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USE OF LEAD CHROMATE AS PHOTOCATALYST FOR DEGRADATION OF BRILLIANT GREEN

ANJANA RAWAL, SHWETA SHARMA, SURBHI BENJAMIN and RITU VYAS[*]

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

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ABSTRACT

The photocatalytic decolorizing of Brilliant green was carried out in the presence of semiconducting lead chromate and the progress of the reaction was observed spectrophotometrically. The effects of various operating variables like pH, concentration of dyes, amount of semiconductor and light intensity on the rate of bleaching was observed. A tentative mechanism has been proposed for the photocatalytic degradation of Brilliant green.

Key words: Photocatalytic degradation, Lead chromate, Photocatalysis.

INTRODUCTION

Wastewater generated from various activities contains different toxic contaminants, which are harmful for both; flora and fauna. The industrial operation generates wastewater containing various pollutants including dyes. Dyes are considered hazardous to the environment because many of them are toxic to living organisms, directly or through their absorption and reflection of sunlight entering the water, which interferes with the growth of aquatic organisms. Furthermore, they impart colour to wastewater, giving rise to aesthetic issues. Organic dyes are used in a wide range of industrial applications (e.g., textiles, food products, cosmetics and pharmaceuticals), so they are frequently found in wastewaters and are increasingly becoming an environmental problem.

The textile activities have a high potential environmental impact, principally due to the release of large volumes of wastewaters that contain high organic charge and strong coloration. Photocatalysis is an evolving field for solving this kind of problem because this technique is very rapid, eco-friendly and effective for treatment of waste water. Therefore, the photocatalyst with a strong oxidizing potential could be postulated.

Many researchers have used ternary oxide as photocatalyst. Fu et al.[1] synthesized nanosized Bi_2WO_6 by a hydrothermal crystallization process. The photoactivities of the as-prepared samples were investigated for the photodegradation of rhodamine-B (RhB). The sample prepared at 180°C exhibited the highest photochemical activity under visible-light irradiation.

The novel $NiFe_2O_4/Bi_2O_3$ heterostructures were prepared by Ren et al.[2] following hydrothermal method by a microwave-assisted method and used for visible-light-driven photocatalytic activity for

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[*] Author for correspondence; E-mail: ritu24vyas@gmail.com

antibiotic degradation. $NiFe_2O_4/Bi_2O_3$ heterostructures exhibited significantly higher visible light photocatalytic activity for the removal of tetracycline in water than that of a single semiconductor. The enhanced photocatalytic performance of the $NiFe_2O_4/Bi_2O_3$ heterostructures was mainly ascribed to the band potential, which matched suitably, followed by efficient charge separation and transfer across the heterostructures interface. Further, the heterostructures can be recovered and recycled under a magnetic field along with good stability.

Kaur et al.[3] synthesized La_2CoO_4 using using lanthanum nitrate and cobalt nitrate as starting reagents with microwave heating for 6 min without calcination step. The synthesized product was characterized by X-Ray powder diffraction (XRD). The photocatalytic behaviour of La_2CoO_4 was studied spectrophotometrically through bleaching of Azure-B and Yellowish orange dyes. The effect of variation of different parameters i.e. pH, amount of La_2CoO_4, concentration of dye and light intensity was studied on the rate of photocatalytic degradation.

Gopalappa et al.[4] investigated the photocatalytic degradation of Brilliant red, an azo textile dye in the presence of $CaMgO_2$ nanoparticles under natural sunlight. Complex metal oxide nanoparticle $CaMgO_2$ was synthesized by solution combustion method. Its band gap energy, particle size and morphology were studied by absorption spectra, XRD and SEM. The photocatalytic activity of these nanoparticles on Brilliant red dye was observed by varying pH, amount of catalyst, dye concentration, etc.

Cheng and Kang[5] synthesized cubic $ZnIn_2S_4$ nanoparticles and hexagonal $ZnIn_2S_4$ flower like microspheres via a facile hydrothermal method by simply changing the metal precursors. The as-prepared samples were characterized by XRD, SEM, TEM and UV-vis DRS. $ZnIn_2S_4$ polymorphs showed photocatalytic activity for the degradation of Methyl orange under visible light irradiation.

Chaneac et al.[6] found bismuth-based oxides such as Bi_2O_3, $BiVO_4$, and Bi_2WO_6 show photocatalytic activity for the degradation of RhB in solution and decomposition of stearic acid under visible light irradiation. They demonstrated that the photocatalytic mechanism is tightly linked to the surface properties of the compounds. For weak acid solids, Bi_2O_3 and $BiVO_4$, the interaction with some pollutants such as RhB and stearic acid is somewhat weak and does not lead to an efficient degradation.

Kumar et al.[7] prepared nanocrystals of europium-doped bismuth tungstate (Bi_2WO_6:Eu) by solvothermal method at 180ºC for 2 hr. The photocatalytic activity of the sample was evaluated by degradation of rhodamine B under sunlight irradiation. It was observed that photocatalytic activity of Eu-doped Bi_2WO_6 showed higher photocatalytic activity in the presence of H_2O_2.

Vijaya et al.[8] prepared Cu^{2+} doped $MnFe_2O_4$ ($Mn_{1-x}Cu_xFe_2O_4$; $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) nanomaterials with different morphologies such as nanoparticles, nanosheets and nanoflakes by the urea assisted one-pot microwave combustion method. X-ray diffraction (XRD) studies showed that the samples have pure cubic spinel phase, and the average crystallite size was found to be in the range of 31-44 nm. The lattice parameter was decreased from 8.477 to 8.455 Å with increasing Cu^{2+} content, which is determined by Rietveld analysis. The morphology of the samples was recorded by high resolution scanning electron microscope (HR-SEM) analysis, and was found to change considerably from nanoparticles to nanosheets and then to nanoflakes with increasing Cu^{2+}. The energy dispersive X-ray (EDX) results showed that the composition of the elements was relevant as expected from the synthesis. The optical properties of the as-prepared nanostructures were also investigated by UV–visible diffuse reflectance spectra (DRS) and photoluminescence (PL) spectra.

Thus, photocatalytic activity of various ternary oxides were observed in the present work. Here, photocatalytic degradation of Brilliant green in presence of lead chromate has been being reported.

EXPERIMENTAL

0.0482 g of Brilliant green was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This stock solution was further diluted. The absorbance of Brilliant green solution was determined with the help of a spectrophotometer at λ_{max} = 630 nm. The dye solution was divided in four beakers.

- The first beaker containing Brilliant green solution was kept in dark.
- The second beaker containing Brilliant green solution was exposed to light.
- The third beaker containing Brilliant green solution and 0.10 g lead chromate was kept in dark, and
- The fourth beaker containing Brilliant green solution and 0.10 g lead chromate was exposed to light.

These beakers were kept for 3-4 hrs and then the absorbance of each solution was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first three beakers remained virtually constant, while the solution of fourth beaker showed a decrease in its initial value. This observation suggests that this reaction requires both; the presence of light as well as semiconductor lead chromate. Therefore, this reaction is a photocatalytic reaction in nature and not chemical or photochemical.

A solution of 1.30×10^{-5} M Brilliant green was prepared in doubly distilled water and 0.10 g of lead chromate was added to it. The pH of the reaction mixture was adjusted to 9.0 and then this solution was exposed to a 200 W tungsten lamp at 60.0 mWcm^{-2}.

A typical run has been presented in Table 1 and graphically represented in Fig. 1.

Table 1: A typical run

pH = 9.0 Lead chromate = 0.10 g
[Brilliant green] = 1.30×10^{-5} M Light intensity = 60.0 mWcm^{-2}

Time (min.)	Absorbance(A)	1 + log A
0.0	0.547	0.7370
5.0	0.400	0.6020
10.0	0.362	0.5514
15.0	0.356	0.5510
20.0	0.297	0.4727
25.0	0.259	0.4132
30.0	0.227	0.3560
35.0	0.196	0.2922
40.0	0.182	0.2600
45.0	0.167	0.2227

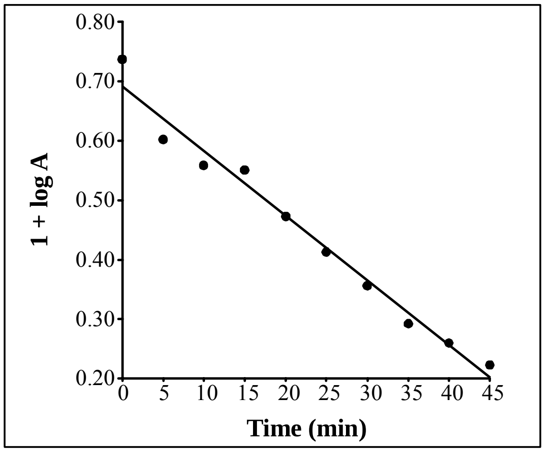

Fig. 1: Typical run

It was observed that there was a decrease in absorbance of Brilliant green solution with increasing time of exposure. A linear plot between 1 + log A v/s time was obtained, which indicates that the photocatalytic degradation of Brilliant green follows pseudo-first order kinetics. The optimum rate constant was found 3.64 × 10^{-5} sec^{-1}. The rate constant for this reaction was measured with the help of equation following equation.

$$k = 2.303 \text{ x slope} \qquad \ldots(1)$$

Effect of pH

The effect of pH on the rate of degradation of Brilliant green solution was investigated in the pH range 6.5-10.5. The results are given in Fig. 2.

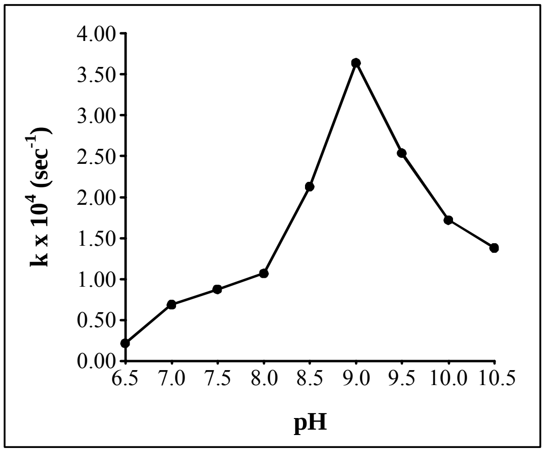

Fig. 2: Effect of pH

It has been observed that the rate of degradation increases with increase in pH upto 9.0 for Brilliant green; further increase in pH resulted in a decrease in the rate of degradation. The increase in the rate of photocatalytic degradation with increase in pH may due to more generation of $^{\bullet}OH$ radicals, which are produced from the interaction of OH^- and hole (h^+) of the semiconductor. These $^{\bullet}OH$ radicals are responsible for the oxidative degradation of dye. After this optimum pH 9.0 ; the rate of reaction decreases because more OH^- ions are available and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of cationic form of Brilliant green will have a force of attraction towards surface of semiconductor. So an enhancement in the rate of degradation was observed. Further increasing the pH, there will be no force of attraction between negatively charged surface of the semiconductor and neutral form of the dye. This will result into a decrease in the rate of degradation.

Effect of dye concentration

The effect of dye concentration was observed by taking different concentrations of Brilliant green. The results are summarized in Fig. 3.

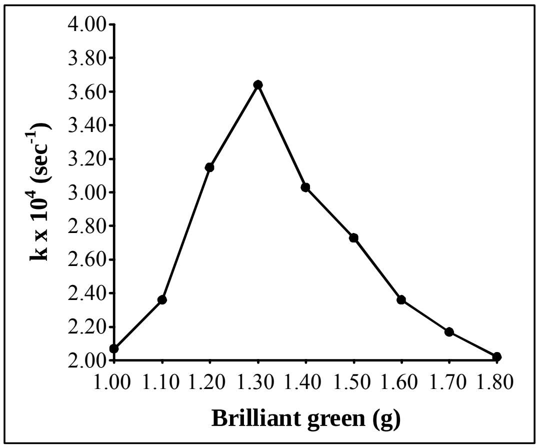

Fig. 3: Effect of dye concentration

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of dye upto a limit i.e. 1.30 × 10^{-5} M for Brilliant green. It may be attributed to the fact that as the dye concentration increases, more dye molecules were available for excitation and consecutive oxidation resulting in degradation. Hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye started acting as an internal filter for the incident light and does not permit the desired light intensity to reach the surface of the photocatalyst; thus, a decrease in the rate of photocatalytic degradation was observed.

Effect of amount of semiconductor

The amount of semiconductor may also affect the degradation of dye and hence, different amounts of lead chromate were used. The results are reported in Fig. 4.

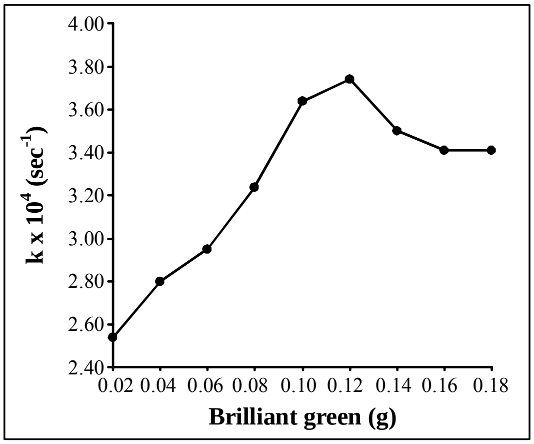

Fig. 4: Effect of amount of semiconductor

It has been observed that the rate of photocatalytic degradation of dyes increases on increasing the amount of semiconductor (lead chromate) but it becomes virtually constant after a particular amount 0.10 g for Brilliant green. This may be explained on the basis that the amount of semiconductor was increased, there was an increase in exposed surface area of the lead chromate, but after a certain limit, increase in amount of photocatalyst will not increase the exposed surface area. It may be considered like a saturation point, above which there is negligible or no effect on the rate of degradation of the dye, as an increase in the amount of semiconductor after this amount will only increase the thickness of the layer at the bottom of the reaction vessels and not the exposed surface area.

Effect of light intensity

The data indicate that as light intensity was increased, the rate of reaction also increases and maximum rate has been found at 60.0 mWcm^{-2}. The results are representing in Fig. 5.

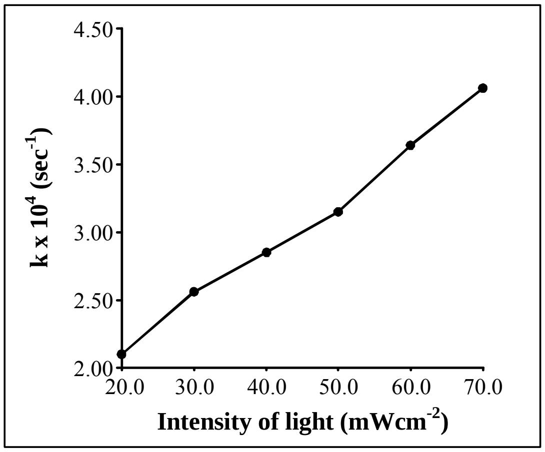

Fig. 5: Effect of light intensity

An almost linear relationship between light intensity and the rate of reaction was observed. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit time per unit area also increases, resulting into higher rate of degradation.

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of dye has been proposed as follows –

Dye (D) absorbs radiation of suitable wavelength and it is excited to its first singlet excited state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting lead chromate (SC) also utilized the incident light energy to excite its electron from valence band to conduction band; 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.

$$^1D_0 \xrightarrow{h\nu} {}^1D_1 \quad \ldots(2)$$

$$^1D_1 \xrightarrow{ISC} {}^3D_1 \quad \ldots(3)$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \quad \ldots(4)$$

$$h^+ + {}^-OH \longrightarrow {}^{\bullet}OH \qquad \ldots(5)$$

$${}^{\bullet}OH + {}^3D_1 \longrightarrow \text{Leuco Dye} \qquad \ldots(6)$$

$$\text{Leuco Dye} \longrightarrow \text{Products} \qquad \ldots(7)$$

The $^{\bullet}$OH radical acts as an active oxidizing species in the degradation of dye as the rate of degradation was adversely affected in the presence of hydroxyl radical scavenger (2-propanol).

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