A SPECTROPHOTOMETRIC ANALYSIS BY SYNTHESIZED NOVEL QUATERNARYPHOTOCATALYST ZrCdPbO_4 FOR MINERALIZATION OF COLOURED POLLUTANT

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ABSTRACT

Coloring carcinogenic dye molecules, which are released in water, pollute it and are not degraded naturally. A novel quaternary photocatalyst ZrCdPbO_4 is synthesized and characterized by different analytical techniques XRD, FESEM, EDS and UV-Vis spectroscopy. This is used as a photocatalyst for the mineralization of carcinogenic Brilliant Green dye. Effect of different factors like pH, the weight of photocatalyst, dye concentration and light intensity are observed. The reaction follows pseudo-first-order rate law and mineralization by $\cdot\text{OH}$ free radical is confirmed. Complete mineralization of the dye is observed.

Keywords: Photocatalyst, FESEM, Mineralization, Pseudo-first-order Kinetics, Free Radical, Brilliant Green.

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INTRODUCTION

The present era is an era of scientific research and development. New researches are being introduced to make the world more comfortable to live in. During carrying out the work, unknowingly, human activities have produced a huge giant in front to face called environmental pollution. The biggest factor polluting our natural resources is synthetic coloring agents i.e. dyes. These dyes are sometimes added to potable water, harming living beings i.e. animals, humans, plants etc.

Canada has 45% of all waterborne outbreaks which are from non-municipal systems.¹ Total 14 sampling points were selected from the Nakdong riverine network of the river Basin during the year 2011. Different factors and their effects on water like temperature, pH, DO, BOD, COD etc was investigated.² Yamuna river pollution had been studied in five locations in Delhi, India. The observations showed a correlation between DO, BOD, COD etc through statistical data analysis.³ Amrita studied the quality of water River Diana by considering the variation of different parameters like Temperature, pH, Conductivity, Alkalinity, Total Dissolved Solids, Dissolved Oxygen and many other factors.⁴ Ferencz and Adalbert measured the contamination levels of pesticides from central Romania and found pesticides in water, soil and foodstuffs samples. Some of them were organochlorine, triazine, carbamate, phenoxy acid and organophosphorus.⁵

Many techniques for removal of these colored contaminants from various resources had been developed in due course of time such as conventional techniques (ozonation, flocculation, coagulation etc.), advanced oxidation processes, photocatalytic techniques etc. and biodegradation process also used for removal of Textile Effluent (STE).⁶

An inexpensive photocatalytic reactor was used in a chemical process that was easily assembled. It used an available fluorescent light with low wattage and utilized a photocatalyst for wastewater treatment.⁷ The reactor used was equipped in such a way that the heat generated by the light source was readily dissipated into water, which was treated. Haloalkanes, esters, aromatics and pesticides were found in drinking water as organic contaminants and their mineralization rate was measured by relative rate methods with the reactions of the hydroxyl radical.⁸ Nadim et al. carried the experiments to study the

effects of temperature and the extent of iron-chelate levels on the mineralization of dissolved polycyclic aromatic hydrocarbons (PAH) in aqueous systems.⁹

Various studies had been carried out in the field of photocatalytic degradation and mineralization. The degradation rate of Brilliant Green was higher over $\text{SnO}_2/\text{TiO}_2$ nanocatalysts than that of TiO_2 .¹⁰ Zinc sulfide quantum dots were used for degradation of BG and about 88 percent degradation was observed.¹¹ Incorporation of copper and cobalt in titanium oxide ($\text{CuCO}_{0.5}\text{Ti}_{0.5}\text{O}_2$ nanocomposite) changes the bandgap and absorption peak in the spectrum (~ 325 nm to 800 nm) which alters the removal of dye.¹² 99 percent degradation of BG was observed in presence of TiO_2 , 87 percent in TiO_2/Zn and 46 percent in presence of TiO_2/Cu .¹³ Decolorization of BG upto 94.8 percent in 120 min, was observed in the presence of ZnO in the sonophotocatalytic process.¹⁴ Visible light irradiation for the degradation of BG dye over monoclinic BiVO_4 in presence of H_2O_2 was carried out and a synergetic effect was observed between BiVO_4 and H_2O_2 in generating more $\cdot\text{OH}$ free radicals.¹⁵ spinel zinc ferrite (SZFO) atomic sheets were synthesized. BG was chemisorbed on the SZFO atomic sheets and mineralized on microwave irradiation.¹⁶ Two percent Nd-doped ZnO showed 98.26 percent degradation of Brilliant Green as compared to others having 1, 3, 4 and 5 percent Nd-doped ZnO nanoparticles.¹⁷ Removal of BG was studied for initial concentration, different irradiation power, the different dosage of H_2O_2 and different dosage of Nb_2O_5 catalyst.¹⁸ Rawal et al. used lead chromate for degradation of BG and different parameters for degradation rate were studied.¹⁹ Molybdenum trioxide (MoO_3) supported on cerium-zirconium oxide ($\text{CeO}_2\text{-ZrO}_2$) was synthesized by co-precipitation process and catalytic behavior of it was tested.²⁰

Literature survey has proved the supremacy of the photocatalytic process of degradation, over others. The present work consists of the synthesis of a novel photocatalyst ZrCdPbO_4 , which with more band gap, has shown strong photocatalytic activity. This is used for the complete mineralization of synthetic dye Brilliant Green. Optimum conditions are extracted for this purpose.

EXPERIMENTAL

Preparation of Photocatalyst

Nitrates of Zr, Cd and Pb (2.49 g, 3.08 g and 3.31 g each respectively) were dissolved in a minimum quantity of distilled water, were mixed and stirred for 2 hours. The solution was filtered and to this, pre-standardized NaOH solution was added drop-wise with continuous stirring. The crystalline precipitate of pale color was obtained. Stirring was continued for another two hours. The precipitate was then allowed to settle for half an hour and supernatant liquid was checked for further precipitation. It was filtered then by Whatman filter paper and was washed with distilled water for several times. The prepared catalyst was dried at 90°C in an oven for 2 hours, grounded and calcined at 500°C for 5 hours. Crystalline pale-yellow colored powder of ZrCdPbO_4 obtained.

Characterization

The study for characterization of ZrCdPbO_4 was carried out by XRD, FESEM, EDS and UV-Vis spectroscopic analytical techniques. The crystalline nature of the compound was analyzed on an X-ray diffraction spectrometer (XRD) (model Rigaku Ultima 4, step size 0.02, scan speed $4^\circ/\text{sec}$, voltage 40KV and current 40mA using Cu Ka 0.154 nm as a radiation source) to obtain diffraction peaks from the sample within a 2θ angle range of $20\text{-}90^\circ$. The morphology and consistency of prepared nanoparticles were examined by field emission scanning electron microscope (FESEM) with an accelerating voltage of 5 kV equipped with EDS (model Hitachi PU8010) image analyzer. The absorption properties were proved using the UV-Vis spectrophotometer (model lambda 750 Perkin Elmer).

Photocatalytic Study

A stock solution of Brilliant Green (BG) was prepared by dissolving 0.120 g in 250 mL distilled water and was diluted by distilled water to obtain the required concentration. pH of the reaction mixture was adjusted by pre-standardized NaOH and HCl and was recorded by pH meter (Hena pen type). Dye solution containing semiconductor was exposed to a 200W tungsten lamp. The absorbance was measured by spectrophotometer (CHINO) at $\lambda_{\text{max}} = 625\text{nm}$. A water filter was used to cut off any side thermal reaction. Experiments carried out showed that light, as well as semiconductors, is necessary for the

mineralization of dye. Effect of pH, the concentration of dyes, weight of semiconductor and intensity of light (solarimeter, CEL 201) on the rate of mineralization of the dye was studied. Maximum mineralization conditions were extracted, and it was observed that the reaction follows pseudo-first-order kinetics. Figure 1 shows the degradation process with time in presence of photocatalyst and light both.

Fig.-1: Photocatalytic Degradation of Brilliant Green containing ZrCdPbO₄ and irradiated by Light

RESULTS AND DISCUSSION

Characterization

The synthesis of many compounds by different methods has been carried out earlier.²¹⁻²⁴ The present work consists of the synthesis of a novel photocatalyst. The Characterization of the prepared photocatalyst ZrCdPbO₄ was carried out and spectral data and images are given in Fig.-2. XRD analysis (Fig.-2a) shows the peaks at 29°, 30.2°, 33.06°, 36°, 38.340°, 49°, 50.3°, 55.33°, 60.2°, 69.29° and crystal planes 111, 200, 220, 222, 310, 311, 321, 400. The peaks of prepared material are in good correlation with the standard XRD peaks of its precursors.^{25,26} XRD calculations show the average particle size to be 28nm. EDS spectra (Fig.-2b) confirmed the presence of Zr, Cd, Pb and O and the molecular formula comes out to be ZrCdPbO₄. FESEM images (Fig.-2c) show the shape of the cluster to be of homogeneous type. The peak in UV-Vis spectrum is obtained at 229nm (Fig.-2d) and calculation through it, gives the value of band gap 5 eV.²⁷ Prepared compounds showed wonderful photocatalytic activities despite greater bandgap. Thus, it was further used for the mineralization of synthetic Brilliant Green dye.

A Typical Run

A solution of dye was prepared and 0.14 g of the photocatalyst was added to it. The solution was then irradiated by 200Watt tungsten lamp with a water filter to cut off the heat reaction. It was observed that the optical density of the solution decreases with an increase in the time of exposure to the radiations. The data are given in Table-1 and Fig.-3. A plot between 1+log O.D. and time was found linear which indicates that mineralization follows pseudo-first-order rate law. The rate of the kinetics of the reaction was calculated by taking slope from the graph:

$$k = 2.303 \times \text{slope}$$

The rate constant obtained was $5.37 \times 10^{-4} \text{ (sec}^{-1}\text{)}$ at optimum conditions, pH 8.5, amount of photocatalyst 0.14 g, the concentration of Brilliant Green $0.6 \times 10^{-5} \text{ M}$ and intensity of light 74.0 mW/cm^2 .

Table-1: A Typical Run

pH= 8.5, [BG] = $0.6 \times 10^{-5} \text{ M}$, ZrCdPbO₄ = 0.14 g, light intensity = 74.0 mW/cm^2

Time (min.)	Optical Density	1+ log O.D.
0	0.232	0.3654
3	0.227	0.3560
6	0.210	0.3222
9	0.194	0.2878
12	0.177	0.2479
15	0.160	0.2041
18	0.146	0.1643

21	0.130	0.1139
24	0.117	0.0681
27	0.108	0.0334

Fig.-2: Analytical techniques (a)-XRD spectra, (b)-EDS analysis. (c)-FESEM images with a resolution of 100nm and 500nm and (d)-UV-Vis spectra

Fig.-3: A Typical Run

Effect of pH

pH is the major factor that alters the rate of reaction. The effect of pH was studied in range 6 to 9 and all other parameters were kept at constant values. Results are given in Table-2 and Fig.-4. The rate of reaction increases with an increase in pH because of addition of more bases increased the number of OH^- ions and so more $\text{OH}^\cdot$ free radicals are formed causing breaks down of conjugation in BG. After attaining a maximum value (at pH 8.5), the rate of reaction decreases with a further increase in pH because a greater number of $\text{OH}^\cdot$ free radicals force the hole electron pair recombination at the surface of the photocatalyst. Thus, a reduction in the rate of reaction is observed.

Table-2: Effect of pH
[BG] = 0.6×10^{-5} M, amount of ZrCdPbO_4 = 0.14 g, light intensity = 74.0 mW/cm^2

pH	Rate Constant $\times 10^4 (\text{sec}^{-1})$
6.0	2.46
6.5	2.90
7.0	3.35
7.5	3.12
8.0	4.02
8.5	5.37
9.0	4.47
9.5	3.58

Fig.-4: Effect of pH

Effect of Amount of Photocatalyst

The amount of photocatalyst is one of the factors affecting the rate of mineralization of BG. It was varied from 0.06 to 0.18 g and other various factors were kept at constant values. The observation data are given in Table-3 and Fig.-5. It was observed that with an increase in amount, the rate of mineralization increases because the exposed surface of the photocatalyst is increased. After the addition of amount 0.14g of the photocatalyst, the rate of reaction decreases because further addition only covers the base of the vessel making it multilayer. The upper layer is exposed to the light and the addition of more amount of photocatalyst generates obstacle in the path of the radiation reaching the surface of the photocatalyst. Thus, a reduction in the rate of the reaction is observed.

Table-3: Effect of Amount of Photocatalyst
[BG] = 0.6×10^{-5} M, pH=8.5, light intensity = 74.0 mW/cm^2

Amount of Semiconductor (g)	Rate Constant $\times 10^4 (\text{sec}^{-1})$
0.06	2.34
0.08	2.67
0.10	3.69
0.12	4.35
0.14	5.37
0.16	3.34
0.18	3.01

Fig.-5: Effect of amount of photocatalyst

Effect of Dye Concentration

The rate of mineralization of BG is affected by the concentration of dye. The study was carried out in the range from 0.2×10^{-5} to 1.4×10^{-5} M and all other factors were set at constant values. The data are given in Table-4 and Fig.-6. It was observed that the rate of reaction increases with an increase in the concentration of BG. It is because, with an increase in dye concentration, a greater number of dye molecules are available for excitation, increasing the rate of reaction. Further increase in concentration (above 0.6×10^{-5} M), decrease in the rate of reaction is observed as dye molecules now start acting as an internal filter which does not allow the desired wavelength to reach the surface of the photocatalyst, resulting in a decrease in the rate of mineralization.

Table-4: Effect of Dye Concentration
pH=8.5, amount of $\text{ZrCdPbO}_4 = 0.14$ g, light intensity = 74.0 mW/cm^2

[BG] $\times 10^5$ M	Rate Constant $\times 10^4 (\text{sec}^{-1})$
0.2	3.82
0.4	4.61
0.6	5.37
0.8	4.61
1.0	4.22
1.2	3.82
1.4	3.82

Fig.-6: Effect of Concentration of BG

Effect of Light Intensity

Light intensity is one of the factors affecting the rate of mineralization. The effect has been observed in the range from 7.0 to 74.0 mW/cm^2 . The observation data are given in Table-5 and Fig.-7. It is evident from data that with an increase in light intensity rate of mineralization increases because the number of

photons striking per unit area increases and a thus higher rate of reaction is observed. Higher intensities were not considered due to thermal side reactions.

Table-5: Effect of Light Intensity
pH= 8.5, [BG] = 0.6×10^{-5} M, pH=8.5, amount of ZrCdPbO_4 = 0.14 g

Light Intensity (mW/cm ²)	Rate Constant $\times 10^4$ (sec ⁻¹)
7.0	2.41
14.0	2.92
40.0	3.41
67.0	4.37
74.0	5.37

Fig.-7: Effect of Light Intensity

Mechanism

A tentative mechanism is proposed where photocatalyst ZrCdPbO_4 excites electrons by absorbing visible light, into the conduction band and holes (h^+) are generated at the valence band. Electrons from OH^- ions are abstracted by holes and $\text{OH}^\cdot$ free radicals are generated. These radicals react with the weaker double bond of dye, breaking its conjugation and initiating a chain reaction of break down. In the present case, Brilliant Green dye is broken down into smaller fragment molecules like carbon dioxide, oxygen, nitrogen and water which were confirmed by various laboratory tests. The participation of hydroxyl free radical was confirmed by scavenger test where the addition of scavenger ceased the mineralization reaction completely.

CONCLUSION

A process of complete mineralization of BG by photocatalyst ZrCdPbO_4 in presence of visible light is found more effective and economic. The process has many advantages over other conventional processes, used for the removal of environmental pollution. These are the following-

- The prepared compound is said green catalyst as it is not affected throughout the mineralization process and is recovered back.
- The process is cost-effective as the starting material is synthesized through precursors.
- The catalyst remains in a heterogeneous phase which can be separated by a simple filtration method and no other matter is added to the source or environment.
- The process uses solar light which is a renewable energy source and so conservation of energy prevails.

- The pollutant organic dye is completely mineralized and produced smaller molecules that do not harm the environment.
- Treated water can be used for irrigation, cooling, washing etc. purposes.
- The photocatalyst can be treated and used again and again, several times for treatment of the pollutant.
- No other chemical or complicated apparatus setup is required for treatment and so this makes the process economic too.

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