Synthesis of a novel Photocatalyst ZrCdPbO$_4$ and its use in Degradation of Toluidine Blue

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Abstract

Synthetic dyes have become an essential constituent in coloring industries like yarn, paper, plastic, wood etc because of their different benefits like low cost, imparting fast color, easily synthesized etc. thus dyes when not consumed completely are excreted in environment and pollute it. Some dyes are proved to be carcinogenetic to human health. Thus the need of the hour is to withdraw them from natural resources by any means. The present work consists of such a process for degradation of Toluidine Blue dye with help of a photocatalyst ZrCdPbO$_4$. This novel photocatalyst is prepared and characterized by different analytical techniques like XRD, FESEM, IR, EDX and UV-Vis etc. Various operational parameters are measured for degradation of the dye like pH, amount of photocatalyst, concentration of dye and light intensity etc. It is observed that the degradation rate follows pseudo first order kinetics and maximum rate constant found is 8.62×10^{-4} (s^{-1}).

Keywords:- Photocatalyst, XRD, FESEM, Toluidine Blue, degradation

I. INTRODUCTION

Different types of dyes are used in various industries. Dyes prepared by natural components are not harmful for human health and are easily biodegradable but synthetic dyes, which are prepared by chemical processes are highly detrimental and also environmental unfriendly. Dyes are classified according to their applications and chemical structure. Chromophores, which are responsible for color imparted by dyes, absorb visible light and electrons get excited from ground state to excited state. In the photocatalytic method this property of chromophores, in combination to the property of photocatalyst helps in breakdown of the chemical bond of chromophores like azo, keto, nitro, nitroso, thio, ethylene etc.

Kamal et al. [1] carried out their studies on volatile organic compounds and these compounds were found to be oxidized by catalytic process. The main sources of these compounds containing C2-C4 alkanes, hexane, cyclohexane, methylcyclohexane, isopropylbenzene, styrene etc. groups, were petroleum refineries, chemical industries, decomposition products in the biosphere and biomass, fuel combustion products, pharmaceutical plants, automobile industries, textile manufacturers, products from solvent processes, cleaning products, printing press excretion, insulating materials, office supplies, printers etc. [2]-[5].

Various gases like formaldehyde, tetrachloroethylene**,** acetaldehyde, ammonia, hydrogen sulfide, benzene were removed from water through photocatalytic process making it safe for further use [6]-[10]. Vijay and Bhardwaj [11] carried out a comparative study and proved the supremacy of ternary semiconductor. It was observed that less time is required to degrade the dye, less amount of semiconductor is used and pH of the solution is less altered for ternary semiconductor, thus causing less alteration to the environmental factors.

Gajbhiye [12] studied textile effluents with very high initial COD and BOD values and effectively treated them using catalytic process. Results showed that the dye molecules could be completely mineralized with the help of photocatalyst which was both economically viable and environment friendly. Kant [13] reported a study of removal dye from textile effluent using activated carbon. Removal by adsorption on two different samples of granular activated carbon was carried out through static batch method as well as continuous flow process. One carbon sample showed higher capacity of adsorption of the dye as compared to second carbon sample. Adsorption was observed more by batch method as compared to continuous flow process. Viswanathan [14] explained effect of normal variables like concentration of oxidizing agent, the concentration of the dye molecules, the amount of catalyst used and intensity of light applied for degradation studies. Other factors affecting the degradation of pollutants are shown in figure-1.
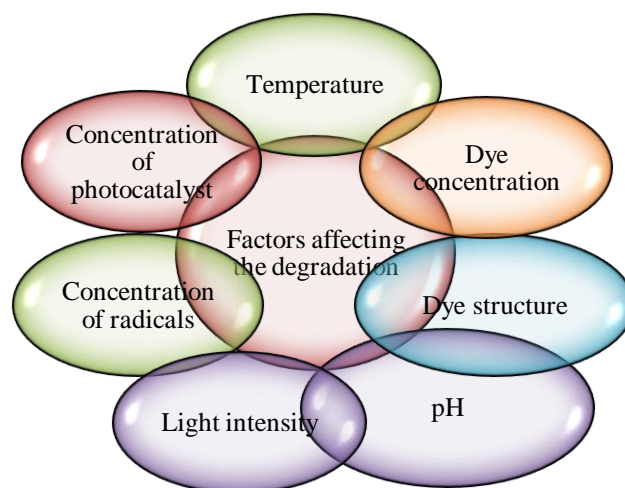
Fig 1: Factors affecting the degradation process

Chakrabarti and Dutta [15] stated that semiconductor photo catalysis often leads topartial or complete mineralization of organic pollutants. Semiconductors catalyze redox reactions in presence of air/O_2 and water when irradiated with UV/visible light. Aggarwal [16] observed that photo catalysis involves generation of electrons (e-) and holes (h^+) by light irradiation which migrate to the surface of the photo catalyst and so work as source for redox reaction and degrade organic pollutants. Different nanostructured photocatalysts like ZnO, CuO-SnO_2 nanocomposite, $ZnFe_2O_4$-modified TiO_2, ZnS, calcium zincate ($CaZnO_2$), TiO_2, $CeFeO_3$, Co_3O_4-ZnO-ZrO_2 ternary nanoparticles, Au doped TiO_2 were used as photocatalytic nanoparticles, nanocomposite and nanotube and played an important role for the degradation of different types of dyes as well as organic pollutants. [17]-[25].

II. MATERIALS AND METHODS

Preparation of photocatalyst - The photocatalyst $ZrCdPbO_4$ was synthesized by co-precipitation method from its precursor nitrates using NaOH as a precipitating agent. The synthesized nanocomposite was characterized by FTIR, FESEM, EDX, XRD, suggesting its bandgap 5eV, average crystal size 28nm and presence of elements Zr, Cd, Pb, O.

Dye solution- Stock solution of the dye Toluidine Blue of 1.0 x 10^{-3} M concentration was prepared by dissolving 0.0675 g of Toluidine Blue in 250.0 mL of doubly distilled water. It was used as a stock solution and was diluted further as required. The solution was then tested for photocatalytic activity which suggested that both light as well as photocatalyst is required for complete degradation of the coloured pollutants.

The absorbance of the solution was found almost constant in presence of sun light alone or in presence of photocatalyst alone. The solution showed a decrease in its optical density as well as color change when it was exposed to light in presence of photocatalyst. Observed data suggested that reaction is neither catalytic degradation nor photo degradation rather it is a photocatalytic degradation process. The desired pH (Hena Pen type pH meter) of the solution was adjusted by addition of prestandardized HCl and NaOH solutions. The progress of photocatalytic reaction was monitored by recording optical density at $Λ_{max}$ 590 nm for regular time intervals using a visible spectrophotometer (CHINO). A water filter was used to cut off the heat reaction. The intensity of light was varied and was measured by solarimeter (CEL 201). The participation of $OH^{.}$ free radicals in the reaction were identified by scavenger test, presence of which ceased the reaction completely. These free radicals were found strong enough to break the different bonds of dye (N=N, C=N, C-N, C=C, C-C etc) thus breaking the conjugation resulting into complete mineralization of the pollutant.

III. RESULT AND DISCUSSION

A. A typical run

Graph between time and 1+log O.D. was plotted and is given in figure 2 and data are in table 1. It was found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant for degradation was determined by -

$$K = 2.303 \times slope$$

Optimum conditions were extracted by experiments. The rate constant was found to be 8.62 x 10^{-4} (s^{-1}), at pH=8.0, amount of catalyst=0.14 g, concentration of Toluidine Blue dye= 2×10^{-5} M and light intensity = 74.0 mW/cm^2. Different rate affecting operational parameters were varied to obtain the optimum rate of reaction for the degradation of Toluidine Blue dye.

Table 1: A typical run

pH= 8.0, Amount of catalyst = 0.14 g, [TB] = 2×10^{-5} M, Light intensity = 74.0 mW/cm^2

Time (min.)	O.D.	1 + log O.D.
0	0.463	0.6655
2	0.450	0.6532
4	0.409	0.6117
6	0.380	0.5797
8	0.304	0.4828
10	0.281	0.4487
12	0.250	0.3979
14	0.225	0.3521
16	0.197	0.2944
18	0.180	0.2552
20	0.161	0.2068

Table 2: Effect of variation of pH

Amount of catalyst = 0.14 g, [TB] = 2×10^{-5} M, Light intensity = 74 mW/cm^2

pH	Rate constant x 10^4 (sec^{-1})
5.5	0.51
6.0	3.99
6.5	4.31
7.0	5.32
7.5	7.31
8.0	**8.62**
8.5	6.63
9.0	6.63
9.5	5.32

Fig 2: A typical run

Fig 3: Effect of variation of pH
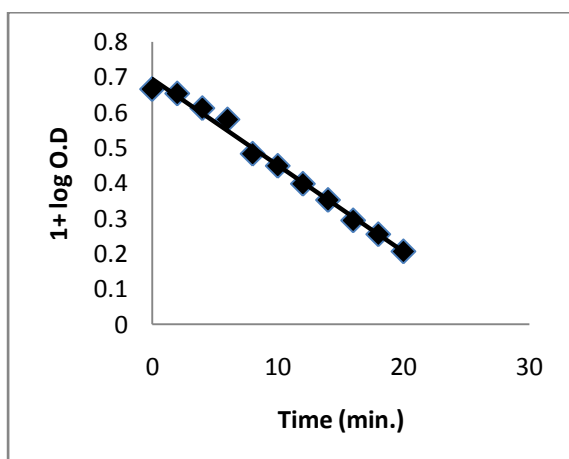
B. Effect of pH

Major factor affecting the rate of degradation of the dye is the pH of the solution. The pH of the solution was varied in both acidic and basic range from 5.0 to 10.0 by intervals of 0.5. The results are graphically reported in figure 3 and table 2. It was observed that rate of photocatalytic degradation increased with increase in pH up to 8.0 and then gradually decreased with increase in pH. The increase in rate is attributed to the availability of more concentration of OH $^-$ ions in solution. After pH 8.0, decrease in reaction rate is observed because repulsion becomes more effective amongst OH$^-$ ions and electrons on semiconductor surface. This repulsion causes the recombination of electrons and holes, which were generated by light irradiation, besides abstracting electrons from OH $^-$species. Thus a decrease in the rate is observed.

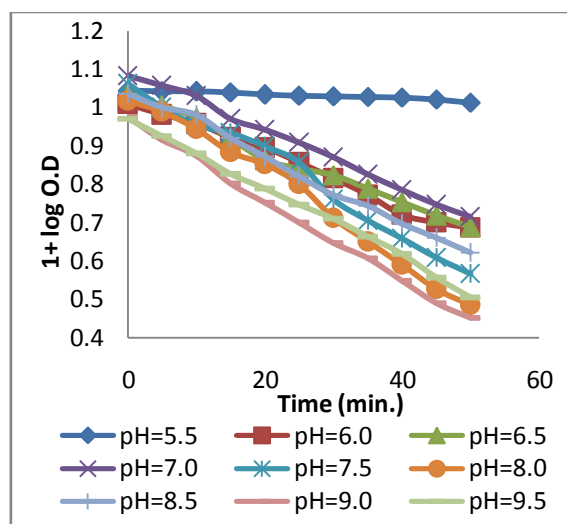## C. Effect of semiconductor amount

The effect of variation of amount of semiconductor was carried out and the highest degradation rate was observed at 0.14 gm of semiconductor. Further increase in amount reduced the rate of reaction. The data are given in table 3 and figure 4. The observations showed that after attaining maximum degradation value, at 0.14g of semiconductor amount, rate of reaction decreased because of formation of multilayers of catalyst in the solution and it promoted the recombination of electrons and holes. Thus reduction in rate of reaction was observed.
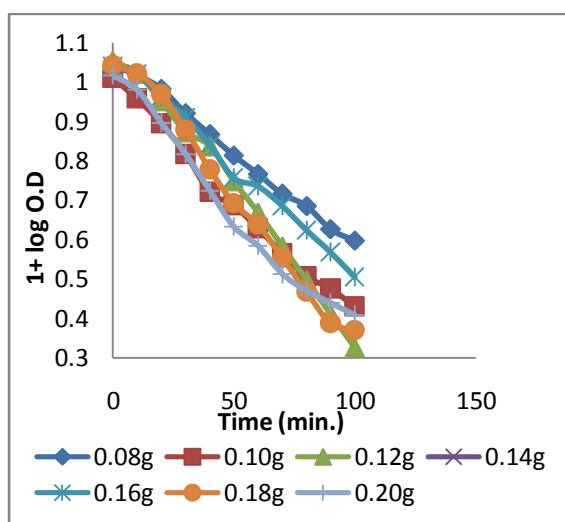
Table 3: Effect of variation of amount of semiconductor

pH= 8.0, [TB] = 2×10⁻⁵ M, Light intensity = 74.0 mW/cm²

Amount of photocatalyst (g)	Rate constant x 10^4 (sec⁻¹)
0.08	4.83
0.10	6.46
0.12	8.06
0.14	**8.62**
0.16	8.06
0.18	7.53
0.20	7.53

Table 4: Effect of variation of dye concentration
pH= 8.0, Amount of catalyst = 0.14 g, Light intensity = 74.0 mW/cm²

[Toluidine Blue] x 10^{-5}M	Rate constant x 10^4 (sec⁻¹)
1.0	7.05
1.5	7.84
2.0	**8.62**
2.5	7.05
3.0	7.05
3.5	5.48
4.0	4.23
4.5	2.82
5.0	2.82

Fig 4: Effect of variation of amount of semiconductor
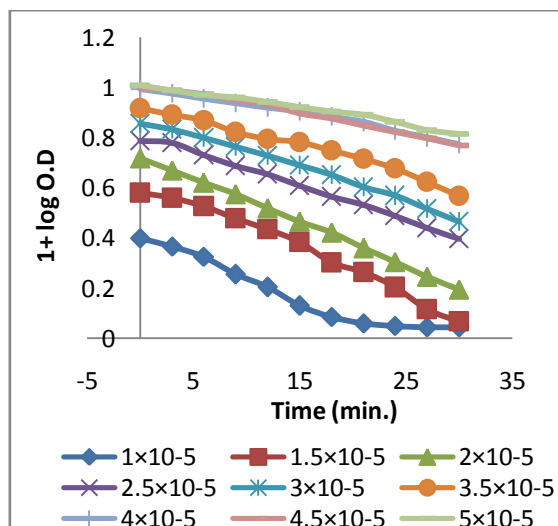
Fig 5: Effect of variation of Toluidine Blue concentration

D. Effect of dye concentration

The effect of dye concentration on degradation was studied by taking different concentration of Toluidine Blue. The resulting data are given in table 4 and figure 5 contains the graphical representation. The observations showed that with increase in concentration of dye, rate of reaction increased up to 2 x 10⁻⁵M. After this, increase in concentration decreased the rate of degradation because of dye molecules themselves started acting as a filter to the incident light. Thus the incident light was not able to cross the crowd of dye molecules and reach up to the photocatalyst at the base of the vessel; as a result the rate of reaction decreases.
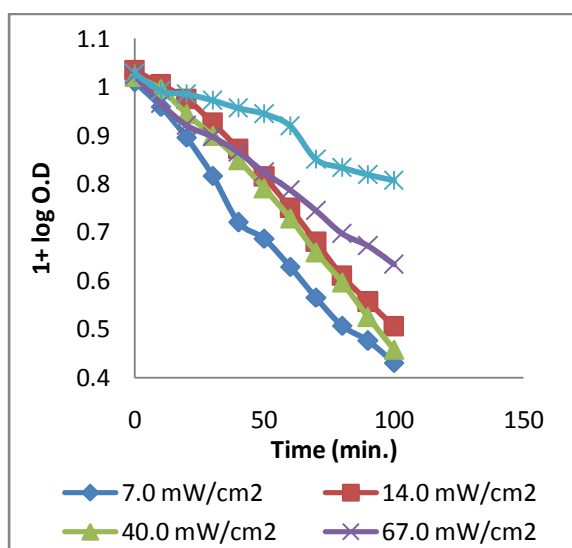
E. Effect of light intensity

Variations of light intensity was carried out and it was observed that rate of photocatalytic degradation increased with increase in light intensity. This fact can be explained by the fact that with increasing light intensity, number of photons increases that strike per unit area per unit time. Rate of photodegradation was observed maximum at light intensity 74.0 mW/cm² for Toluidine Blue dye. Higher light intensity may cause some thermal side reactions therefore were avoided. The data are given in table 5 and graphically represented in figure 6.

*Table 5: Effect of variation of light intensity*

pH= 8.0, Amount of catalyst = 0.14 g, [TB] = 2×10^{-5} M

Light intensity (mW/cm^2)	Rate constant × 10^4 (sec^{-1})
74.0	**8.63**
67.0	7.91
40.0	7.16
14.0	4.31
7.0	2.85

Fig 6: Effect of variation of light intensity

F. Scavenger test

Scavenger test in presence of light and photocatalyst both, was carried out to find out the role of active species and for interpretation of mechanism of degradation of dye. The degradation efficiency of the dye by different free radicals was studied with different scavengers, which is graphically reported in figure 7. It was evident from the data that addition of isopropyl alcohol (hydroxyl radical scavenger) ceased the reaction, confirming the role of hydroxyl radical as an active oxidizing species. A significant reduction in the rate of decomposition (70%) proved that the dye degradation is caused by the hydroxyl radical.
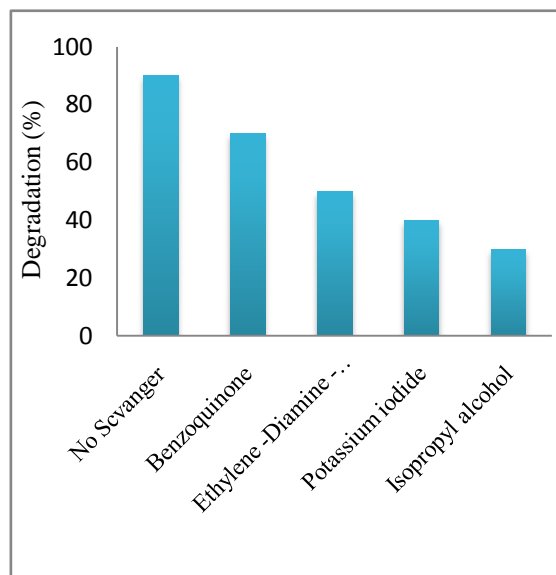
Fig 7: Effect of various scavengers on the degradation of Toluidine blue **(Concentration of BQ, EDTA, KI, IPA= 1 mmol l^{-1})**

IV. MECHANISM

A tentative mechanism of photoctalytic degradation of Toluidine Blue in presence of $ZrCdPbO_4$ catalyst and light both, may be proposed as:

(1) $TB^0 \xrightarrow{h\nu} TB^1$ (Singlet excited state)

$TB^1 \xrightarrow{ISC} TB^3$ (Triplet excited state)

(2) $ZrCdPbO_4 \rightarrow [e^- (CB) + h^+ (VB)]$

$h^+ + {}^-OH \rightarrow {}^\cdot OH$ (oxidation)

$H_2O + h^+ \rightarrow H^+ + {}^\cdot OH$

(3) ${}^\cdot OH + {}^3TB_1 \rightarrow$ Leuco TB
Leuco TB $\rightarrow$ Oxidized Products

Here hν is light photons, ISC is inter system crossing.

Toluidine Blue absorbs desired wavelength of light, gets excited in excited singlet state and by intersystem crossing singlet state get converted into its corresponding triplet state. Simultaeously electrons in $ZrCdPbO_4$ photocatalyst get excited in conduction band and holes are created in valence band. These generated electron hole pairs participate in redox reactions. The scavenger study suggests formation of OH$^\cdot$ free radical which is generated by abstraction of an electron form OH$^-$ ions by the holes generated at semiconductor surface. Hydroxyl free radicals oxidize the organic dye. A chain reaction starts by break down of conjugation resulting

in complete mineralization of dye molecules. The by-products of the reaction are NO_2, CO_2, H_2O etc.

V. CONCLUSION

It is concluded here by that the coloured pollutants are removed from water in heterogeneous photocatalytic degradation process by using solar energy and complete mineralization is observed. It is found that the photocatalytic process is the need of the hour due to following advantages over other processes:-

I. The reaction uses the conventional energy that is sun light. Thus non conventional sources are not exploited and therefore the process becomes eco-friendly.

II. The process removes contaminants from water thus making water useful for many other purposes like washing, cooling, irrigation etc.

III. The process is heterogeneous, thus no extra efforts are put in for separating the photocatalyst from the source.

IV. A chain reaction is initiated of degradation by $OH^{\bullet}$ free radical and so a smaller amount of semiconductor can remove a large amount of pollutant.

V. The medium is heterogeneous and so the semiconductor can be filtered, washed, treated and reused.

VI. The maximum degradation conditions can be extracted by varying different factors.

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