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Photocatalytic degradation of Methylene Blue using a mixed catalyst and product analysis by LC/MS

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ABSTRACT

Cr–Ti binary oxide with 10% molar Cr^{3+} content (Ti–10Cr) was prepared by sol–gel method and characterized by using transmission electron microscope (TEM) and X-ray diffraction analysis (XRD). The photoinduced degradation of Methylene Blue (MB) dye in the presence of Ti–10Cr was studied with UV–vis absorption. The absorption intensity of the dye solution monitored at 668 nm decreased with time upon irradiation in the presence of the catalyst. A maximum degradation efficiency of 70% of the dye was achieved in the presence of Ti–10Cr catalyst at pH 7. Photocatalytic degradation of the dye followed the pseudo-second-order-kinetics. Degradation product analysis was done using the LC–UV/vis–MS technique and the results showed that the dye degradation is initiated by demethylation of the molecule. The intermediates structure was confirmed by tandem mass spectrometric analysis.

1. Introduction

Many industries such as textile, plastics, and paper and pulp generate streams of waste effluents which contain considerable amount of organic dyes. When these compounds are discharged to the main water bodies without any prior treatment, they can cause havoc to the ecological balance in the environment as these molecules have carcinogenic and mutagenic properties towards aquatic organisms and thus pose threat to human life at the end of the food chain [1,2]. The conventional water treatment methods (adsorption, sedimentation, coagulation, etc.) are now being supplemented by advanced oxidation processes (AOPs). The widely used AOPs include photolysis, Fenton method, photofenton, ozonolysis, sonolysis, and photocatalysis [3–6]. All these techniques are versatile in nature and have their own pros and con. However in photocatalysis, one can use the available source of UV radiation from sunlight and in the presence of a suitable catalyst (such as semiconductors), conduct a chemical reaction to degrade the organic pollutant present in wastewater.

Various semiconductors have been tested for their efficiencies towards dye degradation. Some of these include TiO_2, V_2O_5, ZnO, WO_3, CdS, ZrO_2 and their impregnated forms [7–10]. Titanium dioxide mediated photocatalytic oxidation has been applied more extensively for dye studies. This is mainly because of its low cost, stable nature and its optical absorption in the UV region. The use of TiO_2 has also guaranteed good results in detoxification of water samples loaded with molecules like anilines, alcohols, and organochlorides [11,12]. The activity of the catalyst is generally enhanced by adding a secondary dopant to it.

Methylene Blue (MB) is an intensely colored compound which is used in dyeing and printing textiles and is a common water pollutant. In this study an attempt was made to investigate the effect of operational parameters on the photocatalytic degradation of MB in the presence of Cr–Ti binary oxide with 10% molar Cr^{3+} (Ti–10Cr) catalyst. The degraded products were analyzed by using the LC–UV/vis–MS technique.

2. Experimental

The dye under investigation namely Methylene Blue (MB), with a labeled purity of more than 90% was obtained from Sigma–Aldrich and used as such. Deionized water was used to make the dye solutions of desired concentration.

2.1. Catalyst preparation and characterization

Cr–Ti binary oxide with 10% molar Cr^{3+} content (Ti–10Cr) was prepared by sol–gel method according to a procedure described in details elsewhere [13]. In a typical experiment, 6.0 mL (1.76×10^{-2} mol) of Cr^{3+} as chromium (III) nitrate was added gradually to the titanium butoxide solution and the mixture was stirred for 1 h after which 1.0 mL of water was added for hydrolysis. The mixture was stirred for 4 h during which a light green gel was formed which was left standing for 24 h for complete gelation. The

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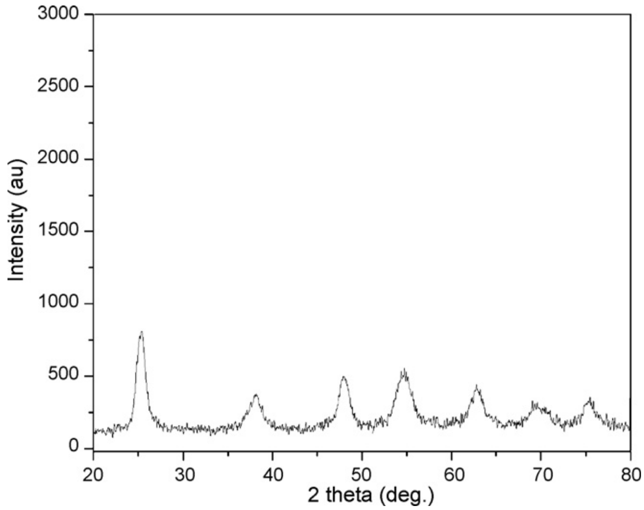
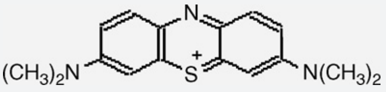


Fig. 1. XRD spectra of Ti–Cr-10 catalyst, Ref. [13].

Table 1
Physical characteristics and molecular structure of Methylene Blue[a].

Dye name	Methylene Blue
Suggested name	Methylene Blue
Abbreviation	MB
C.I. name	Basic Blue 9
C.I. number	52015
Class	Thiazin
λ_{max}	668 nm
Color	Blue
Empirical formula	$C_{16}H_{18}N_3SCl$
Formula weight	319.9 g/mol
Molecular volume (cm^3/mol)	241.9
Molecular diameter (nm)	0.80
Molecular structure	

[a] http://stainsfile.info/StainsFile/dyes/dyes.htm.

solvent was then removed by evaporation in air at 75 °C using a water bath. The solid product was finally dried in an oven at 120 °C for 2 h followed by calcination at 500 °C for 5 h resulting in the final form of a mixed catalyst.

The XRD spectra of the composite after calcinations at 500 °C is shown in Fig. 1 depicts the typical pattern of anatase TiO_2 only, indicating the absence of any segregated chromium oxide and complete dispersion of the chromium ions in the titania matrix. The crystallite size estimated from a TEM micrograph was around 9 nm. The BET surface area of this catalyst was found to be 90 m^2/g by the nitrogen adsorption method, whereas the total pore volume (for pore <100) after calcinations at 500 °C was 0.073 cm^3/g and average pore diameter (for pore <100) after calcinations at 500 °C was 3.3 nm.

2.2. Photodegradation of dye

Dye stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water. A given amount of the catalyst (Ti–10Cr = 0.16 mg) was added to 250 mL of this diluted solution (Methylene Blue = 5×10^{-6} M). The contents of the dye solution were allowed to equilibrate for a given time (usually 15–30 min) in the dark before irradiation. The samples were then irradiated with a UV lamp (UVGL-58, J-129, Upland make) as shown in Fig. 2. The instrument operates at 0.12 A with a UV output at 365 and 254 nm, however, the lamp was used in the 254 nm output mode for these studies. During irradiation, the contents of the solution were agitated continuously so as to maintain a homogeneous environment. After a certain time interval, the cell was drawn away from the UV light and centrifuged and the absorbance of the supernatant solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the rate of decoloration. UV/vis studies were done on a CARY UV/vis spectrophotometer, using a 1 cm quartz cell. Absorbance measurements were recorded in the range of 200–800 nm, and the maximum absorption wavelength experimentally registered at λ = 668 nm for the dye (MB) was used for the calibration curves and further concentration measurements.

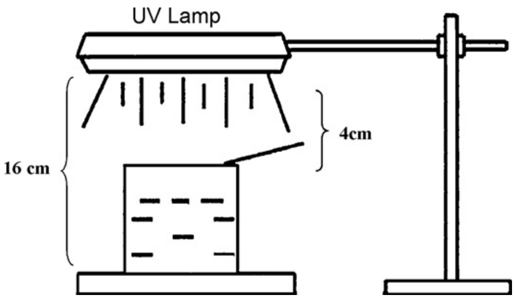


Fig. 2. Apparatus for carrying out photolytic studies of dye solution (container size = 500 mL).

2.3. Product analysis and identification using LC–UV/vis–MS studies

The chromatographic experiments with HPLC–UV/vis system were carried out on a HP 1100 liquid chromatograph (Agilent, USA) using a binary solvent gradient pump and an automatic injector. The dye degradation products were separated by using Agilent Zorbax® SB-C_{18} column 150 mm × 4.6 mm packed with 5 μm particle size. The detection system was a diode array detector (Agilent, USA) with detection range between 200 and 780 nm. The signal acquired from the detector was recorded by HP Chemstation® software. The mobile phase consisted of two solutions namely A and B. Solution A was made from 0.1 M ammonium acetate and acetic acid (pH 5.3), whereas solution B was acetonitrile. The gradient elution was from 5% to 95% in 30 min, the flow rate was 0.8 mL/min and the injection volume was 100 μL.

The gradient HPLC separation was coupled with, ion trap mass spectrometer (Agilent Technologies). The mass spectrometer was equipped with an electrospray ionization source and operated in positive polarity. The ESI conditions were as follows: capillary voltage: 3.5 kV, endplate offset was fixed at 500 V; skimmer at 40 V; trap drive at 53 V; the nebulizer pressure was 70 psi; drying gas flow was 12 L min^{-1} and the drying temperature was 350 °C. The mass range was from 50 to 700 m/z. Tandem MS experiment was done using the Auto MS^n mode wherein Helium gas was used as a collision gas.

3. Results and discussion

In the present work, decoloration and kinetic behavior of Methylene Blue (MB) was investigated followed by product characterization using the LC–UV/vis–MS technique. The structure of the dye is given in Table 1. The λ_{max} value for this dye is 668 nm. For decoloration studies, the λ_{max} of the dye was chosen for further investigations. Initially, experiments were carried out in the absence and presence of either UV light or the catalyst alone. The results showed that either UV light or catalyst alone were not sufficient for the decoloration of this dye.

3.1. Decoloration of dye solution

Dye solution of known concentration was prepared in water and subjected to UV light in the presence of a given amount of a catalyst (either neat TiO_2 or mixed catalyst). The change in the absorption spectra of the dye solution was monitored at regular intervals of time. It was noted that the absorption value of dye became less with irradiation time, thus indicating the decoloration of dye solution. The decrease in absorption value of dye solution can be related in terms of the photodegradation efficiency (η) which was evaluated by using the following relationship [3]:

$$\eta = \left(1 - \frac{A_0}{A_t}\right) \times 100 \tag{1}$$

where A_0 represents the initial absorbance of dyes solution and A_t represents the absorbance of the dye at time t.

3.2. Mechanism of dye decoloration

The photocatalytic decolouration of dyes is well documented in the literature and is believed to involve $^{\bullet}OH$ radicals which are produced in a series of reactions. These radicals then attack the dye molecule and causes it to degrade [14]. In cases where TiO_2 is used as a catalyst, the low photoactivity of the catalyst is believed to be the result of fast recombination of photogenerated electrons and holes. Structural imperfections in the TiO_2 lattice such as spatial distribution of crystallite size, microstrain and crystal orientation may generate trap sites which can act as recombination centers, leading to a decrease in the electrons and holes concentrations.

On the other hand, doping semiconductors with certain transition metal ions improves the electron trapping and inhibits electron–hole recombination. In this case, the presence of transition metals increases the photocatalytic activity either by scavenging electrons that reduces the recombination of charges and therefore favors the $^{\bullet}OH$ formation, or by modifying the surface properties of the material regarding the active sites, presence of defects, etc., which eventually increases the adsorption and favors the interfacial reactions.

The photocatalytic activity of TiO_2 can be enhanced by retarding the electron–hole recombination. The principal method of slowing down the electron–hole recombination is through the incorporation of electron accepting species on the TiO_2 surface such as Mn^{2+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, SiO_2 and V_2O_5 [15–17]. In mixed systems, the degradation of dye is faster than in the single system because the oxidation of dye consumes photo-excited holes promptly and efficiently, thus attenuating electron–hole recombination. In mixed systems this might perhaps be because the recombination is increased by crystallite defects.

Doping with transition metal ions is interesting for inducing a batho-chromic shift of the band gap. The band gap energy is shifted by 2.00 eV in the case of chromium doping [18]. This can be explained by the excitation of an electron of Cr^{3+} into the conduction band of TiO_2. For any photocatalytic reaction, the lifetimes of electrons and holes must be long enough to allow them to reach the surface of the photocatalyst. The addition of transition metal ions produces new trapping sites which affect the lifetime of the charge carriers. A lifetime of 89.3 ms has been reported for pure titania, whereas doping reduces this lifetime to about 30 ms in the case of Cr^{3+} and to about 20 ms with Mo^{5+} [18]. When Cr^{3+} are present in the matrix, the ions are initially oxidised by holes (h^+):

$$Cr^{3+} + h^+ \rightarrow Cr^{4+} \tag{2}$$

followed by the reduction of immobilised holes by free electrons (e^-):

$$Cr^{4+} + e^- \rightarrow Cr^{3+} \tag{3}$$

The above reaction is possible because the potential of the redox pair Cr^{3+}/Cr^{4+} is higher than the potential of the valence band of titania [18].

The above reaction scheme can also be well supported by the photocatalytic chromium cycle which has been reported in the literature [19]. In this cycle, both the main forms of chromium, i.e., Cr(VI) and Cr(III), undergo the photochemical reduction, and the secondary thermal processes are responsible for the ultimate Cr(VI) to Cr(III) reduction or Cr(III) to Cr(VI) oxidation. The re-oxidation of photoreduced chromium species takes place with molecular oxygen. In the photocatalytic degradation process, organic matter, molecular oxygen and UV light are consumed in the chromium cycle, whereas the Cr(III)/Cr(VI) compounds form the catalytic system, which enable the atmospheric oxygen to oxidize and thus degrade organic pollutant.

Table 2
Change in % decoloration of Methylene Blue (MB) with concentration (Ti–10Cr catalyst = 0.16 g/250 mL, time of irradiation = 240 min, pH = 7).

[Dye] (mol/L)	% Decoloration
5×10^{-6}	70
1×10^{-5}	64
2.5×10^{-5}	57
4×10^{-5}	53

Table 3
Change in % decoloration of Methylene Blue with the amount of Ti–10Cr catalyst (Methylene Blue = 5×10^{-6} M, time of irradiation = 240 min, pH = 7).

Catalyst (g/250 mL)	% Decoloration
0.10	60
0.13	65
0.16	70
0.18	66

3.3. Effect of operational parameters on dye degradation

The effect of dye concentration, catalyst amount and pH effect has been reported for various dye degradation studies. These parameters were also studied in the present case and the results are shown in Tables 1–3. Under the experimentally optimized conditions of MB = 5×10^{-6} M, catalyst amount = 0.16 g/250 mL and pH = 7, it was found that 70% of the dye (Methylene Blue, MB) could undergo degradation in 240 min in the presence of Ti–10Cr catalyst as compared to merely 17% degradation in the presence of TiO_2 alone. The present findings on the use of Cr^{3+} doped titania can be supported from the literature review, wherein, it was shown that Rhodamine B undergoes 25% more degradation in the presence of 10% Cr^{3+} doped titania as compared to one in neat titania [18]. At chromium concentrations below 1%, both the lifetime and photocatalytical activity were reported to decrease drastically to a nearly constant low level. The reason for this is that at low concentrations of Cr^{3+}, these ions can occupy regular lattice sites which act as traps. However, at higher ion concentrations of Cr^{3+} ions, the interstitial sites are filled up and thus do not contribute to the recombination [18]. In the present study, higher concentration of chromium ions

Table 4
Effect of pH on Methylene Blue (MB) decoloration (MB = 5 μM, catalyst = 0.16 g/250 mL, irradiation time = 240 min).

pH Value	% Decoloration (240 min)
2	55
7	70
11	60

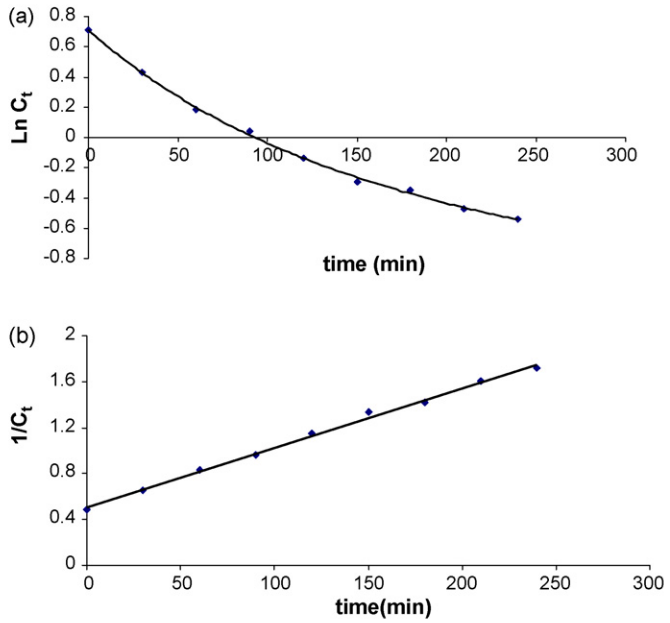


Fig. 3. First-order (a) and second-order (b) plot for the kinetic photodegradation of MB in the presence of Ti–10Cr catalyst

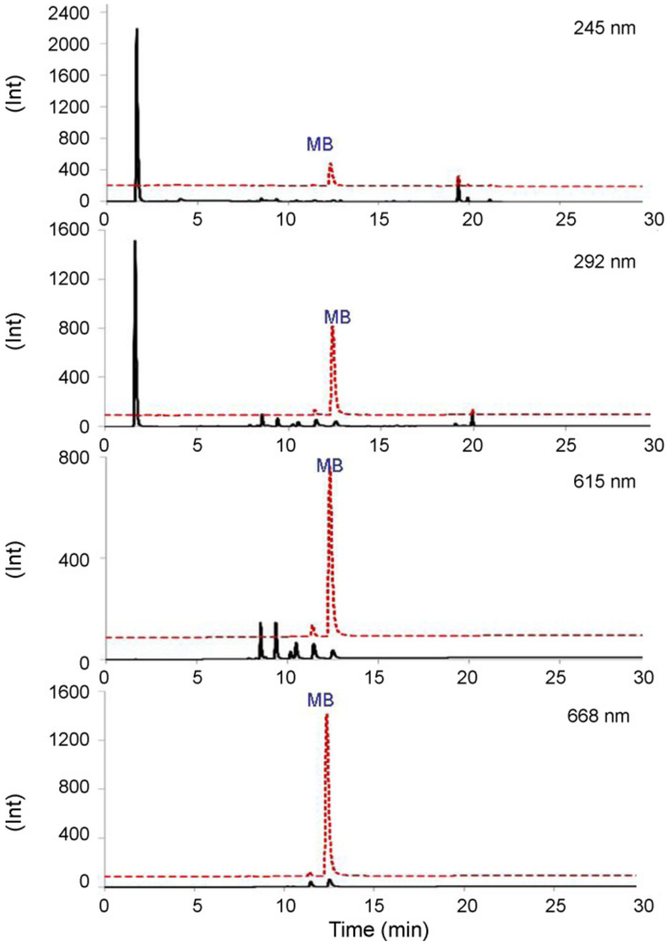


Fig. 4. HPLC chromatograms of Methylene Blue before (- - -) and after (__) photocatalytic degradation monitored at the following wavelengths: 245, 292, 615 and 668 nm ([MB] = 5×10^{-6} M, catalyst = 0.16 g/250 mL).

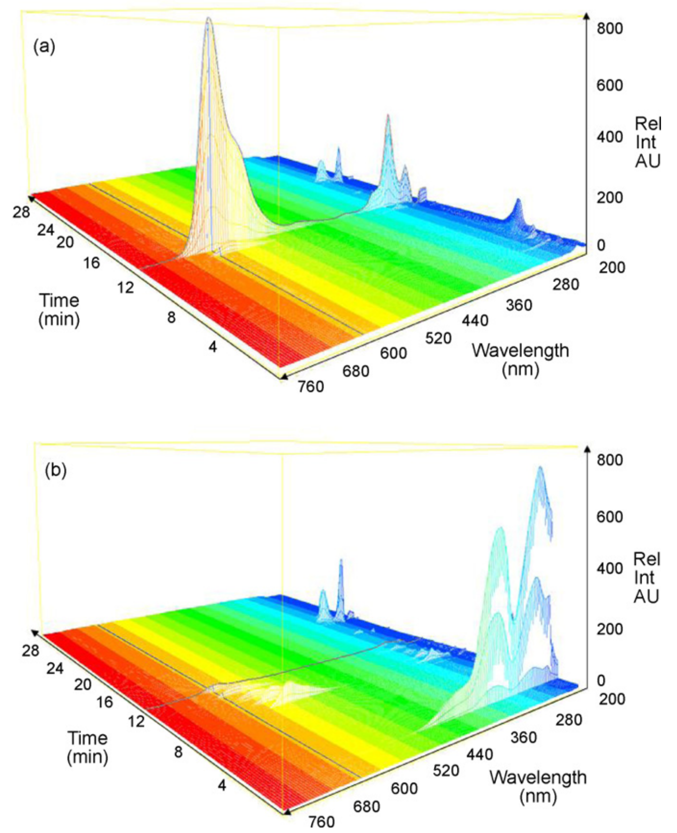


Fig. 5. Three-dimensional plot of HPLC chromatograms with UV/vis analysis of Methylene Blue dye (a) before photocatalytic degradation and (b) after photocatalytic degradation ([MB] = 5×10^{-6} M, catalyst = 0.16 g/250 mL).

was used so that they are completely dispersed into the titania lattice. The 10% of chromium was selected for two reasons: (1) based on characterization of lower and higher chromium contents, it was found that up to 10% Cr^{3+} could be well dispersed in the titania lattice without the formation of any crystalline chromium oxide, (2) 10% chromium resulted in higher surface area than other compositions and also that the anatase phase is retained which is known to be the most catalytically active phase of titania [13] (Table 4).

The average decolorization rate (μg/h) under optimized conditions was also calculated as follows [20]:

$$\text{Average decoloration rate} = \frac{C \times \%D \times 1000}{100 \times t} \tag{4}$$

where C is the initial concentration of dye (mg/L) and D is the dye decoloration (%) after time t (h). In this experiment the average decoloration rate was found to be 276 μg/h.

3.4. Kinetics of photocatalytic decoloration

The decoloration of dye solutions was also subjected to kinetic analysis. Firstly, the data was subjected to first-order-kinetics, which in its usual form is given by

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{app}} \times t \tag{5}$$

where C_0 is the initial concentration value of the dye, C the concentration at time t and k_{app} is the apparent rate constant. A plot of $\ln C$ versus time (t) was plotted as shown in Fig. 3(a). A downward concave curvature observed in this case indicates that first-order-kinetics can be ruled out. However, a linear relationship was observed using the pseudo-second-order-kinetic rate expres-

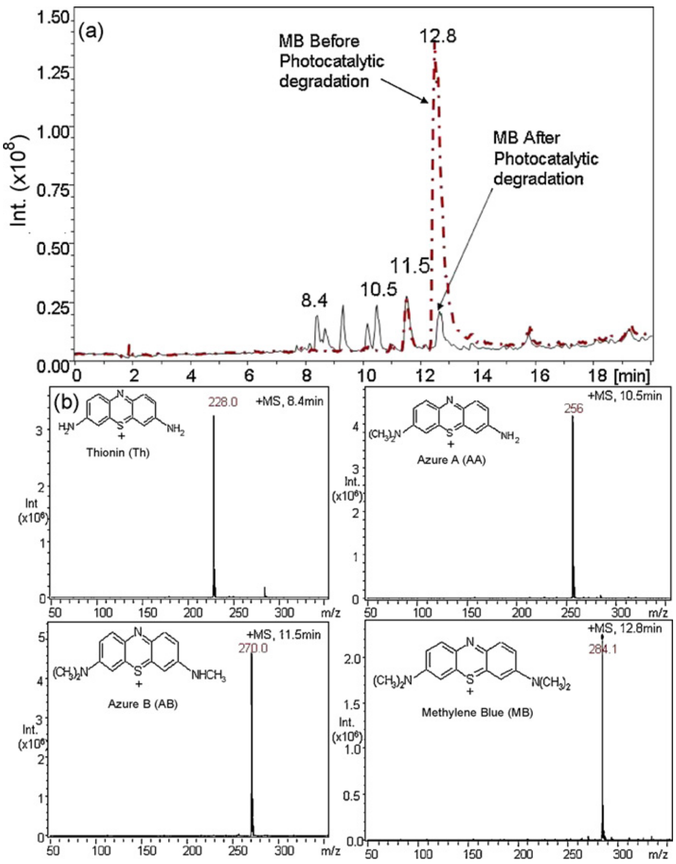


Fig. 6. (a) LC–MS profile of Methylene Blue dye before (—-) and after photocatalytic degradation. (b) Mass spectra of the major detected degradation intermediates eluting at 8.4, 10.5, 11.5 and 12.8 min. ([MB] = 5 × 10^{-6} M, catalyst = 0.16 g/250 mL).

sion [21]:

$$\frac{1}{C_t} = \frac{1}{C_0} + k_{\text{app}} \times t \tag{6}$$

A linear fitting of the data between $1/C_t$ and irradiation time (t) for the dye to the above equation confirmed the applicability of this model with a correlation coefficient value of 0.9961 as shown in Fig. 3(b). The apparent rate constant (k_{app}) obtained from the slope of the plot was 5.2×10^{-3} min^{-1}. A possible explanation for second-order photocatalytic degradation kinetics is the aggregation or dimer formation with increasing MB dye concentration [22]. Similar behavior of second-order-kinetics was also reported in the case of Safranin Orange photodegradation with ZnS and CdS nanoparticles and was explained on the basis of dimerization of the dye under investigation [23].

3.5. LC–UV/vis–MS studies for product analysis

The chromatographic separation of the dye solution recorded initially and after 4 h of photocatalytic treatment was monitored simultaneously at different wavelengths and is shown in Figs. 4 and 5. This experimental data implies that at the end of 240 min irradiation, the wastewater was significantly decolorized or degraded. This is evident by the decrease in the Methylene Blue (MB) peak intensity and the appearance of new peaks detected at lower retention times which correspond to new photocatalytic products of the dye. Consequently, photocatalysis of dye solutions not only caused its decoloration, but also an appreciable degree of destruction in the dye molecule.

Methylene Blue (MB) shows one main band in the visible region, with its maximum absorption at 668 nm with a small shoulder at 615 which is due to dye dimmer [24,25], and two bands in the ultraviolet region located at 245 and 292 nm. The conjugation system between the two dimethylamine substituted aromatic rings through the sulfur and nitrogen is responsible for the absorbance at 668 nm, while the small shoulder at 615 nm has been reported to be due to the absorbance of the dye dimmer; whereas, the substituted benzenes rings have their absorption bands in the ultraviolet region. It was clearly observed that the absorption peak at 668 nm diminished very fast. This indicated a rapid degradation of Methylene Blue (MB) which can be achieved more easily in the presence of Ti–10Cr/UV. The visible band of the Methylene Blue (MB) dye at 615 nm was observed to diminish gradually and at the same time few new bands started showing up at lower retention times (Fig. 4). This indicated the destruction of the parent compound and formation of new compounds that are structurally close to the parent compound with a small structural difference such as one with lesser methyl groups.

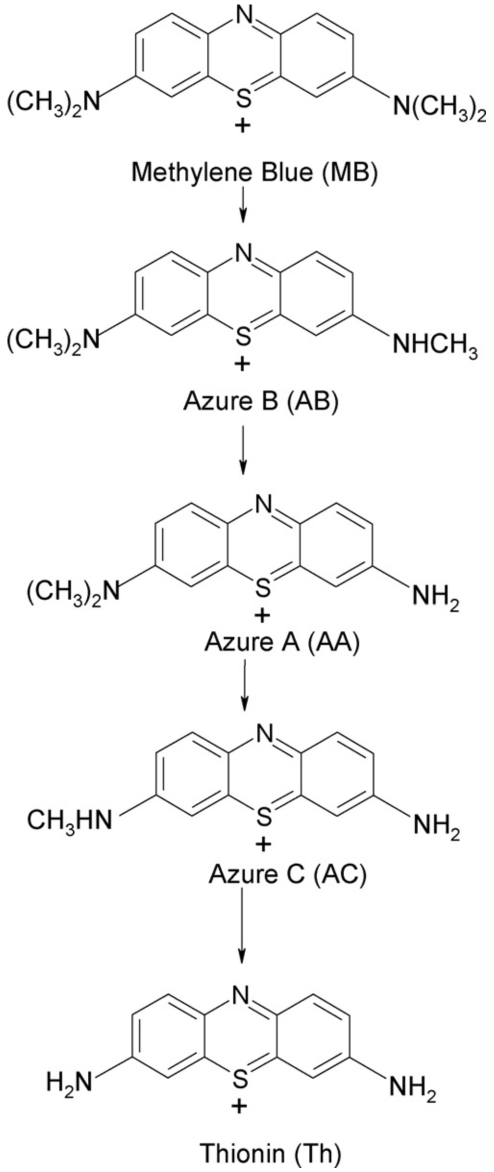


Fig. 7. Demethylation of Methylene Blue dye during photocatalytic degradation process.

To gain insight on the Methylene Blue (MB) dye degradation, the changes in the absorbance values of the dye solution before and after 240 min of irradiation in the wavelength range 200–780 nm as a function of time were plotted in a 3D fashion as shown in Fig. 5.

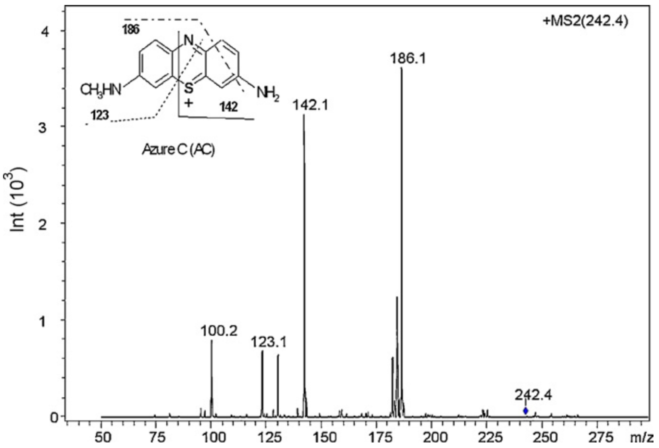


Fig. 8. Tandem mass spectrum of Methylene Blue intermediate degradation product ion m/z 242.

A clear comparison can be seen from this figure in terms of the changing composition of various species which are being formed in different time intervals. One can see a decrease in the absorbance value of the parent molecule with time, while new peaks emerge in the spectra which were collected after 240 min of photocatalytic degradation, thus indicating the formation of some new compounds. The degradation of the dye may possibly be suggested by the qualitative analysis of the samples studied by HPLC before and after photocatalytic degradation. From peak area calculations, it was found that very little dye has survived the degradation process. The amount of dye mineralization was estimated to be 48% as calculated from the peak areas in the HPLC chromatogram, while the remaining 52% of the degraded products were due to intermediate products that were detected at different wavelengths in the HPLC experiment; the later percentage was estimated through the summation of peak areas of the new degradation intermediates detected at various wavelengths.

Further analysis of product formation was done by mass spectroscopic (MS) studies of the degradation intermediate products and the results are shown in Fig. 6. Many peaks of different intensities were observed in addition to the peak of Methylene Blue dye, which indicate the variation in the composition and concentration of the degradation products. Studying some of these intermediate masses and predicting their structure by the cleavage of one or more of the methyl groups substituent on the amine groups, lead to intermediate products that agree in their masses with the eluted intermediates. For instance, the formation of azure A, B and C and thionin (Fig. 7) through the demethylation cleavage during the photocatalytic degradation has been reported in the literature [25,26]. Fig. 6(b) shows the mass spectra of the intermediate degradation products separated at different retention time with the suggested structures. The intermediates structures were confirmed by tandem mass spectrometric analysis, whereas Fig. 8 shows the MSMS spectrum of intermediates with a mass of 242 Da.

4. Conclusion

Cr–Ti catalyst with 10% Cr^{3+} content (Ti–10Cr) was prepared by sol–gel method and used to degrade Methylene Blue (MB) dye in the presence of UV light. The photodegradation of the dye molecules in the presence of this catalyst followed the second-order-kinetics with a degradation efficiency of 70%. The degraded products were analyzed by using the LC–UV/vis–MS technique and it was found that the dye initially undergoes demethylation resulting in the formation of some intermediate products. The intermediates structures were confirmed by tandem mass spectrometric analysis.

Acknowledgments

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