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PHOTOCATALYTIC ACTIVITY OF BARIUM CHROMATE – ZINC OXIDE COMPOSITE FOR DEGRADATION OF CRYSTAL VIOLET

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ABSTRACT

Photocatalytic degradation of dyes and other organic pollutants is an effectively pursued research exercise mainly from the last few years. The variable parameters considered are the concentration of dye solution, the pH of dye solution, amount of the catalyst used and intensity and source of applied light for degradation studies of dye. A tentative mechanism for the reaction has been proposed.

KEYWORDS: Photocatalytic Degradation, Zinc Oxide, Barium Chromate, Crystal Violet Dye.

1. INTRODUCTION

Dyes are broadly used in various industries such as textile industry, food industry, polymer industry, paper industry, cosmetics industry and many more industries. The textile industry has large water consumption and thereby, produces extensive amounts of coloured wastewater. Many dyes are toxic and carcinogenic in nature. Chemical methods for decolorization of wastewater have effective results among physical and biological methods. In chemical methods, the dyes are converted into harmless substances.

Advanced oxidation processes are the most powerful chemical treatment techniques. Recently suggested photocatalysis for organic wastewater treatment by S.I.S. Mashuri el al.[1] The efficiency of numerous homogeneous and heterogeneous photocatalytic processes destructive oxidation of organic compounds of different classes is considered. Oxidative photocatalysis processes (AOPs) for treatment of waste water by R.V. Prihod’ko et al.[2] Advanced oxidation processes hold great commitment to provide substitute for better treatment and protection of environment, are reviewed by A. Al-kdasi et al.[3] A. Kumar et al[4] suggested oxidation rates and efficiency of the photocatalytic process are highly dependent on a number of operational parameters and reviewed on the factors affecting the photocatalytic degradation of hazardous materials. Graphene/$BaCrO_4$ nanocomposites catalysed photodegradation and kinetics study of dyes done by K.H. Kim et al.[5] Effect of different variables on the size distribution of barium chromate nanoparticles and the results shows that, in the synthesis of $BaCrO_4$ nanoparticles, the best performance belongs to sodium citrate given by M. Simiari et al.[6] N. Kapoor et al[7] observed the degradation of evans blue dye by using multi-walled carbon nanotubes (MWCNTs) – barium chromate composite. D.I. Prajapati et al[8] carried out the photocatalytic degradation of malachite green dye using nanosized barium chromate catalyst. K.K. Sivakumar et el[9] studied ZnO/UV induced photocatalytic degradation of textile dye. X. Chen et al[10] synthesized zinc oxide (ZnO) photocatalyst for the efficient and rapid photocatalytic degradation of azo dyes.

C.R. Indulal et al[11] reported potical and photocatalytic studies of zinc strontium oxide nanocomposite for technological applications. F.A. Alharthi et al[12] reported fabrication of graphitic carbon nitride doped zinc oxide nanocomposites, g-C_3N_4/ZnO, (Zn-Us) by using different amount of urea and characterized by X-ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Raman, UV-vis, Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) techniques. P.L. Meena et al[13] synthesized g-C_3N_4/ZnO hybrid nano heterostructures photocatalysts facile grinding, dehydration followed by pyrolysis method. The structural and textural properties of the prepared samples were investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy combine electron dispersive spectroscopy (FESEM-EDS) and UV-visible spectroscopy. K.A. Isai[14] carried out the photocatalytic removal of methylene blue (MB) dye from its aqueous solution by using ZnO and 2%Fe-ZnO nano powder under UV light irradiation and ZnO and 2%Fe-ZnO nanomaterials were prepared by using a low-cost sol-gel method. S.B. Ameur et al[15] reported photocatalytic activities of undoped ZnO, Co (1%) doped ZnO (CZO) and In (1%) doped ZnO (IZO) thin films grown on flexible PEI (Polyetherimide) substrate by spray pyrolysis and increased photocatalytic activity against crystal violet dye. S. A. Umar et al[16] studied 1wt% MgO-ZnO Composite Catalyst for photocatalytic degradation of crystal violet dye. T.A. Garni et al[17] proposed the degradation of methylene blue (MB) and crystal violet (CV) under sunlight irradiation and synthesised Zinc oxide (ZnO) nanoparticles (NPs) using Rosmarinus officinalis leaf extract at 80 ° C (ZnO-80) and 180 ° C (ZnO-180). F. S.A. Suhail et al[18] reported photocatalytic degradation of an aqueous crystal violet dye by using ZnO catalyst in aqueous medium, Photocatalytic degradation of dyes was carried out by using UV radiation as light source. M.A. Habib et al[19] synthesised nanosized ZnO by hydrothermal process and characterized by scanning electron microscopy, X-ray diffraction and laser-induced breakdown spectra measurement techniques and the prepared nanosized ZnO was used to investigate the degradation of crystal violet dye.

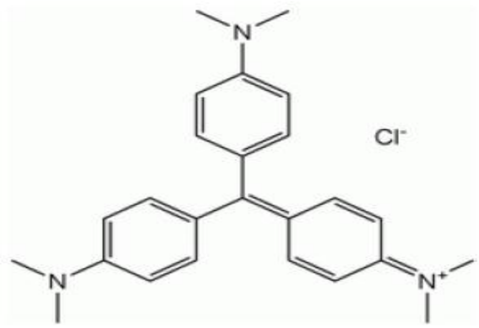

Figure 1: Structure of crystal violet.

2. EXPERIMENTAL

Synthesis of barium chromate

Barium chromate were synthesized by precipitation method and characterized by SEM-EDS techniques. First prepared a separate homogeneous solution of barium chloride and potassium chromate in distilled water. After that mixed both solution under stirring at room temperature. Both solutions react with each other and gives lemon yellow colour precipitation of barium chromate. Then filtered it after 2-3 hours and washed with distilled water 3-4 times. Dried at 60°C.

Zinc oxide

Zinc oxide used from Fisher scientific laboratory grade.

Preparation of composite

Barium chromate and zinc oxide were taken mole to mole and mixed with mechanical method to fine powder.

Characterization of composite

EDX Analysis: Energy-dispersive X-ray spectroscopy (EDS) detects X-rays emitted from the sample during bombardment by electron beam to characterise the elemental composition. The results are reported in table 1 and presented in figure 2.

Table 1: EDS data of barium chromate – zinc oxide.

Element	Series	Norm. C (wt. %)	Atom. C (at. %)
Barium	L-Series	20.03	6.45
Oxygen	K-Series	18.42	50.91
Chromium	K-Series	5.84	4.96
Zinc	K-Series	55.71	37.67
Total		100.00	100.00

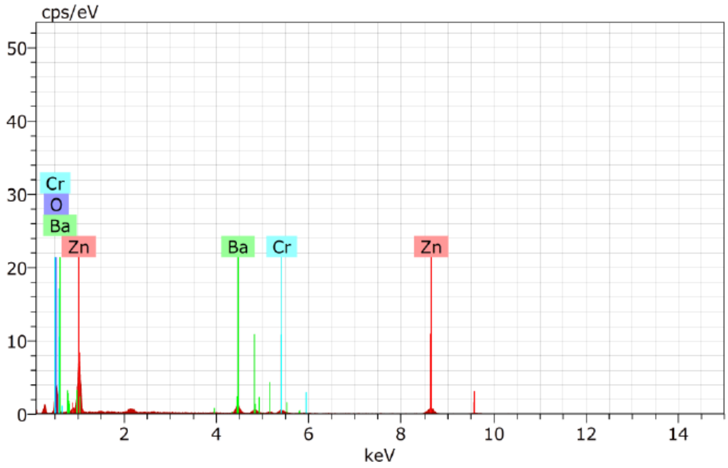

Figure 2: EDS of barium chromate – zinc oxide.

XRD Analysis: X-ray diffraction is a method to determine crystallinity of a compound. The crystal size of the composite was determined by the X-ray diffractometer (XRD). using CuKα radiation ($\lambda = 0.154060$ nm) in the 2θ scanning ranges from 20^0 to 80^0 with a scan rate at 10^0 min^{-1}. The powder XRD pattern of as prepared barium chromate – zinc oxide nanomaterials is given in figure 3.

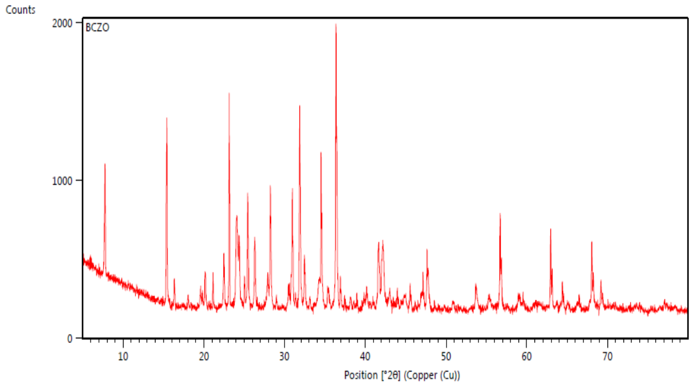

Figure 3: XRD of barium chromate – zinc oxide.

The crystal size (D) was calculated using the Debye-Scherrer's formula:

$D = 0.9\ \lambda/\ \beta \cos\theta$ (1)

Where, λ = The wavelength of x-ray source (λ = 0.1540 nm for CuKα), β (in radians) = The full width at half maximum (FWHM) and θ = The Bragg's angle.

Photocatalytic process

The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of crystal violet dye. A stock solution of dye (1.0×10^{-3} M) was prepared by dissolving (0.0407 gm) of dye in 100 mL of doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics model 335), and the desired pH of the solution was adjusted by the addition of standard 0.1 M sulphuric acid and 0.1 M sodium hydroxide solutions. The reaction mixture containing 0.12 gm photocatalyst was exposed to a 200 W tungsten lamp, and about 3 mL aliquot was taken out every 15 minutes. Absorbance (A) was measured at λ_{max}=590 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM 201). The absorbance of the solution at various time intervals was measured with the help of auto calorimeter (Systronics model LT-114). It was observed that the absorbance of the solution decreases with increasing the time of exposure, which indicates that the concentration of crystal violet dye decreases with increasing time. The calculation of degradation efficiency (φ) was made by the relation:

$$\Psi = 100\frac{A - A_0}{A_0}$$

Here, A_0 is initial absorbance, and A is absorbance after degradation of dye at time t. A plot of 1 + log A versus time was linear following pseudo-first order kinetics. Typical runs are given in Table 2 and graphically presented in Figure 4. The rate constant was calculated by using the expression:

k = 2.303 × slop (2)

Table 2: Typical runs for photocatalytic degradation of crystal violet

pH=9.0, Concentration [crystal violet] =3.5×10^{-5} M,

Composite=0.12 gm, Light intensity=60.0 mWcm^{-2},

Rate constant= 5.32×10^{-5} Sec^{-1} (composite with 2-propanol) and 5.90×10^{-5} Sec^{-1} (composite without 2-propanol).

Time (min)	Composite with 2-propanol		Composite without 2-propanol	
	Abs	1+log A	Abs	1+log A
0	0.741	0.8698	0.713	0.8530
15	0.711	0.8518	0.701	0.8457
30	0.692	0.8401	0.689	0.8382
45	0.679	0.8299	0.651	0.8135
60	0.641	0.8068	0.611	0.7860
75	0.619	0.7916	0.573	0.7581
90	0.588	0.7693	0.534	0.7275
105	0.559	0.7474	0.492	0.6919
120	0.522	0.7176	0.476	0.6776
135	0.498	0.6972	0.449	0.6522
150	0.459	0.6618	0.419	0.6222
K Sec^{-1}	5.32×10^{-5}		5.90×10^{-5}	

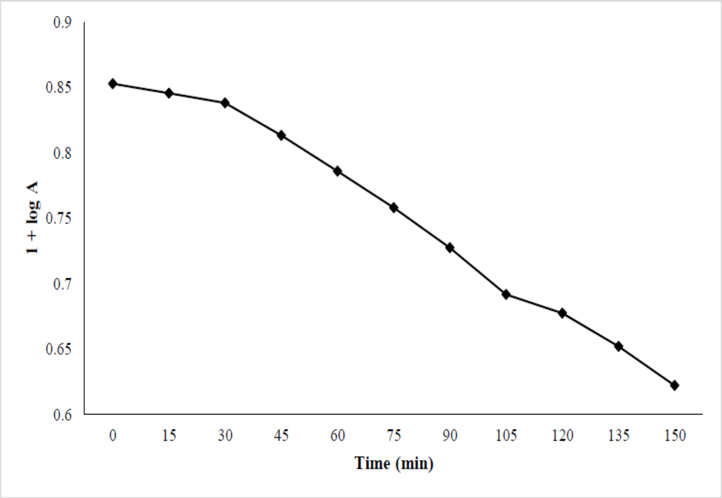

Figure 4: Typical run for photocatalytic degradation of crystal violet.

3. RESULTS AND DISCUSSION

Effect of parameters

(i) Effect of pH

The effect of variation of pH range 4.0 to 9.5 and all other parameters were kept to be identical. The results are given in Table 3 and Figure 5. It was observed that with an increase in pH, the rate of reaction increases. At pH 9.0 rate of reaction was maximum. In this case, the presence of scavenger i.e., 2-propanol does not affect the rate of reaction adversely and hence, it may be concluded that $^{\bullet}$OH radical does not participate in the degradation. It was interesting to observe that barium chromate – zinc oxide composite was active in basic range (6.5-9.0).

Table 3: Effect of pH on photocatalytic degradation of crystal violet.

Concentration [crystal violet] =3.5×10^{-5} M, Composite=0.12 gm,

Light intensity=60.0 $mWcm^{-2}$

pH	**Rate constant, (*k*)× (10^{-5} sec^{-1})**
4.0	2.91
5.0	3.09
5.5	3.48
6.0	3.76
6.5	3.91
7.0	4.12
7.5	4.38
8.0	4.61
8.5	5.11
9.0	**5.90**
9.5	4.86

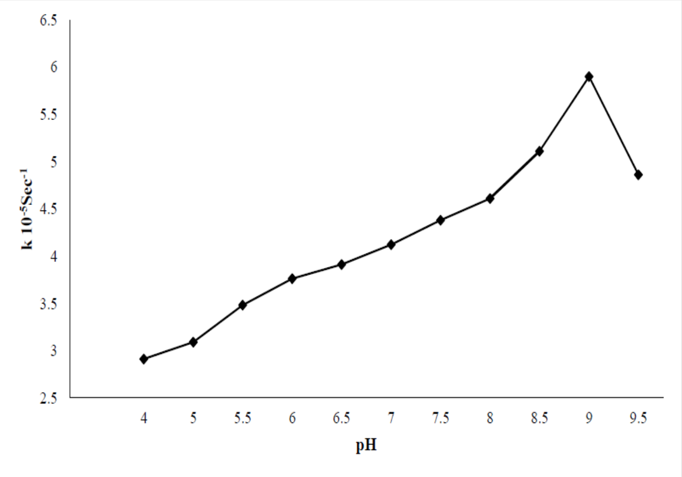

Figure 5: Effect of pH on photocatalytic degradation of crystal violet.

(ii) Effect of concentration of dye solution

The effect of concentration variation of crystal violet dye on its rate of degradation has been observed in the range from 1.5×10^{-5} M to 4.5×10^{-5}M and keeping all parameters to be the same. The results are given in Table 4 and Figure 6. It has been observed that the rate of degradation increases with increasing concentration of dye up to 3.5×10^{-5} M. Further increase in concentration beyond this limit results in a decrease in degradation rate. This may be explained on the basis that on increasing the concentration of dye, the reaction rate increases as more molecules of dyes were available but a further increase in concentration results appearing an internal filter effect which does not permit sufficient amount of light to reach the surface of the photocatalyst thus, decreasing the rate of photocatalytic degradation of crystal violet dye occurs.

Table 4: Effect of dye concentration on photocatalytic degradation of crystal violet:

pH=9.0, Composite=0.12 gm,

Light intensity=60.0 mWcm^{-2}

[Crystal violet] × 10^{-5} M	**Rate constant (k) × 10^{-5}(sec^{-1})**
1.5	2.86
1.7	3.41
2.0	3.96
2.3	4.23
2.5	4.61
2.7	4.88
3.0	5.26
3.3	5.61
3.5	**5.90**
4.0	5.36
4.3	4.95
4.5	4.61

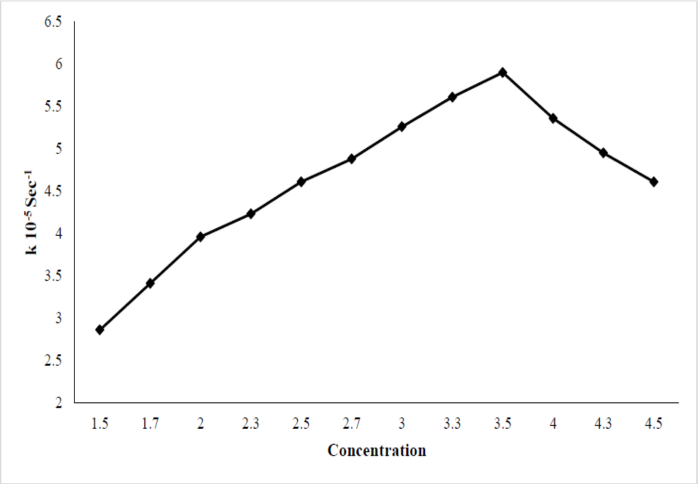

Figure 6: Effect of dye concentration on photocatalytic degradation of crystal violet.

(iii)Effect of amount of photocatalyst

The amount of semiconductor may also affect the rate of degradation of dye and hence, different amounts of semiconductor were taken. The results are the results are reported in Table 5 and Figure 7. It was observed that there was an increase in the rate of photocatalytic degradation with an increase in the amount of semiconductor up to 0.12 g, but after the amount 0.12 g of semiconductor, it becomes almost constant. Beyond this point, the rate of reaction becomes virtually constant. This behaviour may be explained by the fact that with an increase the amount of catalyst, the exposed surface area of catalyst will increase. It may be considered like a saturation point; above which, any increase in the amount of semiconductor had negligible or no effect on the rate of photocatalytic degradation of dye, as an increase in the amount of semiconductor after this saturation point would only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifted to the higher range for larger vessels, while the reverse was true for smaller vessels.

Table 5: Effect of amount of catalyst on photocatalytic degradation of crystal violet.

pH=9.0, Concentration [crystal violet] =3.5×10^{-5} M,

Light intensity=60.0 $mWcm^{-2}$

Photocatalyst (gm)	**Rate constant (k) × 10^{-5}(sec^{-1})**
0.02	3.78
0.04	4.12
0.06	4.67
0.08	5.09
0.10	5.58
0.12	**5.90**
0.14	5.66
0.16	4.79
0.18	4.41
0.20	3.99

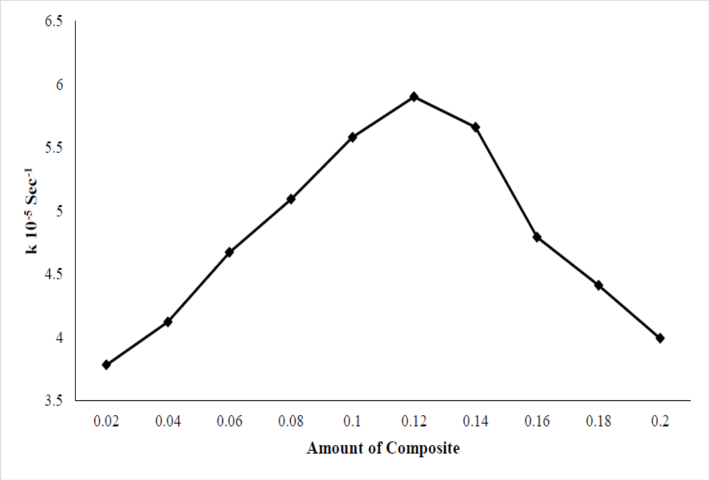

Figure 7: Effect of amount of composite on photocatalytic degradation of crystal violet.

(iv)Effect of intensity of light

The variation in light intensity may also affect the rate of photocatalytic degradation of dye. Hence, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured using Suryamapi (CEL Model SM201). The results are reported in Table 6 and Figure 8. The results showed that with increasing light intensity, the rate of reaction increases and maximum rates were found at 60.0mW cm^{-2} because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor. However, by increasing the intensity above 60.0 mWcm^{-2}, there was a little decrease in the rate. This may be due to some thermal reactions.

Table 6: Effect of light intensity on photocatalytic degradation of crystal volet.

pH=9.0, Concentration [crystal violet] =3.5×10^{-5} M,

Composite=0.12 gm

Light intensity (mW cm^{-2})	Rate constant (k) × 10^{-5}(sec^{-1})
20	2.86
30	3.79
40	4.51
50	4.98
60	**5.90**
70	5.08

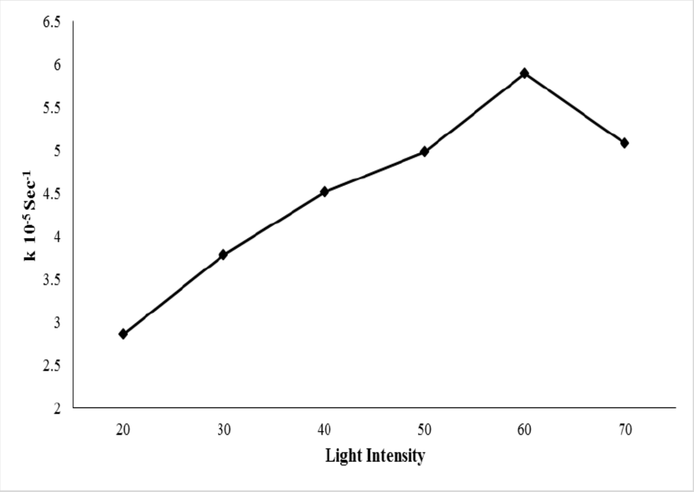

Figure 8: Effect of light intensity on photocatalytic degradation of crystal violet.

Mechanism

On the basis of the experimental observations, a tentative mechanism for photocatalytic degradation of crystal violet dye has been proposed in the presence of barium chromate – zinc oxide composite as follows:

Crystal violet (CV) absorbs radiation of suitable wavelength giving rise to its excited first singlet state after that intersystem crossing (ISC) to the triplet state. The semiconductor barium chromate – zinc oxide also absorbs light energy to excite its electron from the valence band (VB) to conducting band (CB); thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products.

$$^{1}CV_{0} \xrightarrow{h\nu} {}^{1}CV_{1} \tag{3}$$

$$^{1}CV_{1} \xrightarrow{ISC} {}^{3}CV_{1} \tag{4}$$

$$\text{Composite} \longrightarrow e^{-}(CB) + h^{+}(VB) \text{ or } SC^{*} \tag{5}$$

$$H^{+} + {}^{-}OH \longrightarrow \cdot OH \tag{6}$$

$$^{3}CV_{1} + \cdot OH \longrightarrow \text{Leuco CV} \longrightarrow \text{Product} \tag{7}$$

Carrying out the reaction in the presence of $^{\bullet}OH$ radical scavenger, 2-propanol, the reaction rates were unaffected. This unambiguously shows that there was no involvement of $^{\bullet}OH$ radicals in the reactions as an active oxidizing species.

4. CONCLUSION

Barium chromate photocatalyst was synthesized by precipitation method. Barium chromate – zinc oxide composite prepared by mechanical method further characterized to know its morphology. This composite was used for photocatalytic degradation of crystal violet (CV) dye. The experimental results showed that photocatalytic degradation efficiency of crystal violet (CV) was affected by pH, concentration of dye solution, amount of semiconductor and intensity of light. The use of the photocatalyst can be analyzed for the degradation of various pollutants.

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