Undoped and carbon-doped calcium molybdate as photocatalyst for degradation of methylene blue

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Calcium molybdates (undoped and carbon-doped) were synthesized and used as photocatalysts for the degradation of methylene blue. These photocatalysts have been characterized by different techniques such as FE-SEM, EDX and XRD. The progress of the photocatalytic degradation was observed spectrophotometrically. The effect of different parameters such as pH, concentration of dye, amount of semiconductor and light intensity on the rate of degradation of methylene blue was observed. Optimum values were obtained as pH = 8.5, concentration of methylene blue = 1.10×10^{-4} *M*, amount of $CaMoO_4$ = 0.10 g and light intensity = 50.0 mW cm^{-2}. A tentative mechanism for the photocatalytic degradation of methylene blue has been proposed. Scavenger studies indicated that hydroxyl radical is acting as an oxidizing species for this degradation. It was observed that 2% C-doped showed almost 1.4 times better photocatalytic performance than undoped $CaMoO_4$ sample.

Keywords: $CaMoO_4$, photocatalytic activity, methylene blue, degradation, hydroxyl radical, oxidation.

Introduction

Methylene blue is used as a dye and medicine. It is used to treat methemoglobinemia. It was earlier used for treating cyanide poisoning and urinary tract infections, but now it is not recommended. It has many side effects which include headache, vomiting, shortness of breath, confusion, increased sweating, abdominal pain, upset stomach, high blood pressure etc. It goes to nearby water resources like lake, pond, river, etc. making the water colored and toxic. Therefore, it is the need of the day to treat this polluted water by degrading methylene blue by some advanced oxidation process, which is green chemical in nature. Here, the photocatalysis enters the scene.

A facile solid-state metathesis synthesis of copper tungstate ($CuWO_4$) was carried out by Medidi *et al.*[1] followed by ball milling and then preparation of copper tungstate-graphene oxide ($CuWO_4$-GO) nanocomposite using a colloidal blending process. These copper tungstate-graphene
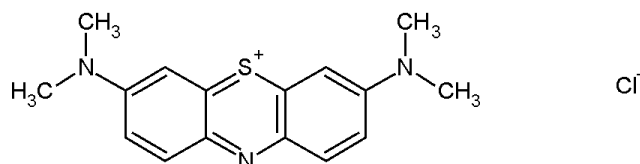

Fig. 1. Methylene blue.

oxide nanocomposites have been used for the photocatalytic degradation of methylene blue under visible light irradiation. This composite showed a band gap of 2.13 eV, which increases range and intensity of light absorption as well as reduction of electron-hole pair recombination in $CuWO_4$ by introducing of GO on to it. Three different forms of modified TiO_2, namely, TiO_2/activated carbon (AC), TiO_2/carbon (C), and TiO_2/PANi, were prepared by Ramli *et al.*[2]. Specific surface area was found in the following order: TiO_2/AC > TiO_2/C > TiO_2/PANi > TiO_2 (179 > 134 > 54 > 9 mg). Photocatalytic performance for the degradation of methylene blue under UV light irradiation was also found to be in same order i.e.

98 > 84.7 > 69%. This order was attributed to the porosity and synergistic effect in the as-prepared samples. Dariani *et al.*[3] designed a photocatalytic reactor to study photocatalytic properties of TiO_2 nanoparticles in photodegradation of methylene blue using UV-A light. Various parameters were evaluated such as: initial dye concentration, mass of TiO_2 nanoparticles, pH, and TiO_2 nano-sized particles. It was observed that on reduction of TiO_2 particles from nano to micro scale, photodegradation becomes very slow. The photocatalytic efficiency for 10 nm TiO_2 nanoparticles was improved to 90% within 1 h and photodegradation was complete in about 2 h, which indicates that the photocatalytic activity increases with increasing surface area.

Three-dimensional flower-like SnS_2(tin sulfide) was synthesized by Balu *et al.*[4] via a facile hydrothermal method. Core-shell structured $SiO_2@\alpha-Fe_2O_3$ nanocomposites were then deposited on the top of these SnS_2 flowers. The photocatalytic behavior of the SnS_2-$SiO_2@\alpha-Fe_2O_3$ nanocomposites was investigated taking the methylene blue as model pollutant. It was reported that an effective photocatalytic activity for the degradation of methylene blue was enhanced especially for the 15 wt% $SiO_2@\alpha-Fe_2O_3$ nanocomposites on SnS_2 flowers. ZnO and 2% Fe-ZnO nanomaterials were prepared by Isai and Shrivastava[5] using a lowcost sol-gel method. It was revealed that as-synthesized nanomaterials have a hexagonal wurtzite structure and their average crystalline size is of the order 22 to 23 nm. The photocatalytic activity of these nanomaterials was monitored spectrophotometrically. The photocatalytic degradation of methylene blue was studied using ZnO and 2% Fe-ZnO nanopowder in presence of UV light irradiation. The effect of various operating parameters such as pH, dye concentration, contact time and catalyst dose was investigated. The maximum degradation of methylene blue was found to be 86% with ZnO and 92% with 2% Fe-ZnO.

Baeissa[6] used a sol-gel method to prepare ZnO nanoparticles, and then a photo-assisted deposition method to deposit indium on the surface of ZnO nanoparticles. The photocatalytic oxidation of methylene blue under visible light irradiation was carried out in the presence of the as-prepared nanoparticles. It was indicated that the indium was well dispersed on the surface of the ZnO nanoparticles and the surface area of the In/ZnO nanoparticles was smaller as compared to ZnO nanoparticles as some of pores of the ZnO nanoparticles were blocked by the deposited metal indium. It was observed that In/ZnO nanoparticles (0.6 wt%) had the lowest band gap and exhibited highest photocatalytic activity for degradation of methylene blue. The performance of these nanoparticles was stable even after reusing it for five times. Vallejo *et al.*[7] synthesized doped ZnO powders using the sol-gel method, and then thin films were fabricated using the doctor blade technique. The photocatalytic degradation of methylene blue was studied in presence of Ag doped ZnO under visible irradiation in aqueous solution. It was reported that the samples were polycrystalline and ZnO was in wurtzite crystalline phase. The Ag-doped ZnO thin films had the lower band gap (2.95 eV). It was revealed that the Ag-doped ZnO thin films had the highest methylene blue photodegradation (45.1%), as compared to that of undoped ZnO thin films (2.7%).

Singh *et al.*[8] studied the degradation of methylene blue in an aqueous solution by nanometallic particles (NMPs). The effects of different parameters were studied such as NMP dosage, pH, concentration of dye and the amount of H_2O_2 on the methylene blue degradation. The highest removal rate achieved was 100% with an initial dye concentration of 5 mg L^{-1}, followed by 99.6% with an initial concentration of 10 mg L^{-1} under following conditions: NMP (0.15 g L^{-1}), concentration of H_2O_2 (100 mM) and temperature (25°C). The degradation of methylene blue followed pseudo-first order kinetics. Visible light active bismuth vanadate ($BiVO_4$) nanoparticles were prepared by Arumugam and Choi[9] via a facile hydrothermal method. The photocatalytic activity of as-prepared $BiVO_4$ photocatalyst was evaluated for the degradation of methylene blue under visible light irradiation. It was reported that about 91.9% degradation was there in 90 min. The effect of varying the experimental parameters was also studied such as catalyst amount, pH, and dye concentration.

Alkaykh *et al.*[10] synthesized nanophotocatalyst $MnTiO_3$ powders via sol-gel technique. Effect of various operating parameters on removal of methylene blue was studied such as amount of photocatalyst, dye concentration, pH and irradiation time. The photodegradation was found to be relatively higher using lower amount (0.005 g) of photocatalyst. It reached rate of 75% and 70% after 240 min for mixed $MnTiO_3/TiO_2$ and pure $MnTiO_3$ nanocatalysts. The photocatalytic degradation of methylene blue followed pseudo-first

order kinetics. These results support use of effective and lowcost $MnTiO_3$ photocatalyst for the decomposition of organic pollutants to water under natural sunlight. A novel catalytic system was developed by Dou *et al.*[11] through activating $NaHSO_3$ with CoO nanoparticles. The CoO nanoparticles were synthesized via a facile one-pot hydrothermal method, which was followed by calcination. The degradation rate of 91.5% for methylene blue was observed in one min, which reached to 99.4% in six min using the $CoO/NaHSO_3$ system. They proposed that sulfate and hydroxyl radicals are responsible for this enhanced degradation of dye with $CoO/NaHSO_3$ system.

Titanate was prepared by Tayeb *et al.*[12] via hydrothermal treatment using TiO_2 and NaOH as precursors. The effect of some operating parameters was also examined. It was reported that the methylene blue degradation was effective in the sample of dye concentration (5 to 10 ppm), catalyst dose (0.25 to 0.50 g) and pH (1.4 to 12.6). The operating parameter values were optimized as: concentration of methylene blue (5.45 ppm), dose of TiO_2 (0.50 g L^{-1}) and pH (11.89). It was revealed that the percentage of degradation was more than 99% under these conditions. Photocatalytic degradation of methylene blue has been investigated by Abdullah *et al.*[13] using polyvinylidene fluoride (PVDF)/TiO_2 membrane. The performance of the membrane followed the order: 9 wt% TiO_2/PVDF > 6 wt% TiO_2/PVDF > 3 wt% TiO_2/PVDF > undoped PVDF. There was a synergistic effect of incorporating the TiO_2 photocatalyst into the PVDF membrane. Rate of degradation of methylene blue followed first order kinetics. Mohabansi *et al.*[14] observed degradation of an aqueous solution of methylene blue dye in presence of titanium dioxide and zinc oxide UV light. The rate of degradation was monitored spectrophotometrically. Effects of some parameters on dye degradation were investigated such as the pH, H_2O_2/COD ratio and the amounts of catalyst. It was revealed that ZnO is a better photocatalyst as compared to TiO_2 in terms of percentage degradation of methylene blue. It was observed that maximum decolorizing efficiency was there in less than 90 min with 50 mg 750 mL^{-1} of ZnO catalyst dose.

Pathak *et al.*[15] used a composite of $CaMoO_4$ with MWCNT to degrade Bismarck brown with optimum rate of 1.87×10^{-4} s^{-1}. Photocatalytic properties of composite of graphene oxide with $CaMoO_4$ has also been reported by Mostafa and Mashkani[16].

Aghajani and Hosseinpour-Mashkani[17] prepared $Ce(MoO_4)_2$@TiO_2 using ultrasonically synthesized $Ce(MoO_4)_2$ nanostructure coupled with TiO_2 nanoparticles. The photocatalytic properties of molybdate-based n-n heterostructure was investigated for the degradation of methyl orange and rhodamine B under UV-Vis light irradiation. It was reported that photocatalytic yield of $Ce(MoO_4)_2$@TiO_2 exhibited a 30% enhancement as compared to $Ce(MoO_4)_2$. DRS results demonstrated that the band gap of $Ce(MoO_4)_2$@TiO_2 was found to be 3.3 eV. About 95 and 93% of methyl orange and rhodamine B were degraded in 50 min, respectively.

Strontium molybdate ($SrMoO_4$) nanostructures were synthesized by Hosseinpour-Mashkani *et al.*[18] via a sonochemical method. They used strontium(II) nitrate and ammonium heptamolybdate tetrahydrate as precursors and glucose and lactose as capping agents. The photocatalytic degradation of methyl orange was observed in presence of nanocrystalline $SrMoO_4$ under ultraviolet light irradiation.

A novel silver-doped tetragonal phase of cadmium molybdate nanoparticles (Ag^0-$CdMoO_4$) were synthesized by them using sonochemical method[19]. Here, sucrose was applied as a green capping agent. Photocatalytic activities of the Ag^0-$CdMoO_4$ samples were evaluated for degradation of methyl orange dye under visible light irradiation and the best photocatalytic activity has been observed with the sample containing 0.5 mol of Ag as compared to other samples.

Hosseinpour-Mashkani *et al.*[20] also synthesized zinc molybdate rod-like nanostructures by precipitation method in the presence of surfactants such as sodium dodecyl sulfate, polyethylene glycol, and cetyltrimethylammonium bromide. Photocatalytic properties of nanocrystalline zinc molybdate were evaluated for the photocatalytic degradation of methyl orange under visible light irradiation.

Experimental

Materials used and method:

Chemicals used:

Methylene blue (Himedia), ammonium molybdate (Thermo Fischer), calcium chloride (Merck), and glucose (Thermo Fischer) were used in present investigations. Double distilled water is used throughout the investigation.

Preparation of photocatalysts:

Undoped calcium molybdate was synthesized by hydrothermal method using Teflon coated autoclave at 200ºC. 4.9 g $(NH_4)_2MoO_4$ and 3.66 g $CaCl_2.2H_2O$ were weighed in stoichiometric proportions. Ammonium molybdate was dissolved in 10 mL doubly distilled water with continuous stirring (solution A) and calcium chloride was also dissolved in 10 mL doubly distilled water (solution B). Solution B was slowly added into the solution A under vigorous stirring for 30 min. Few drops of aqueous NaOH (1 *N*) were added with constant stirring until it gave white colored precipitates. Then it was filtered, washed with water and dried at 80ºC. The resulting solid was calcined for 3 h at 200ºC.

Carbon-doped calcium molybdate was synthesized as follows: 4.9 g $(NH_4)_2MoO_4$, 3.66 g $CaCl_2.2H_2O$ and glucose (0.125, 0.25 and 0.375 g for 1, 2 and 3% carbon doping) were separately dissolved in 10 mL distilled water. Few drops of aq. NaOH (1 *N*) were used. The solution was heated up to 200ºC for 90 min, filtered, washed with water and dried at 80ºC.

Photocatalytic degradation:

Some control experiments were also carried out. 2.5 mL of dye solution ($1.10×10^{-3}$ *M*) was taken in volumetric flask of 250 mL capacity. The solution was diluted with distilled water so that the concentration of dye solution became $1.0×10^{-4}$ *M*. The solution was divided in to four equal parts-

(i) In the first beaker, only dye solution was taken and kept in the dark.

(ii) In the second beaker, only dye solution was taken

and exposed to the light.

(iii) 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.

(iv) 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 few hours, the absorbance of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the solutions of the first three beakers in each case had almost the same absorbance as initial absorbance, while absorbance of reaction mixture in fourth beaker foe each case had considerable decrease in absorbance as compared to its initial value, indicating that undoped calcium molybdate or C-doped (1, 2 and 3%) calcium molybdate and light both are necessary for degradation of methylene blue. 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 (FE-SEM):

The morphology of the particles were 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 2% $CaMoO_4$ were carried out via field emission scanning electron microscopy. The FE-SEM images of the undoped $CaMoO_4$ and C-doped (2%) $CaMoO_4$ (glucose was used as C source) are presented in Fig. 2.

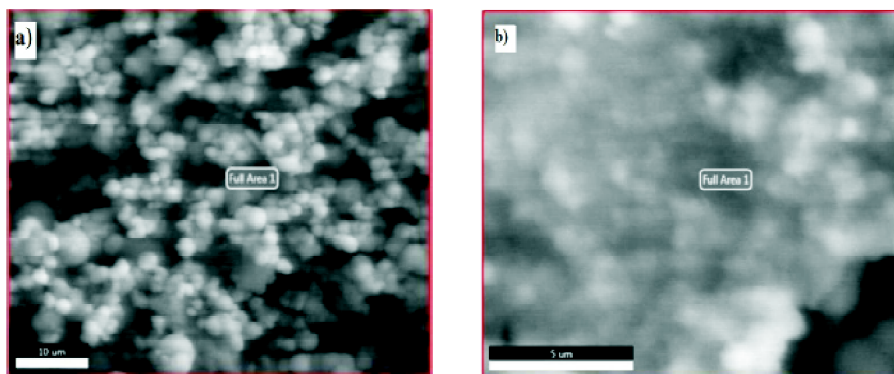**Fig. 2.** FE-SEM Images of (a) undoped $CaMoO_4$ and (b) 2% C-doped $CaMoO_4$.

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 (2%) $CaMoO_4$ are presented in Figs. 3 and 4 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. Hence, it is pure $CaMoO_4$. EDX of C-doped (2%) $CaMoO_4$ 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 $CuK\alpha$ 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 $CaMoO_4$ (2%) are given in Figs. 5 and 6, respectively.
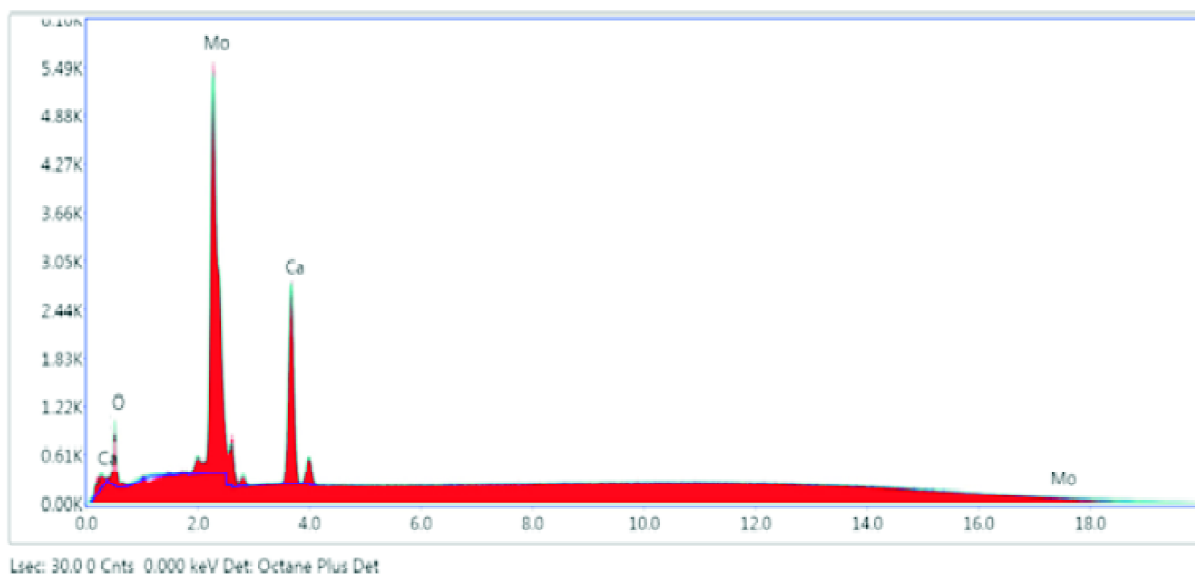
0.0320 g of methylene blue was dissolved in 100.0 mL of
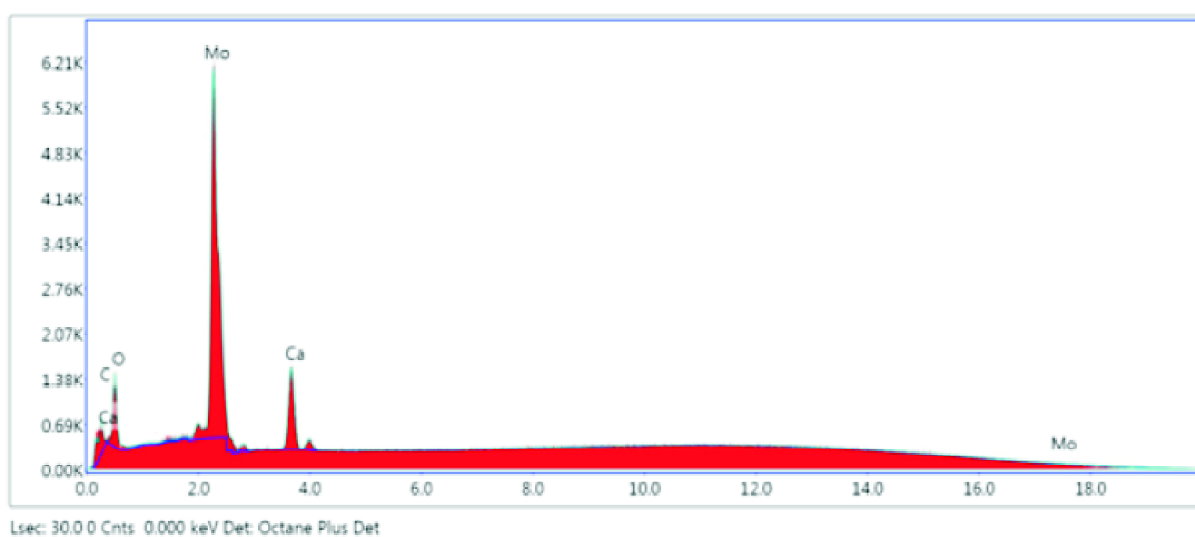

Fig. 3. EDX of undoped $CaMoO_4$.
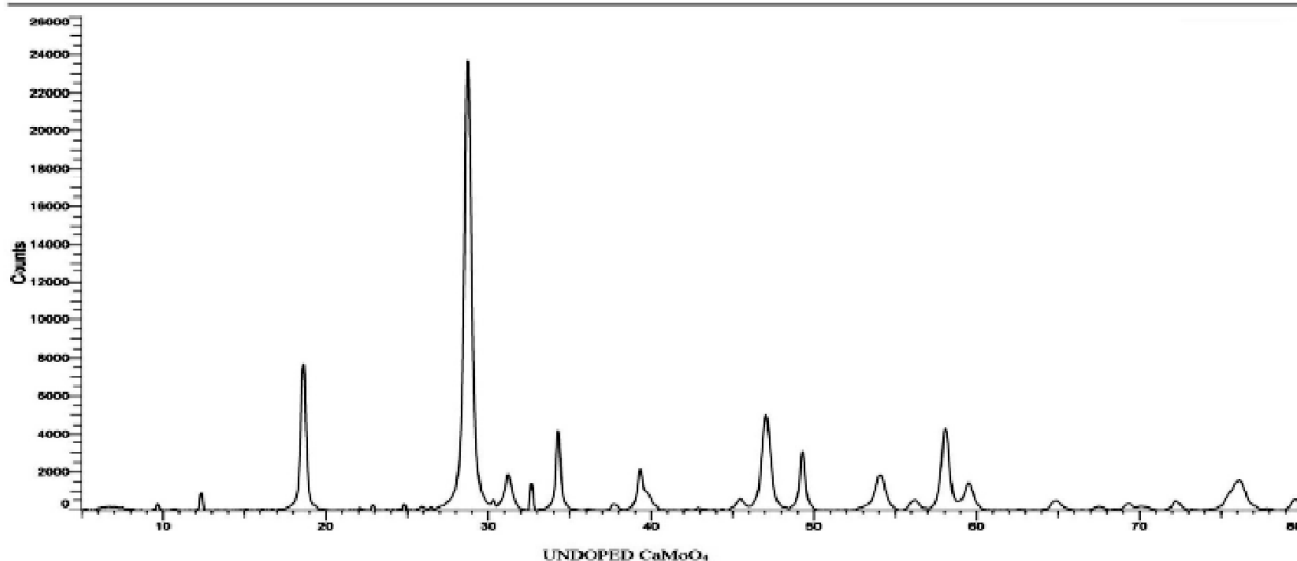

Fig. 4. EDX of 2% C-doped $CaMoO_4$.

Fig. 5. XRD of undoped CaMoO$_4$.
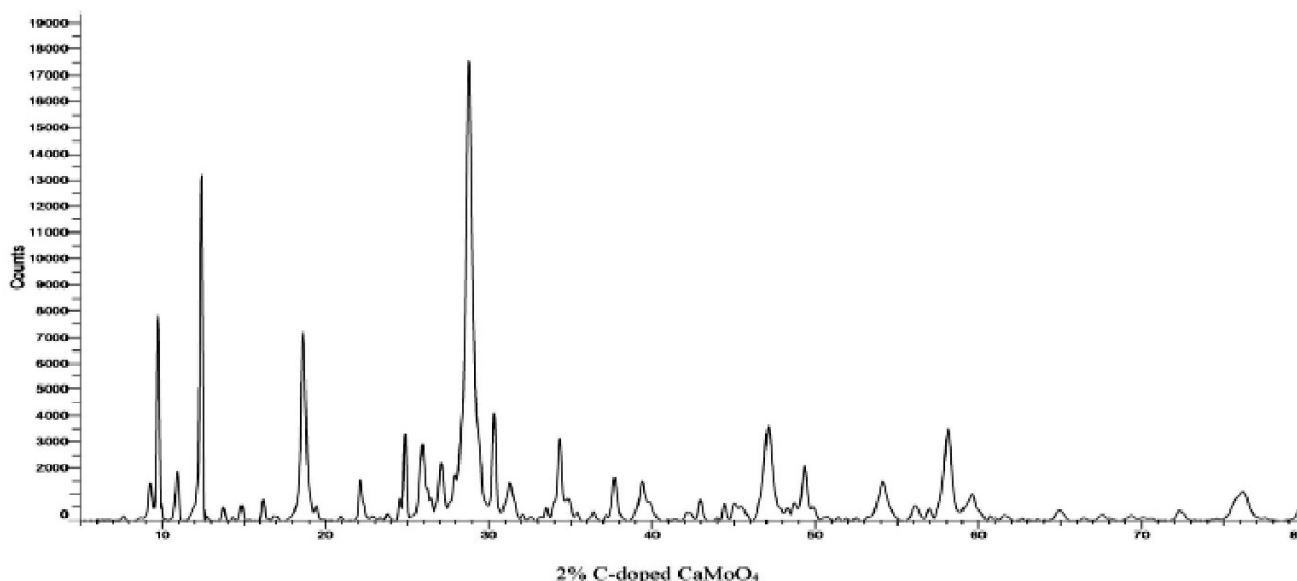
Fig. 6. XRD of 2% C-doped CaMoO$_4$.

doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} *M*. It was used as a stock solution. This solution was further diluted. 50 mL dye solution of 1.10×10^{-4} *M* concentration was taken in a beaker. The pH of this solution was adjusted to 8.5 and 0.10 g of catalyst undoped, 1, 2 or 3% C-doped CaMoO$_4$ 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 2 mL was taken out from the reaction mixture at regular time intervals and its absorbance (*A*) was observed at 665 nm.

It was observed that the absorbance decreases with increasing time of exposure. A plot of $1 + \log A$ versus time was observed to be linear, which shows that the reaction

follows pseudo-first order kinetics. The rate constant was calculated by the rate expression (1).

$$k = 2.303 \times \text{Slope} \tag{1}$$

The results of typical runs for photocatalytic degradation of methylene blue using undoped, 1, 2 and 3% C-doped CaMoO$_4$ are represented in Table 1 and graphically presented in Fig. 7.

Effect of pH:

The effect of pH on the rate of degradation was investigated in pH range 7.5–10.0 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 with an increase in pH, rate of reaction also increases. After attaining the maximum value at pH 8.5, rate decreases with a

Table 1. Typical runs

[Methylene blue] = 1.10×10^{-4} *M*
pH = 8.5
Amount of photocatalyst = 0.10 g
Light intensity = 50.0 mW cm^{-2}

Time	CaMoO$_4$		1% C-Doped CaMoO$_4$		2% C-Doped CaMoO$_4$		3% C-Doped CaMoO$_4$	
(min)	Absorbance (*A*)	1 + log *A*	Absorbance (*A*)	1 + log *A*	Absorbance (*A*)	1 + log *A*	Absorbance (*A*)	1 + log *A*
0	0.708	0.8500	0.724	0.8597	0.708	0.8500	0.708	0.8500
10	0.649	0.8122	0.664	0.8222	0.616	0.7896	0.676	0.8299
20	0.589	0.7701	0.593	0.7731	0.537	0.7300	0.646	0.8102
30	0.539	0.7316	0.537	0.7300	0.472	0.6739	0.608	0.7839
40	0.487	0.6875	0.491	0.6911	0.414	0.6170	0.582	0.7649
50	0.447	0.6503	0.434	0.6375	0.355	0.5502	0.549	0.7396
60	0.409	0.6117	0.389	0.5899	0.315	0.4983	0.517	0.7135
70	0.373	0.5717	0.355	0.5502	0.282	0.4502	0.496	0.6955
80	0.337	0.5276	0.303	0.4814	0.240	0.3802	0.473	0.6749
90	0.309	0.4900	0.286	0.4564	0.211	0.3243	0.447	0.6503

Rate constant (*k*) for:
Undoped CaMoO$_4$ = 1.59×10^{-4} s^{-1}
1% C-Doped CaMoO$_4$ = 1.73×10^{-4} s^{-1}
2% C-Doped CaMoO$_4$ = 2.22×10^{-4} s^{-1}
3% C-Doped CaMoO$_4$ = 8.32×10^{-5} s^{-1}
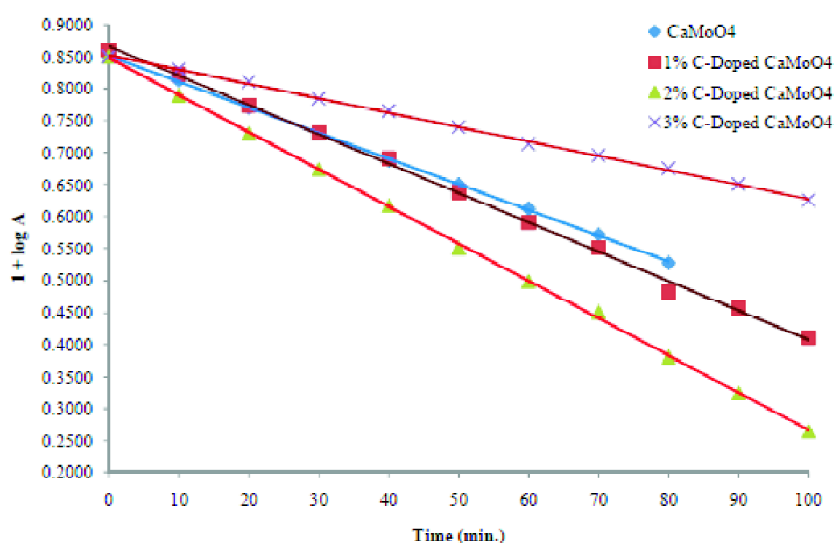
Fig. 7. Typical runs.

Table 2. Effect of pH

[Methylene blue] = 1.10×10^{-4} M   Light intensity = 50.0 mW cm^{-2}
Amount of photocatalyst = 0.10 g

pH	CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	1% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	2% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	3% C-Doped CaMoO$_4$ Rate constant (k)×10^5 (s^{-1})
7.5	1.16	1.06	1.61	5.41
8.0	1.40	1.37	1.84	7.17
8.5	1.59	1.73	2.22	8.32
9.0	1.26	1.21	1.01	7.80
9.5	1.01	0.98	0.82	7.07
10.0	0.82	0.74	0.65	6.32

further increase in pH. In this case, the presence of scavenger (2-propanol) affect the rate of reaction adversely and hence, it may be concluded that •OH radicals do participate in the degradation as an active oxidizing species.

Effect of dye concentration:

The effect of variation of concentration of methylene blue on its degradation rate has been observed in the range from 0.5×10^{-5} to 1.30×10^{-5} M for undoped 1, 2 and 3% C-doped CaMoO$_4$ keeping all other parameters same. The results are given in Table 3. It has been observed that the rate of degradation increases with increasing concentration of dye up to 1.10×10^{-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 further increasing concentration of dye, 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. 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.

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 reported 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 (0.10 g), for; undoped and 1, 2 and

Table 3. Effect of dye concentration

pH = 8.5   Light intensity = 50.0 mW cm^{-2}
Amount of photocatalyst = 0.10 g

[Methylene blue] ×10^4 M	CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	1% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	2% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	3% C-Doped CaMoO$_4$ Rate constant (k)×10^5 (s^{-1})
0.50	0.53	0.62	0.72	5.00
0.60	0.60	0.70	0.84	5.48
0.70	0.72	0.81	0.97	5.74
0.80	0.89	0.94	1.03	6.33
0.90	1.00	1.12	1.44	7.00
1.00	1.26	1.54	1.68	7.41
1.10	1.59	1.73	2.22	8.32
1.20	1.02	1.24	1.66	7.20
1.30	0.86	0.93	1.30	6.36

Table 4. Effect of amount of photocatalyst

pH = 8.5   Light intensity = 50.0 mW cm^{-2}

[Methylene blue] = 1.10×10^{-4} *M*

Photocatalyst (g)	CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	1% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	2% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	3% C-Doped CaMoO$_4$ Rate constant (k)×10^5 (s^{-1})
0.04	0.73	0.76	1.06	6.83
0.06	0.90	0.98	1.41	7.16
0.08	1.06	1.34	1.77	7.84
0.10	1.59	1.73	2.22	8.32
0.11	1.60	1.73	2.22	8.31
0.12	1.59	1.74	2.20	8.32
0.13	1.59	1.73	2.22	8.31
0.14	1.60	1.74	2.22	8.32

Table 5. Effect of light intensity

pH = 8.5   [Methylene blue] = 1.10×10^{-4} *M*

Amount of photocatalyst = 0.10 g

Light Intensity (mW cm^{-2})	CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	1% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	2% C-Doped CaMoO$_4$ Rate constant (k)×10^4 (s^{-1})	3% C-Doped CaMoO$_4$ Rate constant (k)×10^5 (s^{-1})
30.0	0.84	0.99	1.64	6.12
40.0	1.17	1.32	1.83	7.65
50.0	1.59	1.73	2.22	8.32
60.0	1.32	1.64	2.01	8.06
70.0	1.11	1.46	1.88	7.86

3% C-doped CaMoO$_4$. But after this point, the rate of reaction becomes virtually constant and it shows saturation likebehavior. This may be explained on the basis that with an increase in the amount of photocatalyst, the exposed surface area of photocatalyst will increase and therefore, 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 plateau was obtained.
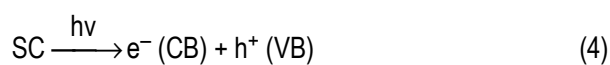
Effect of light intensity:

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 70.0 mW cm^{-2}. The observations are presented in Table 5. The results indicate that the 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 explained on the basis 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 start some side thermal reactions and therefore, higher intensities of light have been avoided.

Mechanism:

On the basis of experimental observations, the following tentative mechanism has been suggested for photocatalytic degradation of methylene blue.

$$^1MB_0 \xrightarrow{h\nu} {}^1MB_1 \tag{2}$$

$$^1MB_1 \xrightarrow{ISC} {}^3MB_1 \tag{3}$$

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

$$h^+ + OH^- \rightarrow {}^\bullet OH \tag{5}$$

$$^{\bullet}OH + {}^{3}MB_{1} \rightarrow \text{Leuco-MB} \qquad (6)$$

$$\text{Leuco-MB} \rightarrow \text{Products} \qquad (7)$$

where, MB = methylene blue and SC = undoped as well as 1, 2 and 3% carbon-doped $CaMoO_4$.

First of all, methylene blue is excited to its first excited singlet by absorbing radiations of suitable wavelength. Then, 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 behind a hole in valence band. As this hole is electron deficient and medium in also alkaline and more OH^- ions are there, it will abstract an electron from ^-OH ions to generate $^{\bullet}OH$ radical. These radicals are very strong oxidant and non-selective also and therefore, they will attack triplet state of methylene blue converting it into its leuco (colorless) form. Leuco form of methylene blue will degrade to some smaller almost harmless products like carbon dioxide, water, SO_4^{2-}, NO_3^- and Cl^- ions.

Conclusion

Undoped as well as 1, 2 and 3% carbon-doped $CaMoO_4$ were prepared and used for action of photocatalytic degradation of methylene blue. 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 a slight adverse effect on rate of degradation on increasing the amount of carbon dopant above this value (2%). The optimum conditions for degradation of methylene blue are: pH = 8.5, concentration of methylene blue = 1.10×10^{-4} M, photocatalyst = 0.10 g and light intensity = 50.0 mW cm^{-2}. A mechanism of photocatalytic degradation has been proposed involving hydroxyl radicals as an active oxidizing species. The participation of hydroxyl radicals was confirmed by scavenger studies using 2-propanol, where rate of degradation was drastically reduced.

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