compounds should be considered. Therefore, in addition to absorbance measurements for decolorization studies, it is necessary to analyze the degree of mineralization of the azo dye 4BS to evaluate the degradation level applied under UV irradiation using SrTiO₃/CeO₂. COD values have been related to the total concentration of organics in the solution and the decrease of COD reflects the degree of mineralization.

As can be seen from Fig. 1, the maximum mineralization efficiencies obtained after 240 min of irradiation was 69%, indicating that there is still a residual amount of organic compounds, consisting of low mass molecules such as aldehydes and carboxylic acids [29] in the treated solution. The rate of decolorization was noticeably faster than that of COD. Decolorization of the dye does not mean that it has been oxidized completely into CO_2 and H_2O , which is because, in most cases, reaction intermediates are formed in solution during the degradation of the dye.

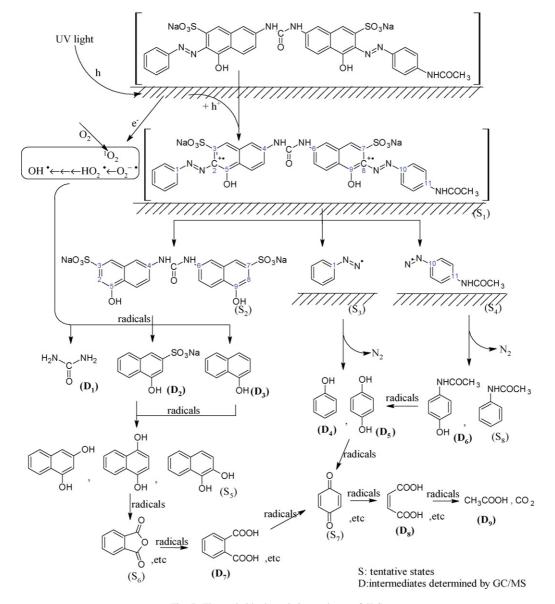


Fig. 5. The probable degradation pathway of 4BS.

3.9. Degradation mechanism

Table 1 shows the proposed structures of by-products found by means of GC/MS analysis of samples collected after different times of reaction. Only urea was detected in reaction samples without pH adjustment and others were detected after the pH value of the solution was adjusted to 2.0 by HCl. A reaction mechanism based on the above results is proposed in Fig. 5.

Initially, the dye molecules adsorbed onto the catalyst surface might be excited by positive holes to form compound S_1 . The photogenerated conduction band electrons were trapped by water or oxygen molecules, leading to the formation of radicals such as $O_2^{\bullet-}$, HOO[•] and [•]OH. These free radicals with a high oxidation potential were the predominant species contributing to the degradation of the dye.

Cleavage of the C (2)–N and C (8)–N bonds seems to occur first on the dye molecule and led to formation of compounds S_2 , S_3 and S_4 . This is supported by the fact that compounds D_1 , D_2 and D_3 were not detected, while compounds D_4 , D_5 and D_6 were detected in the sample collected at 1 h.

The compound S_2 had a nitrogen atom located in site 4 or site 6 (or both) of the aromatic ring, which were substituted by H to yield compounds D_1 , D_2 and D_3 . The compounds D_2 and D_3 could be further oxidized by active radicals yielding compound S_5 and generating S_6 by the breakdown of the aromatic ring and then compounds D_7 and S_7 were formed.

Compounds S_3 and S_4 adsorbed on the surface of the catalyst may dissociate the azo group to give the corresponding compounds (D_4 , D_5 , D_6 and S_8). Compounds D_4 and D_5 were subsequently produced by hydrolytic decomposition of compounds D_6 and S_8 and could be further oxidized to quinone. Destruction of quinone by radicals gave maleic acid, acetic acid, etc.

4. Conclusions

A SrTiO₃/CeO₂ system in aqueous dispersions under UV irradiation can easily decolorize and degrade 4BS. Compared to the photocatalyst SrTiO₃, SrTiO₃/CeO₂ had been found to be more efficient. In addition, SrTiO₃/CeO₂ could be reused for dye degradation with slightly less efficiency. The decolorization rates were determined and shown to be affected by the initial concentration of dye, the catalytic dose, the light intensity and the pH. Complete dye decolorization could be achieved within 60 min with a SrTiO₃/CeO₂ concentration of 1.5 g/L, pH of 12.0, initial dye concentration of 100 mg/L, UV power of 250 W and air flow rate of $0.15 \text{ m}^3/\text{h}$, while 69% of the wastewater COD was removed after 240 min of irradiation. The addition of KI resulted in an inhibitory effect on decolorization of 4BS. Intermediate products, including urea, (4-hydroxynaphthalene-2-sulfonato-kO) sodium, 1-naphthol, phenol, hydroquinone, N-(4-hydroxyphenyl) acetamide, phthalic acid, maleic acid, and acetic acid were detected by GC/MS.

Therefore, the results obtained by experiment confirm that $SrTiO_3/CeO_2$ is an effective catalyst for the photocatalytic degradation of azo dyes. The photocatalytic process may be applied as a new methodology for reducing the levels of other

organic chemicals in aqueous solution. More work is needed to determine the precise mechanisms for the reaction reported here, and the clear effectiveness achieved by the use of the catalyst is worthy of further study and may form the basis of important techniques for environmental treatment.

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