Use of Undoped and Carbon-Doped Calcium Molybdate for degradation of basic Fuchsin: A Green Chemical Route

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Abstract

Calcium molybdate (undoped and carbon-doped) has been used as photocatalyst for the degradation of basic fuchsin. Calcium molybdate is a ternary photocatalyst. The reaction was monitored spectrophotometrically.

The effect of various operating parameters on rate of degradation was observed such as pH, concentration of dye, amount of semiconductor and light intensity. Optimum conditions were: pH = 9.0, concentration of basic fuchsin = 4.00 × 10^{-4} M, amount of $CaMoO_4$ = 0.08 g and light intensity = 50.0 mWcm^{-2}. A tentative mechanism for the photocatalytic degradation of basic fuchsin has been proposed which involves hydroxyl radicals as the oxidant. 2% C-doped was found to show better photocatalytic performance than undoped, 1 and 3% C-doped samples.

Keywords: $CaMoO_4$, Photocatalytic activity, Basic fuchsin, Degradation, Hydroxyl radical, Oxidation.

Introduction

Basic fuchsin is a fluorescent dye which contains a mixture of rosaniline, pararosaniline, magenta II and new fuchsine. It is used for the detection of acid-fast bacilli and is quite common in the Ziehl Neelsen staining technique. It also stains mucopolysaccharides and glycoproteins and also tracks proteins in acidic pH systems. Alkaline fuchsin solution is used in propylene glycol in the diagnosis of dental caries. Its side effects are irritation in eyes.

Ning et al[1] prepared Fe_3O_4/SiO_2 core-shell nanoparticles via co-precipitation and sol-gel methods. Then this catalyst was used for degradation of basic fuchsin in wastewater by H_2O_2. It was found that coating of SiO_2 on Fe_3O_4 nanoparticles could stabilize the Fe_3O_4 in aqueous solution dramatically. It was reported that almost complete degradation could be achieved within 5 min. These Fe_3O_4/SiO_2 core-shell nanoparticles were stable and also exhibited excellent recyclability even after repeated use.

Wang et al[2] synthesized 3D hierarchically porous perovskites $LaFe_{0.5}M_{0.5}O_3$-CA (M = Mn, Cu) in a two-step method. They used polymethylmethacrylate (PMMA) as template and supporting with carbon aerogel. As-prepared composites were used in microwave catalytic degradation of fuchsin basic in wastewater. It was reported that the catalytic degradation of dye could be remarkably improved by coating with CA. The dye removal fitted well with pseudo-first order model and the degradation rate constants were found to increase with initial pH value while it decreases with initial basic fuchsin concentration. All the catalysts presented can be recycled and are stable in repeated use. Radical scavenger studies indicated that hydroxyl radicals played important role in the catalytic degradation.

Taamallah et al[3] investigated effects of several operating parameters on the efficiency of ultrasonic process such as initial concentration of dye, ultrasonic power and temperature. Experiments were also conducted in the presence of tert-butyl alcohol (radical scavenger). It was reported that initial degradation rate was increased by a factor of 2.8 when the power was increased from 30 to 90 W. The presence of salts has practically no significant effect on the efficiency of removal of dye. It was confirmed that hydroxyl radical was the main active species involved in the degradation of this compound. Huang et al[4] prepared a visible light active photocatalyst of S-doped graphene quantum dots (S-GQDs) via a facile hydrothermal synthesis. They used 1, 3, 6-trinitropyrene and Na_2S as precursors. An excellent photocatalytic performance of S-GQDs was observed for degradation of basic fuchsin under visible light irradiation.

Lan et al[5] studied removal of basic fuchsin from aqueous solutions using ultrasound. The effects of different operating parameters such as ultrasound power (200 W–500 W), initial pH (3–6.5) and temperature (15 - 60°C) were evaluated on the ultrasonic degradation. The degradation of basic fuchsin was found to obey pseudo-first order reaction kinetics. It was reported that 84.1% extent of degradation could be achieved at initial dye concentration 10 μmol L^{-1}, ultrasound power 400 W, ultrasound frequency 25 kHz, dosage of Fe(II) 4 mg L^{-1}, initial pH 6.5 and temperature 22°C. The rate of degradation of fuchsin basic was significant on addition of radical scavenger.

The g-C_3N_4/Ag_3VO_4 hybrid photocatalysts were prepared by Wang et al[6] via by anchoring Ag_3VO_4 on the surface of g-C_3N_4. It was reported as Ag_3VO_4 nanoparticles were well distributed on the surface of g-C_3N_4 and g-C_3N_4/Ag_3VO_4 heterojunctions were formed. As-prepared g-C_3N_4/Ag_3VO_4 hybrid materials exhibited much higher photocatalytic activity for basic fuchsin as compared to g-

C_3N_4 and Ag_3VO_4 optimal rate constant was found to be 0.92 h^{-1} which was almost 11.5 and 6.6 times higher as compared to pure g-C_3N_4 and Ag_3VO_4 respectively. It was found that h^+ and $O_2^{\bullet-}$ were generated in the photocatalytic process and these played a key role in degradation of basic fuchsin.

A high-performance photocatalyst of AgBr–Ag_3PO_4/MWCNTs was fabricated by Wang et al[7] chemical precipitation method. They used hexadecyltrimethyl ammonium bromide $(NH_4)_2HPO_4$ and $AgNO_3$ in the presence of MWCNTs. The photocatalytic activity of the photocatalyst was evaluated by decomposing mixed dye of basic fuchsin and basic red 9. It was reported that about 99% decolorization and 47% mineralization could be achieved under visible light irradiation in 10 min. $H_4SiW_6Mo_6O_{40}/SiO_2$ was sensitized by H_2O_2 solution by Yu et al[8] and catalytic activity improved significantly. Degradation of basic fuchsin was taken as a model pollutant to evaluate influencing factors on the photodegradation reaction.

The optimal conditions achieved were: Initial concentration of basic fuchsin 8 mg L^{-1}, pH 2.5, catalyst dosage 4 gL^{-1} and light irradiation time 4 h. The degradation rate of basic fuchsin was 98% under optimum conditions. The catalyst maintained its photocatalytic activity for degradation of dye even after four cycles.

Kurt et al[9] prepared graphene nanosheets and then these were successfully decorated with platinum (Pt) and palladium (Pd) nanoparticles. It was revealed that the graphene-metal nanocomposites exhibited higher free radical scavenging activity. It was also reported that the graphene-metal nanocomposites could be successfully used for the photocatalytic removal of fuchsin and indigo carmine in presence of light. The photocatalytic degradation of two cationic triarylmethane dyes (crystal violet and basic fuchsin) was examined by Li et al[10] in aqueous TiO_2 suspensions under visible light irradiation.

Material and Methods

Chemicals used: Basic fuchsin (Himedia), ammonium molybdate (Thermo Fischer), calcium chloride (Merck) and glucose (Thermo Fischer) were used in present investigations. Double distilled water was used to make solutions throughout the experiment.

Preparation of photocatalysts: Pure and 1, 2 and 3% carbon-doped calcium molybdate were prepared via hydrothermal methodas reported earlier.[11]

Photocatalytic degradation: Some control experiments were also carried out. 2.5 mL of dye solution (1.10 x 10^{-3}) was taken in volumetric flask of 100 mL capacity. The solution was diluted with distilled water so that the concentration of dye solution became 1.0 x 10^{-4} M. The solution was divided into four equal parts:

- In the first beaker, only dye solution was taken and kept in the dark.
- In the second beaker, only dye solution was taken and exposed to the light.
- In the third beaker, 0.10 g undoped calcium molybdate or C-doped (1, 2 or 3%) calcium molybdate (photocatalyst) was added to the dye solution and kept in dark.
- In the fourth beaker, 0.10 g undoped calcium molybdate or C-doped (1, 2 or 3%) calcium molybdate (photocatalyst) was added to the dye solution and exposed to the light.

After 3-4 hours, the absorbance of the solution in each beaker was measured with the help of a spectrophotometer. It was observed the solutions of the first three beakers (in each case) had the same absorbance as its initial absorbance while absorbance of reaction mixture in fourth beaker (for each case) had significant decrease in absorbance as compared to its initial value. This indicates that undoped calcium molybdate or C-doped (1, 2 and 3%) calcium molybdate and light both are necessary for degrading basic fuchsin. Hence, this was concluded that the reaction is photocatalytic in nature and not chemical and photochemical.

Results and Discussion

Characterization

Field Emission Scanning Electron Microscopy (FESEM): The morphology of the particles was examined using Field Emission Scanning Electron Microscope (Nova NanoSEM, model) operated at a voltage of 15 kV. The microstructural characterization of undoped $CaMoO_4$ and C-doped 3% $CaMoO_4$ was carried out via field emission scanning electron microscopy. The FESEM images of the undoped $CaMoO_4$ and C-doped (3%) $CaMoO_4$ (glucose was used as C source) are presented in fig. 1.

Energy Dispersive X-Ray Analysis (EDX): EDX analysis was performed to study the chemical composition of the samples. EDX spectra of undoped $CaMoO_4$ and C-doped (3%) $CaMoO_4$ are presented in figs. 2 and 3 respectively. An estimation of carbon content in C-doped $CaMoO_4$ was also obtained from EDX measurements. It is clear from these figures that undoped $CaMoO_4$ contains only Ca, Mo and O and no other impurity was present there. Hence, it is pure $CaMoO_4$. EDX of C-doped (3%) $CaMoO_4$ showed a peak of carbon confirming the doping of carbon.

X-Ray Diffraction Analysis (XRD): XRD of as-prepared $CaMoO_4$ composite was recorded by the X-ray diffractometer (XRD) (P analytical X Pert Pro) using CuKα radiation (λ = 1.54060 nm) in the 2θ scanning ranges from 20° to 80° with a scan rate at 10° min^{-1}. The applied voltage and current were 40 KV and 40 mA respectively. The powder XRD pattern of As-prepared $CaMoO_4$ composite and C-doped $CaMoO_4$ (3%) are given in figs. 4 and 5 respectively.

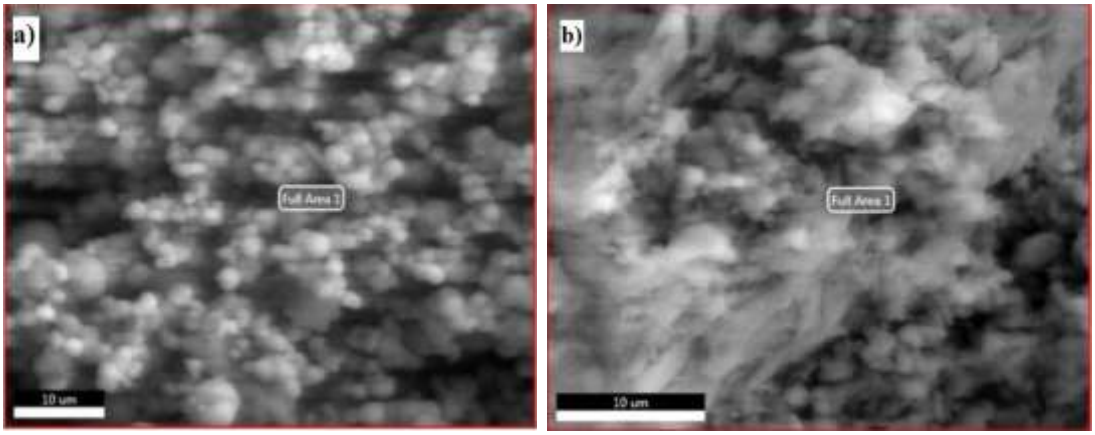

Fig. 1: FE-SEM Images of (a) Undoped $CaMoO_4$ (b) 3% C-doped $CaMoO_4$

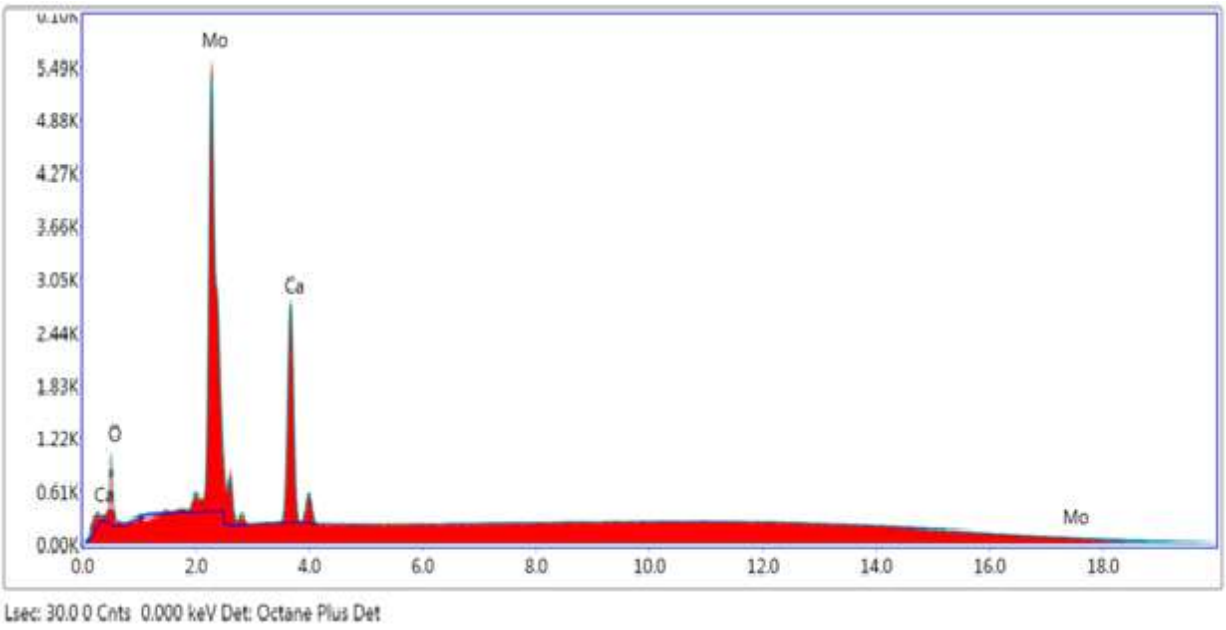

Fig. 2: EDX of Undoped $CaMoO_4$

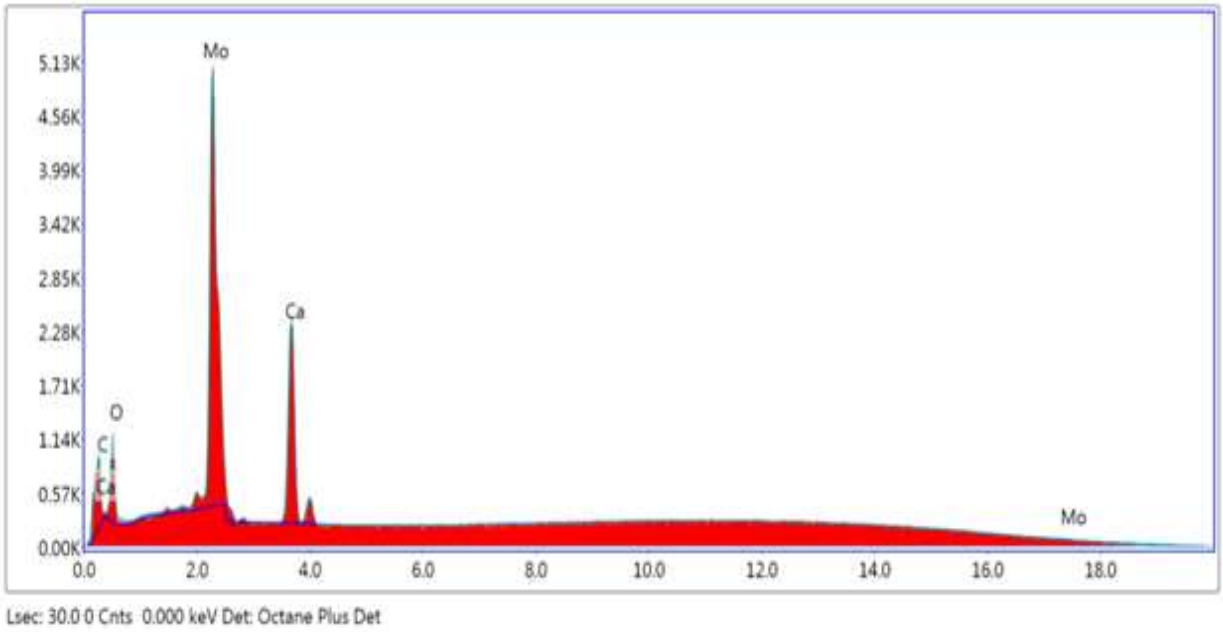

Fig. 3: EDX of 3% C-doped $CaMoO_4$

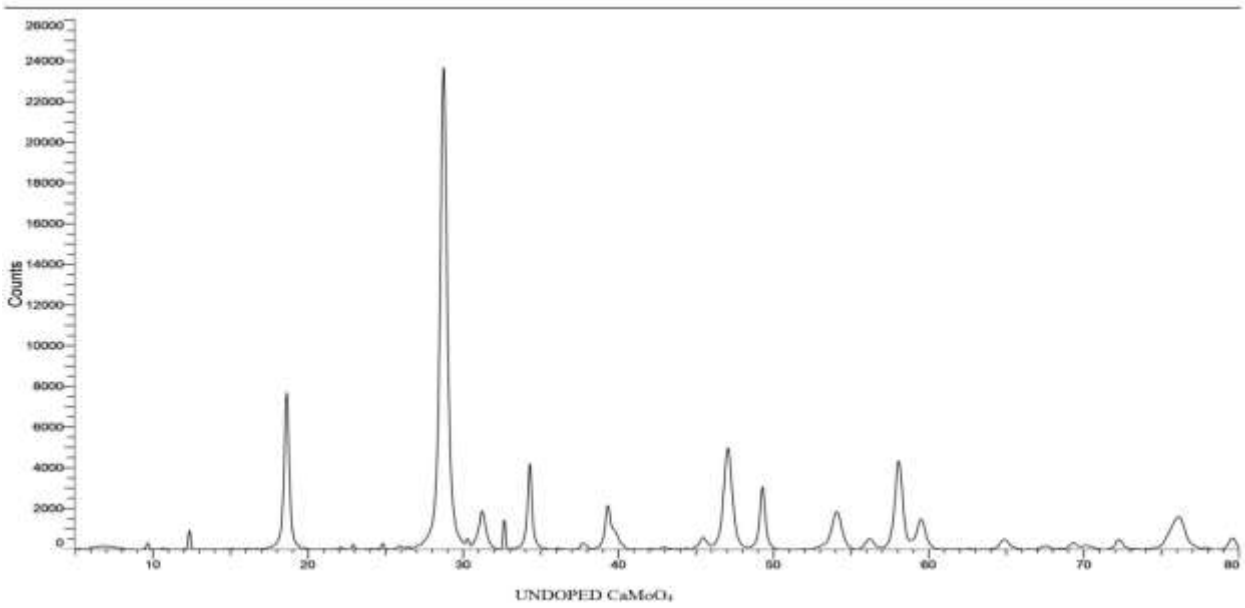

Fig. 4: XRD of Undoped $CaMoO_4$

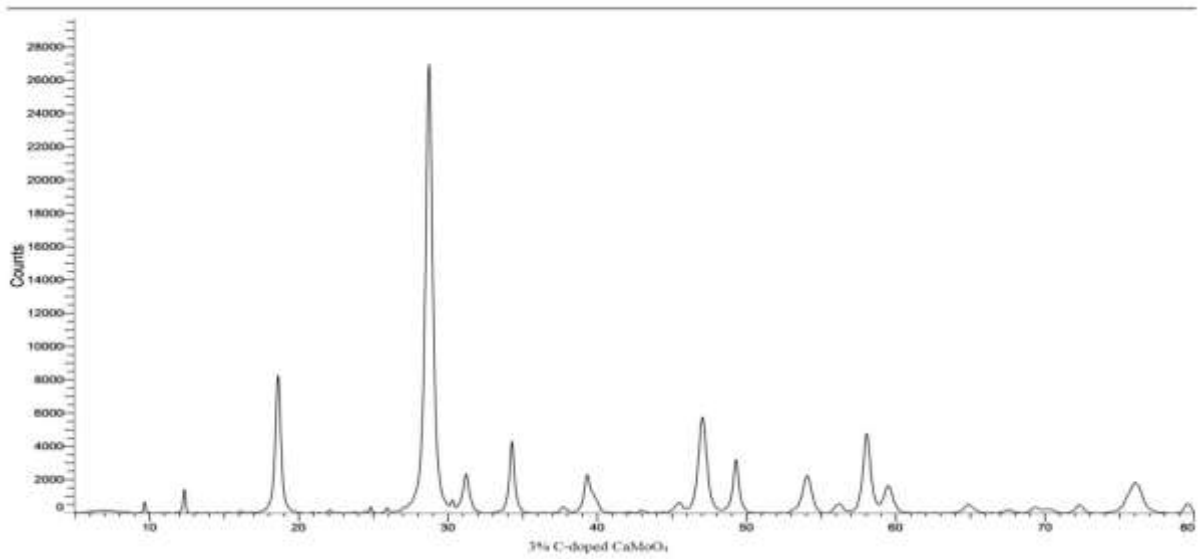

Fig. 5: XRD of 3% C-doped $CaMoO_4$

Experimental: 0.0338 g of basic fuchsin was dissolved in 100.0 mL of doubly distilled water so that the concentration of stock solution of dye was 1.0 x 10^{-3} M. This solution was further diluted as and when required. 50 mL dye solution of 4.00×10^{-4} M concentration was taken in a beaker. The pH of this solution was adjusted to 9.0 and 0.08 g of catalyst. Undoped, 1, 2 or 3% C-doped $CaMoO_4$ were added in it separately. Now, this reaction mixture was exposed to a 200 W tungsten lamp. A water filter was used to cut off thermal radiations. An aliquot of 3 mL was taken out from the reaction mixture at regular time intervals and its absorbance (A) was observed at 545 nm.

It was found that the absorbance decreases with increasing time of exposure. A plot of 1 + log A versus time was found to be linear which shows that the reaction follows pseudo-first order kinetics. The rate constant was calculated by the rate expression.

$$k = 2.303 \times \text{slope} \quad (1)$$

The same procedure was followed using catalyst C-doped $CaMoO_4$. The results of typical runs for photocatalytic degradation of basic fuchsin using undoped, 1, 2 and 3% C-doped $CaMoO_4$ are represented in table 1 and graphically presented in fig. 6.

Effect of pH: The effect of pH on the rate of degradation was observed in pH range 7.5–10.5 for undoped 1, 2 and 3% C-doped $CaMoO_4$, keeping all other parameters identical. The results are summarized in table 2. It was observed that rate of reaction also increases on increasing pH. After

reaching a maximum value at pH 9.0, rate decreases with a further increase in pH. In this case, the presence of scavenger (2-propanol) affected the rate of reaction adversely and hence, it may be concluded that •OH radicals are participating in the degradation as active oxidizing species.

Effect of dye concentration: The effect of variation of concentration of basic fuchsin rate has been observed in the range from 3.2×10^{-4} to 4.6×10^{-4} M for undoped 1, 2 and 3% C-doped $CaMoO_4$ keeping all other parameters same. The results are reported in table 3. It has been observed that the rate of degradation increases with increasing concentration of dye up to 4.00×10^{-4} M for undoped, 1, 2 and 3% C-doped $CaMoO_4$.

Further increase in concentration beyond this limit resulted in a decrease in degradation rate. This may be explained on the basis that on increasing the concentration of dye, the rate of reaction increases as more molecules of dyes were available for excitation and energy transfer but on increasing concentration of dye further, the rate of reaction decreases.

This may be explained on the basis that after reaching an optimum concentration, the dye may start acting as an internal filter itself and it will not permit the desired light intensity to reach the surface of the photocatalyst and as a result, the rate of photocatalytic degradation decreases.

Table 1
Typical runs

[Basic fuchsin] = 4.00×10^{-4} M **Amount of photocatalyst = 0.08 g**
pH = 9.0 **Light intensity = 50.0 mWcm^{-2}**

Time (min)	$CaMoO_4$		1% C-Doped $CaMoO_4$		2% C-Doped $CaMoO_4$		3% C-Doped $CaMoO_4$	
	Absorbance (A)	1+log A	Absorbance (A)	1+log A	Absorbance (A)	1+log A	Absorbance (A)	1+log A
0	0.537	0.7300	0.413	0.6160	0.501	0.6998	0.450	0.6532
5	0.501	0.6998	0.355	0.5502	0.380	0.5798	0.417	0.6201
10	0.473	0.6749	0.302	0.4800	0.288	0.4594	0.390	0.5911
15	0.450	0.6532	0.257	0.4099	0.240	0.3802	0.371	0.5694
20	0.426	0.6294	0.209	0.3201	0.177	0.2480	0.345	0.5378
25	0.417	0.6201	0.178	0.2504	0.141	0.1492	0.316	0.4997
30	0.398	0.5999	0.155	0.1903	0.107	0.0294	0.298	0.4742

Rate constant (k) for:
Undoped $CaMoO_4$ = 1.71 x 10^{-4} sec^{-1}
1% C-Doped $CaMoO_4$ = 5.46 x 10^{-4} sec^{-1}
2% C-Doped $CaMoO_4$ = 8.53 x 10^{-4} sec^{-1}
3% C-Doped $CaMoO_4$ = 2.37 x $10^{-4}$$sec^{-1}$

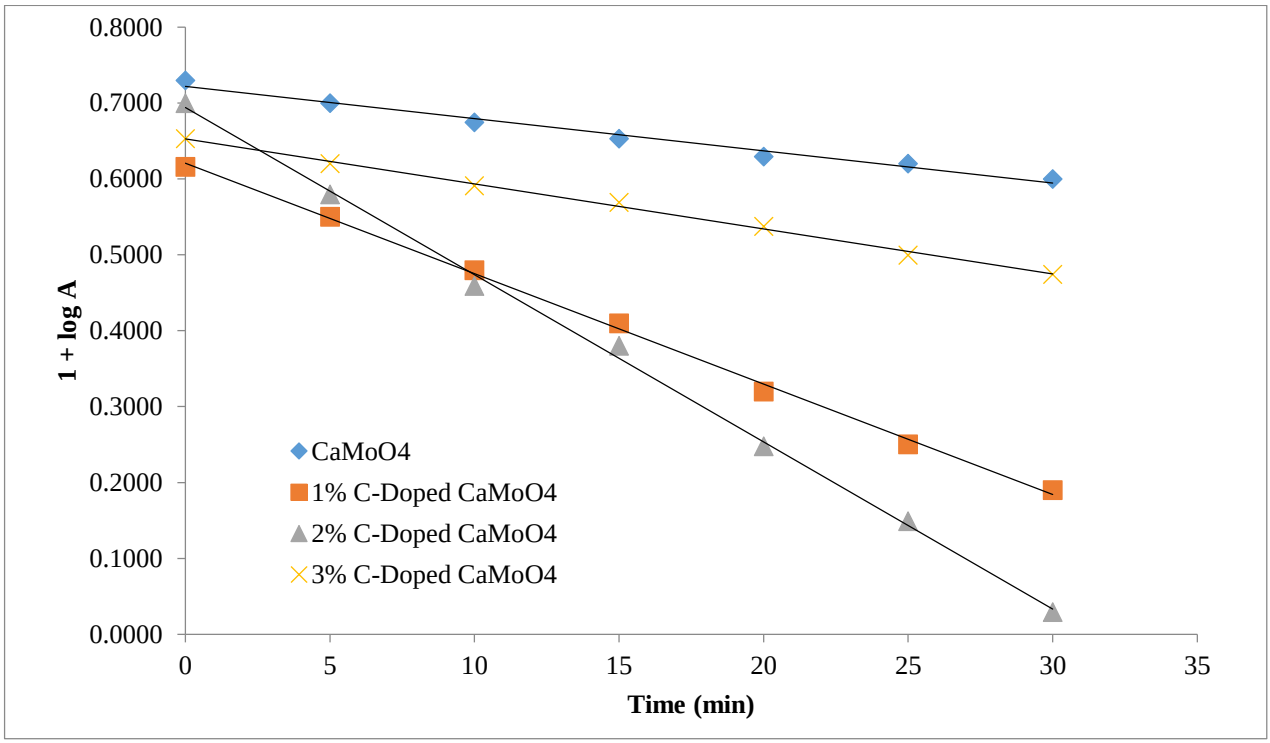

Fig. 6: Typical runs

Table 2
Effect of pH

[Basic fuchsin] = 4.00 × 10^{-4} M **Light intensity = 50.0 mWcm^{-2}**
Amount of photocatalyst = 0.08 g

pH	$CaMoO_4$	1% C-doped $CaMoO_4$	2% C-doped $CaMoO_4$	3% C-doped $CaMoO_4$
	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})
7.5	0.47	2.98	6.01	0.76
8.0	0.84	3.81	6.94	1.03
8.5	1.33	4.99	7.87	1.88
9.0	1.71	5.46	8.53	2.37
9.5	1.14	4.98	7.66	1.88
10	0.82	3.45	6.02	1.02
10.5	0.47	2.88	5.11	0.66

Table 3
Effect of dye concentration

pH = 9.0 **Light intensity = 50.0 mWcm^{-2}**
Amount of photocatalyst = 0.08 g

[Basic Fuchsin] × 10^4 M	$CaMoO_4$	1% C-doped $CaMoO_4$	2% C-doped $CaMoO_4$	3% C-doped $CaMoO_4$
	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})
3.2	0.65	2.90	5.22	0.88
3.4	0.81	3.38	6.03	1.07
3.6	1.03	4.27	7.12	1.65
3.8	1.40	5.11	8.04	2.01
4.0	1.71	5.46	8.53	2.37
4.2	1.34	5.07	8.10	2.06
4.4	1.02	4.39	7.31	1.45
4.6	0.78	3.96	6.44	0.98

Table 4
Effect of amount of photocatalyst

pH = 9.0 **Light intensity = 50.0 mWcm^{-2}**
[Basic fuchsin] = 4.00 × 10^{-4} M

Photocatalyst (g)	$CaMoO_4$	1% C-doped $CaMoO_4$	2% C-doped $CaMoO_4$	3% C-doped $CaMoO_4$
	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})	Rate constant (k) × 10^4 (sec^{-1})
0.04	0.99	3.16	6.04	1.04
0.06	1.06	4.80	7.44	1.89
0.08	1.71	5.46	8.53	2.37
0.10	1.70	5.45	8.54	2.37
0.11	1.71	5.46	8.53	2.36
0.12	1.72	5.47	8.52	2.37
0.13	1.71	5.46	8.53	2.38
0.14	1.71	5.46	8.53	2.37

Effect of amount of photocatalyst: The effect of variation of the amount of photocatalyst on the rate of dye degradation has been observed in the range from 0.04 to 0.14 g and the results are summarized in table 4. It was observed that the rate of degradation increases on increasing the amount of photocatalyst, but up to a certain amount of photocatalyst (0.08 g) for undoped and 1, 2 and 3% C-doped $CaMoO_4$. But after this point, the rate of reaction becomes virtually constant and it shows saturation behavior. This may be explained on the basis that as the amount of photocatalyst was increased, the exposed surface area of photocatalyst will also increase. As a result, the rise in the rate of reaction has been observed, but with further increasing the amount of photocatalyst, only the thickness of the layer will increase

(and not the exposed surface area) and hence, a saturation like behavior was observed.

Effect of light intensity: The effect of light intensity on the rate of degradation of dye was also investigated by changing the intensity of light from 30.0 to 80.0 mWcm^{-2}. The observations are presented in table 5. The data indicated that the rate of reaction increases with increasing light intensity and maximum rate was found at 50.0 mW cm^{-2} for undoped, 1, 2 and 3% C- doped $CaMoO_4$. It may be due to the fact that as the light intensity was increased, the number of photons striking per unit time per unit area of photocatalyst will also increase resulting in higher rate of degradation. Further increase in the light intensity may initiate some side thermal reactions and therefore, higher intensities of light have been avoided.

On the basis of experimental observations, a tentative mechanism has been proposed for photocatalytic degradation of basic fuchsin.

$$^1BF_0 \xrightarrow{h\nu} {}^1BF_1 \quad (2)$$

$$^1BF_1 \xrightarrow{ISC} {}^3BF_1 \quad (3)$$

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

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (5)$$

$$^{\bullet}OH + {}^3BF_1 \rightarrow \text{Leuco-BF} \quad (6)$$

$$\text{Leuco-BF} \rightarrow \text{Products} \quad (7)$$

where BF = Basic duchsin and SC = Undoped, 1, 2 and 3% carbon-doped $CaMoO_4$.

First of all, basic fuchsin is excited to its first excited singlet by absorbing radiations of suitable wavelength state. It relaxes in its triplet excited state through intersystem crossing. Calcium molybdate also absorbs light to excite electron from its valence band to conduction band; thus, leaving a hole in valence band. As this hole is electron deficient and medium is also alkaline (more OH^- ions are there), it will abstract an electron from ^-OH ions to generate $^{\bullet}OH$ radicals. These radicals are very strong oxidant and non-selective also and therefore, they will attack triplet state of basic fuchsin converting it into its leuco (colorless) form. Leuco form of basic fuchsin is less stable and it will degrade to some small almost harmless compounds like carbon dioxide, water, NO_3^- or $NO_2^-$and Cl^- ion.

Table 5
Effect of light intensity
pH = 9.0 **Amount of photocatalyst = 0.08 g**
[Basic fuchsin] = 4.00 × 10^{-4} M
MECHANISM

Light Intensity (mW cm^{-2})	**$CaMoO_4$**	**1% C-Doped $CaMoO_4$**	**2% C-Doped $CaMoO_4$**	**3% C-Doped $CaMoO_4$**
	Rate constant (k) × 10^4 (sec^{-1})	**Rate constant (k) × 10^4 (sec^{-1})**	**Rate constant (k) × 10^4 (sec^{-1})**	**Rate constant (k) × 10^4 (sec^{-1})**
30.0	0.46	3.17	6.45	1.05
40.0	1.08	4.23	7.85	1.86
50.0	1.71	5.46	8.53	2.37
60.0	1.43	5.07	8.12	2.04
70.0	1.06	4.11	7.23	1.47
80.0	0.87	3.09	6.11	1.09

Conclusion

Undoped as well as 1, 2 and 3% carbon-doped $CaMoO_4$ could successfully degrade basic fuchsin photocatalytically. It was found that photocatalytic activity of $CaMoO_4$ increases on carbon doping but the maximum rate of degradation was observed with 2% C-doped $CaMoO_4$. There was adverse effect on rate of degradation on increasing the amount of carbon dopant above this value (3%). The optimum conditions for degradation of basic fuchsin are: pH = 9.0, concentration of basic fuchsin = 4.00 x 10^{-4} M, photocatalyst = 0.08 g and light intensity = 50.0 mW cm^{-2}.

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