Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2023, 12 (1): 33-41

(International Peer Reviewed Journal)

Study on Photocatalytic Degradation of Crystal Violet from Water by Using Calcium Chromate–Zinc Oxide Composite

Sneha Paliwal* and Neetu Shorgar

Department of Chemistry, PAHER University, Udaipur-313003 (Raj.) **INDIA**

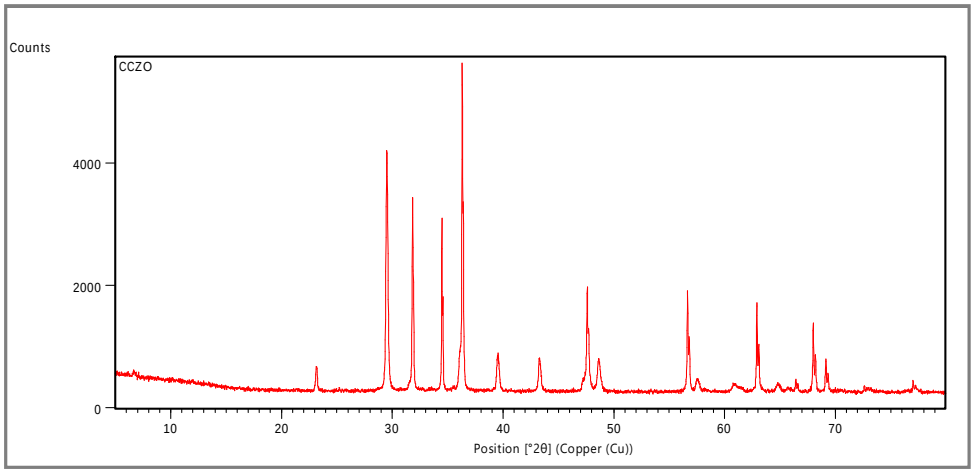
Email: snehaplw@gmail.com

Accepted on 16th January, 2023

ABSTRACT

Numerous photocatalysts have been used for the removal of various dyes from their aqueous solutions. Calcium chromate - zinc oxide composite was used as a photocatalyst for the degradation of crystal violet dye. Effect of different parameters that affect the rate of reaction, such as pH of dye solution, concentration of dye, amount of semiconductor and intensity of light were studied. A tentative mechanism for the photocatalytic degradation of dye has been proposed, where hydroxyl radical has been observed as an active oxidizing species.

Graphical Abstract:



XRD of calcium chromate-zinc oxide.

Keywords: Photocatalytic Degradation, Zinc Oxide, Calcium Chromate, Crystal Violet Dye.

INTRODUCTION

In today's world water pollution is a major problem, which caused in different aspects. Water is predominantly contaminated by dyes which are using in textile industries, paper industries, food industries etc. Human activities including industrialization and agricultural practices contributed

immensely in no small measure to the degradation and pollution of the environment which adversely has an effect on the water bodies that is a necessity for life. Water pollution is an environmental problem that is of major concern to the world at large researched by Owa [1]. Human contribution to water pollution is enormous by way of defecating; dumping of refuse, industrial wastes and washing of clothes etc.

Novel CuO/Ag_3PO_4 nanocomposites synthesized by co-precipitation method. Palpandi *et al*., [2] suggest that the CuO/Ag_3PO_4 has sphere like structure reveals strong absorption in visible region and it has exceedingly great photocatalytic activity for the photodegradation of amaranth under visible light irradiation. The photocatalytic pastime enhancement of CuO/Ag_3PO_4 is related to the efficient separation of electron hole pairs.

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. The photodegradation of crystal violet dye was investigated under UV and sunlight irradiations. Doping and excitation energy effects on photocatalytic efficiencies are discussed by Ameur *et al*., [3]. The photocatalytic degradation of fast green was studied by Jat *et al*., [4] under visible light using SnO_2-TiO_2.Thiscomposite was prepared by hydrothermal method using stannic chloride (hydrate) as precursor forSnO_2 quantum dots. It has more photocatalytic activity than titania nanopowder for degradation of fast green. Reduced grap hene oxide with a combination of copper sulphide (rGO-CuS composite) is used to remove crystal violet photo catalytically from waste water. The photocatalytic performance of rGO/CuS composite and CuS was evaluated by using a model system of crystal violet studied by Ruchi *et al*., [5].

Sahoo *et al*., [6] suggested the photocatalytic degradation of Crystal Violet, a triphenyl methane dye (also known as Basic Violet 3) in aqueous solutions was investigated with Ag^+ doped TiO_2 under UV and simulated solar light. The dye degradation using untreated TiO_2 and Ag^+ doped TiO_2 was compared. It was found that Ag^+ doped TiO_2 is slightly more efficient. Alkaim *et al*., [7] worked on titanium dioxide particles TiO_2 (Hombikat UV 100) doped with 0.5 % of Pt, Rh and Ru metals. They are prepared by photo deposition method. The adsorption and photocatalytic degradation of CV dye over bare TiO_2, Pt/TiO_2, Pd/TiO_2, Rh/TiO_2 and Ru/TiO_2, has been studied. The addition of Pd or Pt dramatically increases the adsorption and photocatalytic degradation of CV dye.

Jangid *et al*., [8] investigated the photocatalytic degradation of Evans blue under visible light in the presence of $SrCrO_4$ as a photocatalyst. Strontium chromate was synthesized by precipitation method in a wet chemical process. Results showed that strontium chromate has the highest catalytic activity in basic medium. The potential of calcinated and uncalcinated zinc oxide as an effective photocatalyst for the degradation of malachite green dye (MG) from aqueous medium using UV light studied by Maureen *et al*., [9]. Methyl orange dye has been successfully degraded in the presence of ZnO photocatalyst. The results obtained in the present study show the efficiency of AOP's in removing dyes, this process has proved its superiority to other conventional methods of wastewater treatment, in the presence of bio recalcitrant compounds proposed by Chowdhury *et al*., [10].

Reddy *et al*., [11] synthesized$ZnWO_4$ photocatalyst with the help of combustion method by taking $Zn(NO_3)_2$, Na_2WO_4. $2H_2O$ are taken as oxidant and glycine as fuel. The obtained phase pure monoclinic ZnWO4 photocatalyst was used to degrade Rhodamine-B under visible light irradiation. Isai *et al*., [12] synthesized ZnO and 2%Fe-ZnO nanomaterials by using a low-cost sol-gel method. 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 was studied.

Sivakumar *et al*., [13] synthesized ZnO for the photocatalytic degradation of textile dye under various experimental conditions through UV irradiation. The photocatalytic activity of graphene oxide (GO) and zinc oxide composite was explored by Gupta *et al*., [14]. The composites were prepared in

three different ratios: GO:ZnO (1:1), (1:2) and (2:1) by mechanochemical method (grinding) of the two components.Durmus *et al*., [15] synthesized graphene oxide/zinc oxide (GO/ZnO) nanocomposite by the decoration of thermally expanded and chemically oxidized graphite oxide nanosheets with zinc oxide (ZnO) nanoparticles synthesized via two-step sol-gel deposition method and used as an effective photocatalyst for degradation of basic fuchsin (BF) dye. Bhatt *et al*., [16] reported SnO_2 quantum dots/TiO_2 nanospheres composite frameworks are excellent candidates as photocatalyst due to their strong visible-light absorbing ability, high tunability, high specific surface areas and semi conductive properties. Herein, a visible-light driven SnO_2 quantum dots/TiO_2 nanospheres composite has been prepared by bottom-up approach.

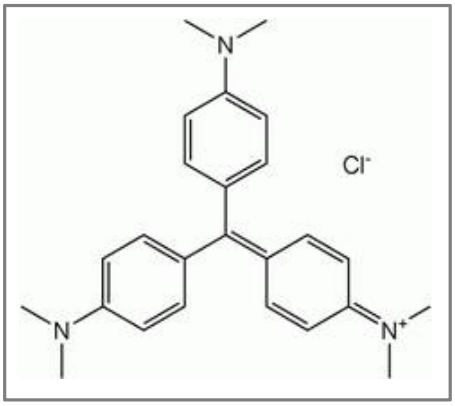


Figure 1. Structure of Crystal Violet.

MATERIALS AND METHODS

Synthesis of calcium chromate: Calcium chromate were synthesized by precipitation method and characterized by SEM-EDS techniques. First prepared a separate homogeneous solution of calcium chloride and sodium chromate in distilled water. After that mixed both solutions under stirring at room temperature. Both solutions react with each other and give pale yellow colour precipitation of calcium chromate. Then filtered it after 2-3 h and washed with distilled water 3-4 times. Dried at 80°C to 100°C.

Zinc oxide: Zinc oxide used from Fisher scientific laboratory grade.

Preparation of composite: Calcium 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 calcium chromate – zinc oxide

Element	Series	Norm. C (wt. %)	Atom. C (at. %)
Zinc	K-Series	56.00	28.39
Oxygen	K-Series	28.33	58.69
Calcium	K-Series	15.46	12.79
Chromium	K-Series	0.22	0.14
Total:		100.00	100.00

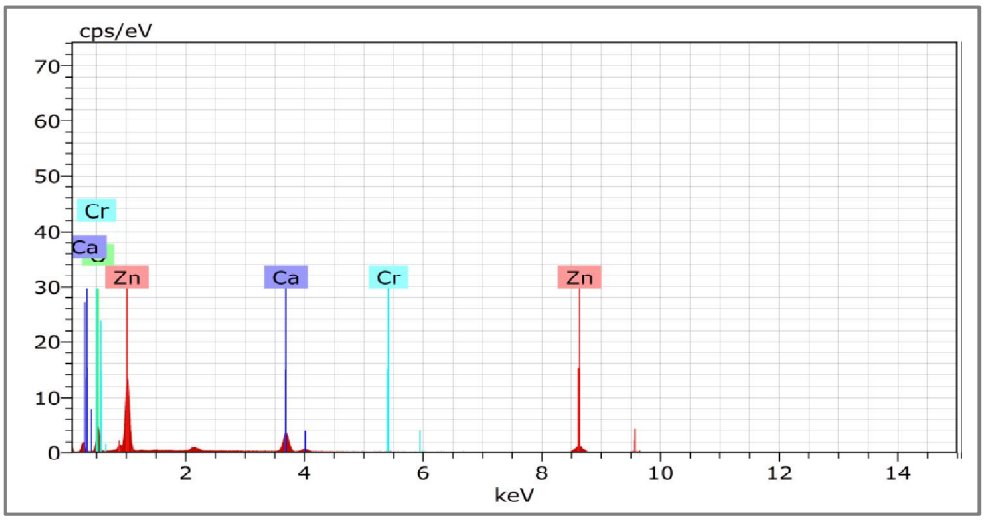


Figure 2. EDS of calcium chromate-zinc oxide.

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 (λ = 0.154060 nm) in the 2θ scanning ranges from 20° to 80° with a scan rate at 10^0 min^{-1}. The powder XRD pattern of as prepared calcium chromate – zinc oxide is given in figure 3.

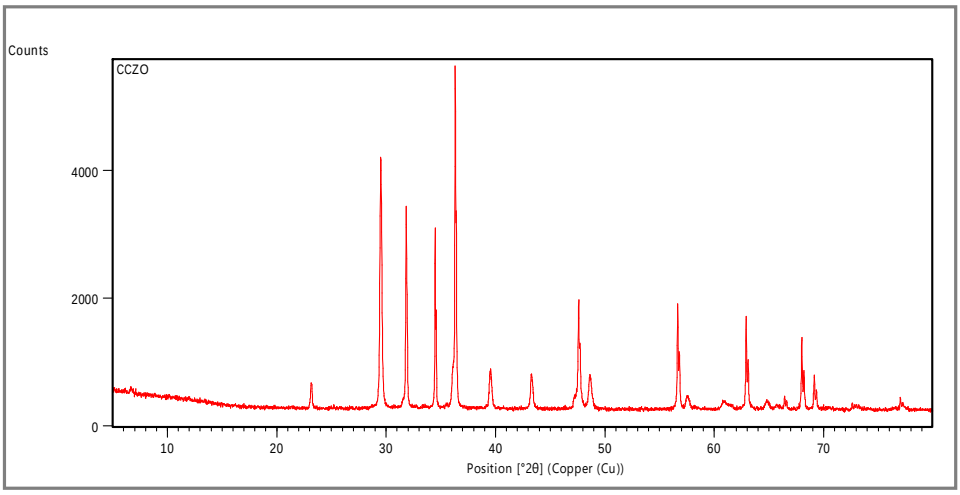


Figure 3. XRD of calcium chromate-zinc oxide.

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

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

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 x 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 0.10 gm photocatalyst was exposed to a 200 W tungsten lamp, and about 3 mL aliquot was taken out every 15 min. 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

$$\Psi = 100\frac{A-A_0}{A_0} \quad (2)$$

Here, A_0 is initial absorbance, and A is absorbance after degradation of dye at time t. A plot of 1 + logA 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:

$$k = 2.303 \times \text{slope} \quad \ldots(3)$$

Table 2. Typical runs for photocatalytic degradation of Crystal violet

pH = 8.5, Concentration [Crystal violet] =3.0 × 10^{-5} M, Composite = 0.10gm, Light intensity = 50.0 mWcm^{-2}, Rate constant = 6.10×10^{-5} Sec^{-1} (composite with 2-propanol) and 6.69×10^{-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	0.729	0.8627	0.723	0.8591
15	0.701	0.8457	0.706	0.8488
30	0.689	0.8382	0.687	0.8369
45	0.647	0.8109	0.649	0.8122
60	0.611	0.7860	0.621	0.7930
75	0.586	0.7678	0.592	0.7723
90	0.547	0.7379	0.546	0.7371
105	0.521	0.7168	0.499	0.6981
120	0.498	0.6972	0.457	0.6599
135	0.473	0.6748	0.429	0.6324
150	0.421	0.6242	0.396	0.5976
k Sec^{-1}	6.10×10^{-5}	--	6.69×10^{-5}	--

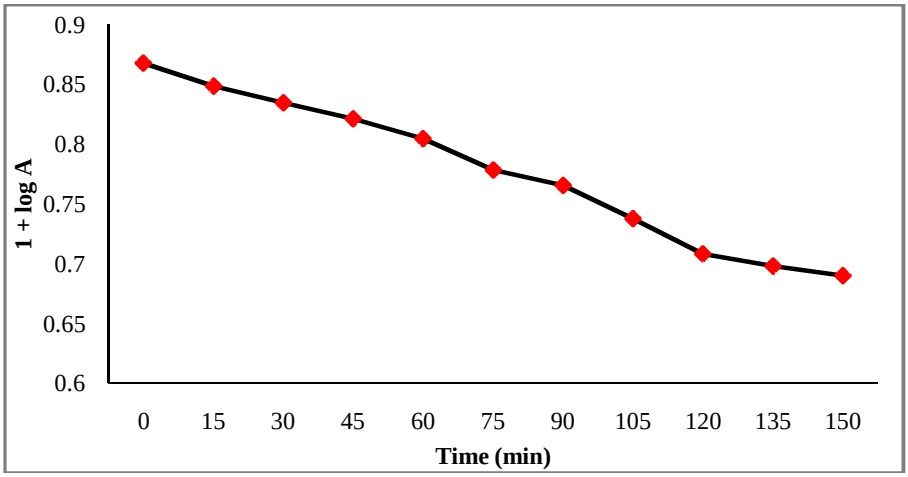
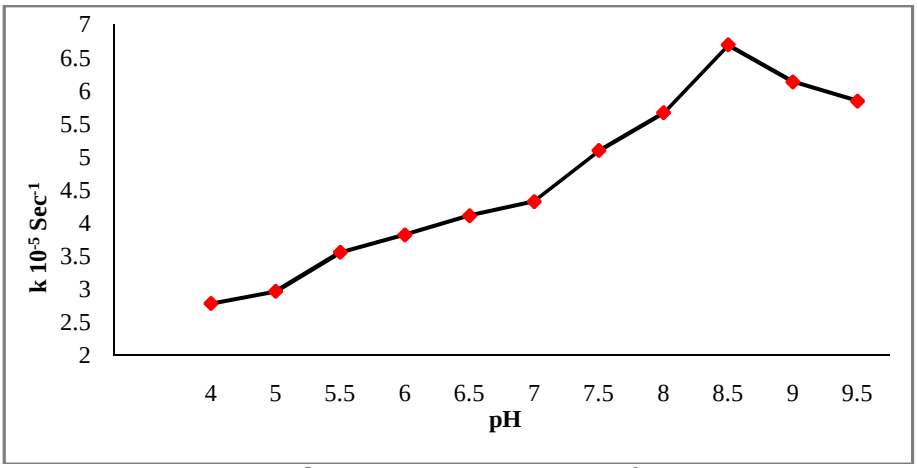


Figure 4. Typical run for photocatalytic degradation of crystal violet.

RESULTS AND DISCUSSION

Effect of parameters:

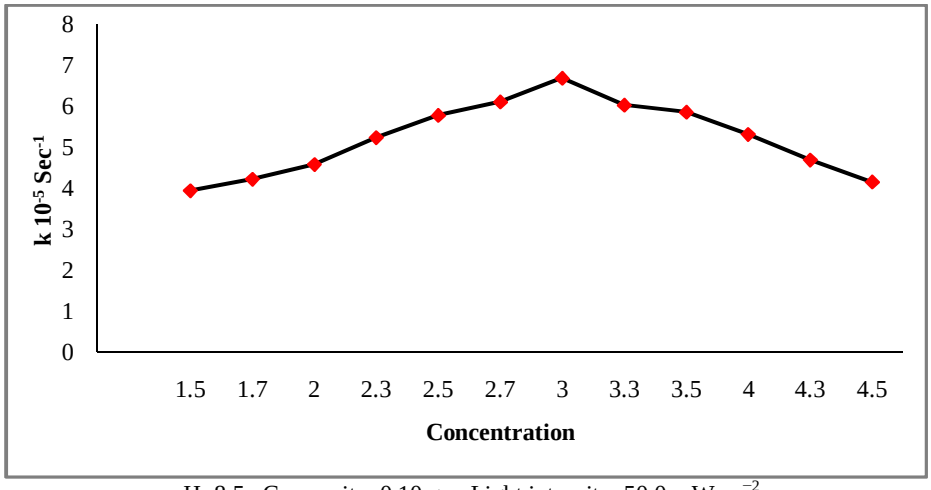
Effect of pH: The effect of variation of pH range 4.0 to 9.5 and all other parameters were kept to be identical. The results are given in figure 5. It was observed that with an increase in pH, the rate of reaction increases. At pH 8.5 rate of reaction was maximum. In this case, the presence of scavenger 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 calcium chromate–zinc oxide composite was active in basic range (6.5-9.5).



[Crystal violet]=3.0×10^{-5}M, Light intensity=50.0mWcm^{-2}, Composite=0.10gm,

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

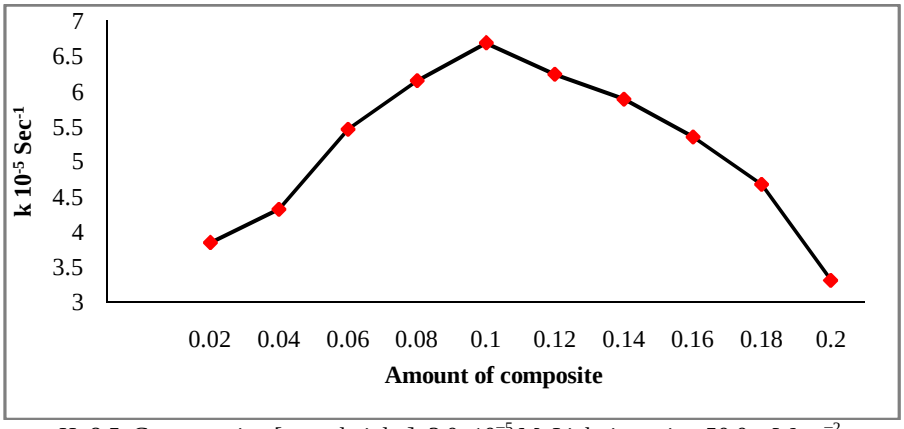
Effect of Concentration of Dye Solution: The effect of concentration variation of crystal violet dye on its rate of degradation has been observed in the range from 1.5×10^{-5} M to 4.5×10^{-5} M and keeping all parameters to be the same. The results are given in figure 6. It has been observed that the rate of degradation increases with increasing concentration of dye up to 3.0×10^{-5} M. Further increase in concentration above 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.



pH=8.5, Composite=0.10 gm, Light intensity=50.0 mWcm^{-2}

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

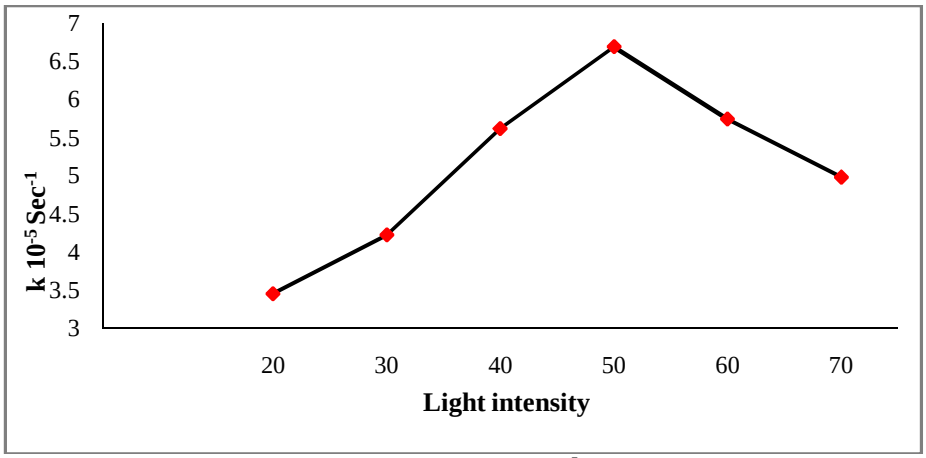
Effect of Amount of Photocatalyst: The amount of semiconductor may also affect the rate of degradation of dye and hence, different amounts of semiconductor were taken. The results are the results are reported in figure 7. It was observed that there was an increase in the rate of photocatalytic degradation with an increase in the amount of semiconductor up to 0.10 g, but after the amount 0.10 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.



pH=8.5, Concentration [crystal violet]=3.0×10^{-5} M, Light intensity=50.0 mWcm^{-2}

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

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 figure 8. The results showed that with increasing light intensity, the rate of reaction increases and maximum rates were found at 50.0 mWcm^{-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 50.0 mWcm^{-2}, there was a little decrease in the rate. This may be due to some thermal reactions.



pH=8.5, Concentration [crystal violet]=3.0×10^{-5} M, Composite=0.10 gm

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 calcium 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 calcium 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.

$$^1CV_0 \xrightarrow{h\nu} {}^1CV_1 \quad \ldots(3)$$

$$^1CV_0 \xrightarrow{ISC} {}^3CV_1 \quad \ldots(4)$$

$$\text{Composite} \rightarrow e^-(CB) + h^+(VB) \text{ or } SC^* \quad \ldots(5)$$

$$H^+ + {}^-OH \rightarrow {}^{\bullet}OH \quad \ldots(6)$$

$$^3CV_1 + {}^{\bullet}OH \rightarrow \text{Leuco CV} \rightarrow \text{Product} \quad \ldots(7)$$

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.

APPLICATION

This study is very useful for removal of pollutants from industrial wastewater such as dye industries, pharma industries, paper industries etc.

CONCLUSION

Calcium chromate photocatalyst was synthesized by precipitation method. Calcium chromate-zinc oxide composite prepared by mechanical method further characterized to know its morphology. This composite was used for photocatalytic degradation of crystal violet dye. The experimental results showed that photocatalytic degradation efficiency of crystal violet 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.

REFERENCES

1. S. Poovaragan, R. Sundaram, C. M. Magdalane, K. Kaviyarasu, M. Maaza, Photocatalytic F. D. Owa, Water pollution: sources, effects, control and management, *Mediterr. J. Soc. Sci.*, **2013**, 4(8), 65-65.
2. K. Palpandi, K. Eswaran, B. Kavitha, Novel sphere CuO/Ag_3PO_4 nanocomposites with enhanced visible lightphotocatalytic activity for degradation of amaranth, *J. Applicable Chem.*, **2020**, 9(2), 229-239.
3. S. B. Ameur, H. BelHadjltaief, B. Duponchel, G. Leroy, M. Amlouk, H. Guermazi and S. Guermazi, Enhanced photocatalytic activity against crystal violet dye of Co and In doped ZnO thin films grown on PEI flexible substrate under UV and sunlight irradiations, *Heliyon*, **2019**, 5(6), e01912.

4. K. K. Jat, J. Bhatt, S. C. Ameta, Photodegradation of fast green by using SnO_2 quantum Dots/ TiO_2 nanoparticles composite, *J. Applicable Chem.*, **2019**, 8(1), 139-145.
5. Ruchi, A. K. Rai, M. Gupta, R. Ameta, S. C. Ameta, Reduced graphene oxide/CuS nano-composite: an efficient photocatalyst for degradation of crystal violet, *J. Nanosci. Tech.*, **2019**, 5(2), 673-675.
6. C. Sahoo, A. K. Gupta, A. Pal, Photocatalytic degradation of crystal violet (C.I. basic violet 3) on silver ion doped TiO_2, *Dyes Pigm.*, **2005**, 66(3), 189-196.
7. A. F. Alkaim, M. B. Alqaraguly, Adsorption and photocatalytic degradation of crystal violet dye in the presence of different metals doping on TiO_2, *J. Appl. Chem.*, **2013**, 2(2), 291-303.
8. M. Jangid, S. C. Ameta, A. Sharma, Photodegradation study of evan's blue in presence of strontium chromate, *J. Applicable Chem.*, **2018**, 7(5), 1291-1299.
9. C. O. O. Maureen, O. J. Nnaemeka, A. N. Basil, O. E. Emeka, Photocatalytic degradation of a basic dye using zinc oxide nanocatalyst, *Int. lett. chem. phys. astron.*, **2018**, 81, 18-26.
10. M. I. H. Chowdhury, M. S. Hossain, M. A. S. Azad, M. Z. Islam, M. A. Dewan, Photocatalytic degradation of methyl orange under UV using ZnO as catalyst, Int. *J. Sci. Eng. Res.*, **2018**, 9(6), 1646-1649.
11. M. R. Reddy, J. Suresh, G. Ravi, Factors effecting visible light photocatalytic degradation of rhodamine-B using $ZnWO_4$ synthesized by combustion method, *J. Applicable Chem.*, **2018**, 7(3), 695-701.
12. K. A. Isai and V. S. Shrivastava, Photocatalytic degradation of methylene blue using ZnO and 2% Fe-ZnO semiconductor nanomaterials synthesized by sol-gel method: a comparative study, *J. Water Environ. Nanotechnol.*, **2019**, 4(3), 251-262.
13. K. K. Sivakumar, M. H. Basha, Nandhini, ZnO/UV induced photocatalytic degradation of textile dye, *Res. J. Chem. Environ.*, **2021**, 25(5), 160-165.
14. M. Gupta, J. Bhatt, Ruchi, R. Ameta, S. C. Ameta, Use of graphene oxide-zinc oxide composite in photocatalytic degradation of victoria blue B, *J. Nanosci. Tech.*, **2019**, 5(2), 702-705.
15. Z. Durmus, B. Z. A. Kurt, Durmus, Synthesis and characterization of graphene oxide/zinc oxide (GO/ZnO) nanocomposite and its utilization for photocatalytic degradation of basic fuchsin dye, *Chemistry Select*, **2019**, 4(1), 271-278.
16. J. Bhatt, S. Benjamin, R. Ameta, S. C. Ameta, Enhancement of photodegradation of picric acid (2,4,6-Trinitrophenol) by fabrication of visible-light-active SnO_2 quantum dots/TiO_2 nanospheres composite, *J. Applicable Chem.*, **2019**, 8(4), 1805-1812.