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Visible Light Induced Photocatalytic Degradation of Bismarck Brown using $CaMoO_4$-MWCNT Composite

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ABSTRACT

Photocatalytic degradation of bismarck brown has been studied using synthesized calcium molybdate-multiwalled carbon nanotube ($CaMoO_4$-MWCNT) composite. The prepared catalyst was characterized by FESEM, XRD, EDS, FT-IR and UV-visible techniques. This composite showed better photocatalytic activity as compared to pure $CaMoO_4$ and MWCNT. Different rate affecting parameters were studied and optimized as pH = 8.0; dye concentration = 2.0×10^{-4} M; amount of composite = 0.08 g; light intensity = 40.0 $mWcm^{-2}$. The rate constant for photocatalytic degradation of bismarck brown was observed as k = 1.87×10^{-4} sec^{-1}.

1. Introduction

Carbon nanotube (CNT) based nanotechnologies have found an application in water treatment, such as sorbents, catalyst, filters or membranes. CNTs, with their high surface-active site to volume ratio and controlled pore size distribution, have an exceptional sorption capability and high sorption efficiency compared to conventional granular and powder activated carbon [1].

Dalt et al. synthesized TiO_2-ZnO/MWCNT nanocomposites and applied it for photodegradation of an organic dye [2]. Dinesh et al. studied sonophotocatalytic treatment of bismarck brown G dye in the presence of Fe (o)-doped TiO_2 and found that the highest degradation of dye with the smallest amount of catalyst [3]. Emman et al. investigated photocatalytic degradation and adsorption of bismarck brown G dyes using spinel co-catalyst $(Co,Ni)_3O_4/Al_2O_3$[4]. Tak et al. studied photocatalytic reduction of bismarck brown dye using copper hexacyanoferrate (II) [5].

Amalraj and Pius studied photocatalytic degradation of alizarin red S and bismarck brown R using titanium dioxide photocatalyst [6]. Kamil et al. used MWCNT for adsorption of bismarck brown R dye from an aqueous solution [7]. Gole and Alhat investigated the degradation of bismarck brown dye using effects of photocatalysis and microwave and their sequential combination [8]. Devi et al. studied photodegradation of diazo dye bismarck brown by advanced photo-Fenton process using zero valent metallic iron [9]. Hussein et al. used zinc oxide for photocatalytic degradation of aqueous solutions of bismarck brown G [10]. Boruah et al. studied the photocatalytic activity of the Fe_3O_4@V_2O_5/rGO towards the degradation of harmful cationic bismarck brown and anionic acid orange 7 dyes under direct sunlight irradiation [11]. Preetha and Shanthi studied photodegradation of bismarck brown and rhodamine B dyes from aqueous solutions using iron oxide nanoparticleas photocatalyst [12]. Qu et al. [13] introduced Fe_2O_3 nanoparticles into the multiwalled carbon nanotubes and studied adsorbent properties of these magnetic MWCNTs in case of methylene blue and neutral red dyes. Yu et al. observed the effect of carbon nanotubes on the adsorption and the photocatalytic properties of TiO_2 (P25) for the treatment of procion red MX-5B, procion yellow HE4R, and procion red HE3B [14]. Kumar et al. used bacterial strain AKIP-2 for bioremediation of Evan's blue dye [15]. In the present investigation calcium molybdate-multiwalled carbon nanotube ($CaMoO_4$-MWCNT) composite has been used for photocatalytic degradation of bismarck brown. The structure of bismarck brown is shown in Fig. 1. The observations revealed the better performance of composite as compared to pure $CaMoO_4$ and MWCNT.

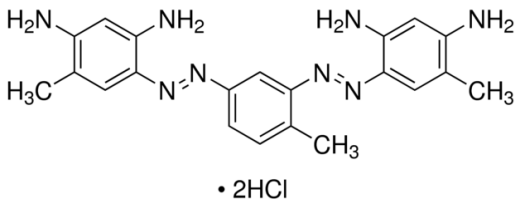

Fig. 1 Structure of bismarck brown

2. Experimental Methods

2.1 Material and Methods

MWCNT was purchased from United Nanotech Innovations Pvt. Ltd. Bangalore. Calcium chloride was purchased from Finar and ammonium molybdate and Evans blue from HiMedia. Systronics digital pH meter 335 was used to measure pH and Systonics spectrophotometer (Model-106) was used to measure absorbance. A 200 W tungsten lamp was used for irradiation purpose.

2.2 Preparation of $CaMoO_4$ (Calcium Molybdate)

Solution A was prepared by mixing 5 g molybdenum trioxide, 12 mL of 6 N NaOH solution and 6 N nitric acid. On the other hand, solution B was prepared by dissolving 3.8 g of calcium chloride in 9 mL doubly distilled water. Thereafter, solutions A and B were mixed. As obtained product of calcium molybdate was washed with hot distilled water thrice. This was filtered and dried in an oven at 80-100 °C for 3-4 hr. Calcium molybdate was obtained in the form of white crystalline powder.

2.3 Preparation of Composite

Composite was prepared by mixing 2 g of each MWCNT and $CaMoO_4$. The mixture was ground in agate mortar pestle. Photocatalytic performance was evaluated by degradation of bismarck brown dye under visible light. The degradation of dye was monitored spectrophotometrically.

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2.4 Characterization of Composite

2.4.1 FESEM Analysis

The field emission scanning electron microscopic (FESEM) analysis was conducted by Hitachi-PU 5.0 kV, which provides information of the sample surface i.e. morphology. The compositions of natural and manufactured materials with higher resolution are shown in Fig. 2. From these figures, the formation of composite is clear where the composite contains both the structures of MWCNT (thread like structure) and $CaMoO_4$ (spherical particles).

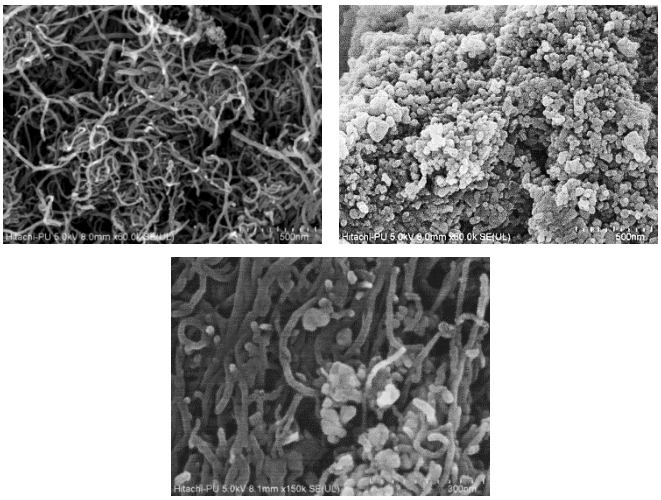

Fig. 2 FESEM of (a) MWCNT (b) $CaMoO_4$ (c) $CaMoO_4$–MWCNT composite

2.4.2 EDS Analysis

Energy-dispersive X-ray spectroscopy (EDS) detects X-rays emitted from the sample during bombardment by electron beam to characterize the elemental composition. It is based on an interaction of source of X-ray excitation and sample. The EDS analysis of sample shows that the composite contains carbon (wt.%) = 55.59, calcium (wt.%) = 2.74, molybdenum (wt.%) = 5.03 and oxygen (wt.%) = 6.87.

2.4.3 XRD Analysis

X-rays diffraction pattern of $CaMoO_4$-MWCNT composite was performed by XPERT-PRO Model X-ray diffractometer and shown in Fig. 3. Average particle size of the crystalline composite powder was calculated by Debye-Scherrer's equation and it was found 17.95 nm. This size shows the formation of nanoparticles.

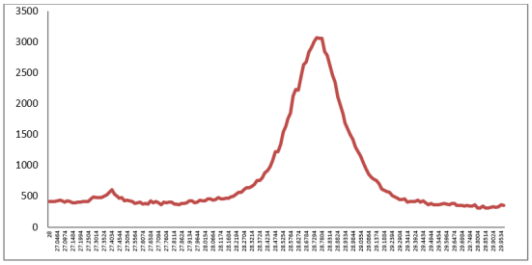

Fig. 3 XRD of MWCNT-$CaMoO_4$

2.4.4 FTIR Analysis

FT-IR was recorded on FT-IR Spectrophotometer Model RZX (Perkin Elmer). FTIR spectrum of the composite shows a band at 1222.1 cm^{-1}, which confirms the presence of C–O stretching vibrations as supported by Evans and Wharf studies [16].

2.4.5 UV Analysis

UV Analysis of composite was recorded with UV-VIS-NIR Detector Lambda 900 (Perkin Elmer). UV spectrum indicated bending vibration of $[MoO_4]^{2-}$ in the range from 200-230 nm. This observation is supported by Mitchell reports [17].

2.4.6 Photocatalytic Degradation

The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of bismarck brown dye. A stock solution of dye (1.0×10^{-3} M) was prepared by dissolving 0.0460 g of dye in 100 mL doubly distilled water. This stock solution was further diluted (2.0×10^{-4}M). The absorbance of bismarck brown solution was determined with the help of a spectrophotometer at λ_{max} = 420 nm. The pH of the reaction mixture 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 N sulphuric acid and 0.1 N sodium hydroxide solutions.

3. Results and Discussion

A decrease in absorbance of bismarck brown solution was observed with increasing time of exposure. A plot of 1 + log A against time was found to be linear (Fig. 4), which indicates that the catalytic degradation of dye follows pseudo–first order kinetics. The rate constant was calculated by using the equation, k = 2.303 × slope.

Typical runs for the degradation of bismarck brown by MWCNT, $CaMoO_4$ and MWCNT-$CaMoO_4$ have been presented in the Table 1 and graphically presented in Fig. 4.

Table 1 A typical run at pH = 8.0, $CaMoO_4$-MWCNT composite = 0.08 g, [Bismarck brown] = 2.0×10^{-4} M, Light intensity = 40.0 $mWcm^{-2}$

Time	$CaMoO_4$-MWCNT Composite		$CaMoO_4$		MWCNT	
(min)	Abs (A)	1 + log A	Abs. (A)	1 + log A	Abs. (A)	1 + log A
0	0.275	0.4393	0.275	0.4393	0.275	0.4393
10	0.245	0.3892	0.257	0.4099	0.264	0.4216
20	0.223	0.3483	0.241	0.3820	0.248	0.3945
30	0.197	0.2945	0.224	0.3502	0.234	0.3692
40	0.176	0.2455	0.208	0.3181	0.219	0.3404
50	0.155	0.1903	0.189	0.2765	0.208	0.3181
60	0.137	0.1367	0.180	0.2553	0.195	0.2900
70	0.124	0.0934	0.166	0.2201	0.186	0.2695
80	0.112	0.0492	0.154	0.1875	0.173	0.2380
90	-	-	0.143	0.1553	0.164	0.2148
100	-	-	0.135	0.1303	0.154	0.1875
110	-	-	0.125	0.0969	0.145	0.1614
120	-	-	0.115	0.0607	0.137	0.1367

Rate constant (k) with CaMoO4-MWCNT Composite = 1.87 × 10-4 s^{-1}
Rate constant (k) with CaMoO4= 1.21 × 10-4 s^{-1}
Rate constant (k) with MWCNT= 9.67 × 10-5 s^{-1}

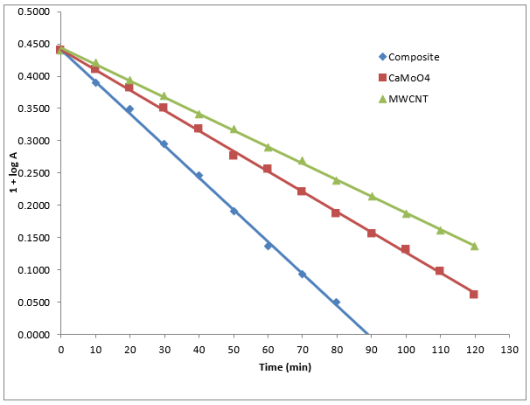

Fig. 4 Typical run

Table 2 Effect of pH at $CaMoO_4$-MWCNTcomposite = 0.08 g, [Bismarck brown] = 2.0×10^{-4} M, Light intensity = 40.0 $mWcm^{-2}$

pH	Rate constant (k) × 10^4 (s^{-1})
5.0	0.87
5.5	1.33
6.0	1.37
6.5	1.50
7.0	1.56
7.5	1.59
8.0	1.87
8.5	1.77
9.0	1.59
9.5	1.50

3.1 Effect of pH

The effect of variation of pH was studied in the range 5.0-9.5. The results are summarized in a Table 2. From the observations, it was observed that as the pH was increased from 5.0, the highest rate was observed at pH 8.0, but the rate of degradation decreases with a further increase in pH. An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\bullet-}$. An increase in the rate of photocatalytic degradation of dye

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with the increase in pH may be due to the availability of more $O_2^{\bullet-}$ radicals. After pH 8.0, a decrease in the rate of photocatalytic degradation of the dye may be due to the repulsion force faced by bismarck brown molecules (anionic form) with the negatively charged surface of the semiconductor (due to absorption of more OH^- ions on the surface of the photocatalyst).

3.2 Effect of Dye Concentration

The effect of dye concentration on the photocatalytic degradation of bismarck brown was observed in the range of 1.4×10^{-4} to 2.6×10^{-4} M and results are reported in Table 3.

Table 3 Effect of dye concentration at pH = 8.0, $CaMoO_4$-MWCNTcomposite = 0.08 g, Light intensity = 40.0 $mWcm^{-2}$

[Bismarck brown] × 10^4 M	Rate constant (k) × 10^4 (s^{-1})
1.40	0.62
1.60	0.80
1.80	1.50
2.00	1.87
2.20	1.70
2.40	0.62
2.60	1.00

As the concentration of the dye was increased, it was observed that the dye degradation was also increased but after 2.00×10^{-4} M (optimum condition), the photocatalytic degradation showed a declining behaviour. Here, the dye molecule will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel. As a consequence, the degradation rate was retarded.

3.3 Effect of Amount of $CaMoO_4$-MWCNT Composite

The effect of variation of the amount of catalyst on the rate of dye degradation has been studied in the range from 0.02 to 0.14 g. The results of variation of rate constant with composite are represented in Table 4.

Table 4 Effect of amount of $CaMoO_4$-MWCNT composite pH = 8.0, [Bismarck brown] = 2.0×10^{-4} M, Light intensity = 40.0 $mWcm^{-2}$

Amount of composite (g)	Rate constant (k) × 10^4 (s^{-1})
0.02	0.45
0.04	0.67
0.06	0.89
0.08	1.87
0.10	1.78
0.12	1.66
0.14	1.43

It was observed that as the amount of photocatalyst was increased, the rate of photocatalytic activity was also increased because its exposed surface area increased. The rate of degradation was found to be optimum at 0.08 g of the semiconductor. After this amount the degradation rate of the dye was decreased. It can be explained by the fact that there are close multilayers of composite at the bottom of beaker, which leads to recombination of electron-hole pair. This recombination reduces the photocatalytic activity of composite and it will result in a decrease in rate of degradation.

3.4 Effect of Light Intensity

The distance between the light source and exposed surface area of photocatalyst was varied from 20.0 to 70.0 $mWcm^{-2}$ to determine the effect of light intensity on the photocatalytic degradation. Rate constants with different light intensity are represented in Table 5.

Table 5 Effect of light intensity pH = 8.0, $CaMoO_4$-MWCNT composite = 0.08 g, [Bismarck brown] = 2.0×10^{-4} M

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^4 (s^{-1})
20.0	0.85
30.0	0.91
40.0	1.87
50.0	1.52
60.0	1.36
70.0	0.83

It was observed that photocatalytic degradation of bismarck brown was found maximum at 40.0 $mWcm^{-2}$. This increase in photocatalytic degradation is due to increase in number of photons striking per unit area per unit time. After this optimum value of light intensity, the decrease in photocatalytic activity was observed by increasing light intensity further. This may be because of thermal side reactions and therefore, higher light intensities were avoided.

3.5 Mechanism

On the basis of the observations, a tentative mechanism for photocatalytic degradation of bismarck brown may be proposed as,

$$^1BB_0 \xrightarrow{h\nu} {}^1BB_1 \quad (1)$$

$$^1BB_1 \xrightarrow{ISC} {}^3BB_1 \quad (2)$$

$$SC \xrightarrow{h\nu} e^- (CB) + h^+ (VB) \quad (3)$$

$$O_2 + e^- \longrightarrow O_2^{\bullet-} \quad (4)$$

$$O_2^{\bullet-} + {}^3Dye_1 \longrightarrow \text{Leuco Dye} \quad (5)$$

$$\text{Leuco Dye} \longrightarrow \text{Products} \quad (6)$$

Bismarck brown absorbs radiation of suitable wavelength and it is excited to its first excited singlet state followed by inter system crossing (ISC) to its triplet state. On the other hand, the semiconducting $CaMoO_4$ also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This electron from conduction band is abstracted by dissolved oxygen to generate superoxide anion radical ($O_2^{\bullet-}$). This $O_2^{\bullet-}$ reduced dye molecules present in leuco form, which ultimately degrades in less harmful products. The observations of typical run were also performed in the presence of 2-propanol, where the rate of dye degradation was not affected, which also confirms the role of $O_2^{\bullet-}$ as reducing agent.

4. Conclusion

The feasibility of photocatalytic degradation of bismarck brown dye was tested using synthesized $CaMoO_4$-MWCNT composite as photocatalyst. The experimental results indicated that degradation efficiency of dye was affected by pH, concentration of dye, amount of composite and light intensity. In the present work, $CaMoO_4$-MWCNT composite was successfully used as a photocatalyst for degradation of Bismarck brown and also the comparative study showed that the performance of composite was better than the individual components i.e. $CaMoO_4$ and MWCNT. The use of $CaMoO_4$-MWCNT composite may be explored for removal of a variety of other industrial effluents in future.

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