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Photocatalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using Ag^+ doped TiO_2

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Abstract

The photocatalytic degradation of a mixture of two dyes: Crystal Violet (CV), also known as C.I. Basic Violet 3, which is a cationic triphenylmethane dye and Methyl Red (MR), which is an anionic azo dye was studied using untreated TiO_2 and silver ion doped TiO_2 under UV irradiation. To increase the photocatalytic efficiency of TiO_2 and to make its separation from the treated effluent after degradation easier, it was doped with silver ion using liquid impregnation method. The degradation of the dyes in the mixture was measured spectrophotometrically at their respective λ_{max} values. The degradation kinetics fitted well to the Langmuir–Hinselwood pseudo first order rate law. The effects of pH and different interfering substances like Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, Ca^{2+}, Fe^{2+}, humic acid, O_2 and electron acceptors like H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ on the degradation were also investigated. Several mixtures of these dyes prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the V/V ratios of 1:1, 1:5 and 1:10 degraded by >99% on UV irradiation for 90 min in the presence of Ag^+ doped TiO_2 and about 70% under similar conditions in presence of TiO_2. COD removal was measured at regular intervals to quantify the mineralization of the dye. Above 86% mineralization was observed using 90 min irradiation.

Keywords: Ag^+ doped TiO_2; Crystal violet; Dye degradation; Methyl red; Photocatalytic

1. Introduction

The removal of colour from the wastewater coming from different industries is a current issue of discussion and regulation all over the world [1,2]. Dyes are used in many industries like textile, paper, plastic, leather, ceramic, cosmetics, ink, food processing etc [3]. There are many classes of dyes such as acidic, basic, neutral, azo, disperse, direct, reactive etc. [4]. Out of these dyes azo dyes are most frequently used. These contain one or more azo bonds (−N=N−) in their structure [5]. Triphenylmethane dyes are the next in the list. Some of these dyes are toxic and potentially carcinogenic [6]. About 15% of dyes of the total world production are lost during synthesis and processing with wastewater [7].

Several studies on the physical, chemical and biological degradation of dye containing wastewater have been reported in the literature [8,9]. Physical methods do not degrade the pollutants but they only transfer them from the liquid phase to the solid phase, thus causing secondary pollution. Chemical methods have been proved to be expensive as they require high dosage of chemicals and produce large quantity of sludge.

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Biodegradation of dyes has been shown to be ineffective [10–12].

Heterogeneous photocatalysis has been used in the recent years as a promising method for the removal of toxic organic and inorganic contaminants from industrial wastewater, since it not only degrades the pollutants but also causes their complete mineralization to CO_2, H_2O and mineral acids [13–15]. Out of the various semiconductor photocatalysts used TiO_2 has been found to be the most suitable because of its non-toxic, insoluble, inexpensive and highly reactive nature [16]. The main disadvantage of this method is the separation and recycling of the fine catalyst particles from water after dye degradation. The rapid recombination of electron–hole pair also limits the efficiency of TiO_2. To eliminate the above difficulties the photocatalyst is sometimes immobilized on a transparent support [17] or is doped with small concentration of metal or metal ion [18]. Immobilization decreases the photocatalytic efficiency of TiO_2 whereas metal or metal ion doping enhances it decreasing the recombination of electron–hole pair.

There are very limited studies on the degradation of mixture of dyes. Hence the photocatalytic degradation of a mixture containing Crystal Violet (CV), a cationic dye and Methyl Red (MR), an anionic dye using silver ion doped TiO_2 under UV irradiation is undertaken in the present study. Both the investigated dyes are extensively used in the textile, paper and leather industries and medicines. Both are mutagen, mitotic poisons and suspected carcinogens [19]. TiO_2 has been doped with silver ion in order to improve its photocatalytic efficiency and settleability. Silver ion doping is done by liquid impregnation method [20]. The dyes are mixed in various ratios and their degradation is investigated. The degradation is investigated under varying pH and also in the presence of common interfering substances. COD removal is studied to examine the extent of mineralization. The effects of various electron acceptors like H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ on the degradation are also studied.

2. Materials and methods

2.1. Materials

CV was purchased from BDH, England and MR was from Merck India. Their molecular structures are shown in Fig. 1a and b, respectively. The photocatalyst used was titanium dioxide obtained from Merck India, mainly anatase of average particle size about 1 μm (from SEM). All the solutions were prepared using double distilled water. The catalyst was doped with silver ion using silver nitrate (99.9% pure) from S.D. Fine Chem. Other chemicals used in the study viz. NaOH, HNO_3, H_2SO_4, NaCl, Na_2SO_4, $NaNO_3$, Na_2HPO_4, $CaCl_2$, $FeSO_4$, $K_2Cr_2O_7$, $FeSO_4(NH_4)_2SO_4$, H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ were purchased from Merck India and were of analytical reagent grade. Humic acid was obtained from Aldrich.

2.2. Instrumentation

The following instruments viz., Systronics spectrophotometer 106, Thermo Spectronic UV1 spectrophotometer, UV fluorescent lamp (16 W), solar light simulating Philips tungsten-halogen lamp (250 W), JEOL JSM-5800 scanning electron microscope (SEM), Gallenkamp revolving centrifuge, Berghof COD digester, Cyberscan 510 digital pH meter, Remi magnetic stirrer and Sartorius electronic balance were used during the studies.

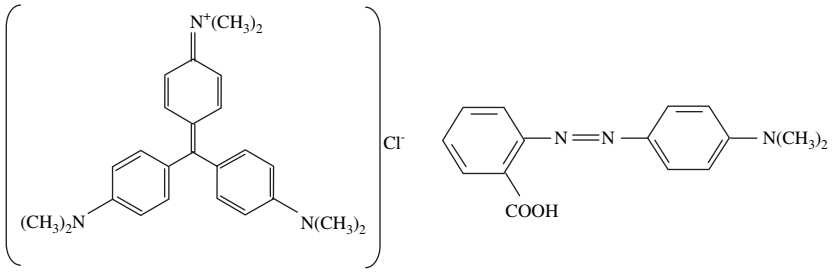
2.3. Preparation of photocatalyst

TiO_2 was doped with silver ion in 1% molecular ratio by dissolving 0.01 mol of $AgNO_3$ in 100 ml of water in a porcelain crucible and then adding 0.99 mol of TiO_2 to it with continuous stirring. The solution was then allowed to stand for 24 h and was heated at 100 °C for 12 h in an incubator to evaporate water out. The dried solids were ground in an agate mortar and calcined at 400 °C for 6 h in a muffle furnace [20]. This method is called liquid impregnation method. In this method the metal ions get deposited on the surface of the photocatalyst as conformed by the SEM analysis.

2.4. Experimental procedure

Each of the aqueous solutions of the mixture of CV and MR (60 ml) prepared by mixing CV solution (5×10^{-5} mol dm^{-3}) and MR solution (7.5×10^{-5} mol dm^{-3}) in the V/V ratio of 1:1, 1:5 and 1:10 was added with untreated TiO_2 and Ag^+ doped TiO_2 at a dose of 1 g/l and subjected to adsorption study by stirring in the dark. At regular time intervals aliquots were taken and centrifuged. The concentration of the two dyes in the mixture after adsorption was measured spectrophotometrically. Direct photolysis of the mixture was also studied by subjecting it to UV irradiation in the absence of photocatalyst.

The experimental set up for photocatalytic degradation consisted of a 500 ml borosil beaker placed on a magnetic stirrer above which a low pressure UV fluorescent light (16 W) emitting UV light of wavelength ~ 365 nm was placed. The height and the diameter of the beaker was 12 cm and 8 cm, respectively. Aqueous solutions (60 ml) of the mixture of dyes CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) mixed in the V/V ratio 1:1, 1:5 and 1:10 were taken in the beaker and Ag^+ doped TiO_2 (1 g/l) and untreated



(a) (b)

Fig. 1. Structure of: (a) Crystal Violet and (b) Methyl Red.

TiO_2 were added separately to them. The depth of the dye solution in the beaker was 1.7 cm and the distance of the light source from the upper level of dye solution was 10.5 cm. The solutions were stirred in the dark for 30 min to establish the adsorption equilibrium. The zero time readings were then taken and the solutions were irradiated. Aliquots were taken at 15 min time intervals and centrifuged to separate the catalyst from the solution. The solutions were then analysed spectrophotometrically.

2.5. Analysis

The percent degradation of CV and MR in the mixture was found out spectrophotometrically at their respective λ_{max} of 590 nm and 430 nm at pH 6.4 (pH of the reaction mixture). To quantify the extent of mineralization of the mixture, COD was measured at regular time intervals using closed reflux titrimetric method [21]. The pH of the solution was adjusted using 1 N HNO_3 and 1 N NaOH solutions. After complete degradation the effluents were tested for the presence of silver ion by the addition of 1 N NaCl solution and observing the precipitate if any [22].

3. Results and discussion

3.1. Catalyst characterization

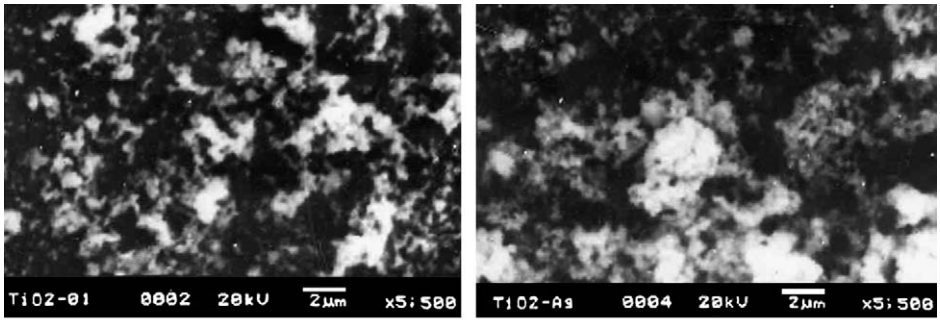
Both the photocatalysts TiO_2 and Ag^+ doped TiO_2 were characterized by the scanning electron microscope to determine the average particle size and chemical composition of TiO_2 and Ag^+ doped TiO_2. The micrographs taken at 5500 times magnification are shown in Fig. 2a and b. The average particle size was found to be about 1 μm. The compositions of TiO_2 and Ag^+ doped TiO_2 were found to be as follows:

TiO_2: Si − 1.84% (atomic); Ti − 98.16% (atomic).
Ag^+ doped TiO_2: Si − 1.73% (atomic); Ti − 97.32% (atomic); Ag − 0.95% (atomic).

The above analysis shows that all the silver ions added are deposited on the surface of TiO_2.

3.2. Study of absorption spectra

From the absorption spectra of CV (5×10^{-6} mol dm^{-3}) and MR (3.75×10^{-5} mol dm^{-3}) taken separately (Fig. 3a) and mixture of CV (5×10^{-6} mol dm^{-3}) and MR (3.75×10^{-5} mol dm^{-3}) (Fig. 3b) it is evident that the λ_{max} and maximum absorbance values of both CV and MR do not change on mixing. There are two distinct peaks for CV and MR. Therefore the degradation of CV and MR in the mixture can be studied separately at their corresponding λ_{max} values of 590 nm and 430 nm. The molar extinction coefficients of CV and MR are 362,533 and 19,233 at the above wavelengths and pH of the reaction medium 6.4. The degradation of two dyes and also their mixture have been tested separately and no interference has been found.



(a) (b)

Fig. 2. SEM micrographs of: (a) TiO_2 and (b) Ag^+ doped TiO_2.

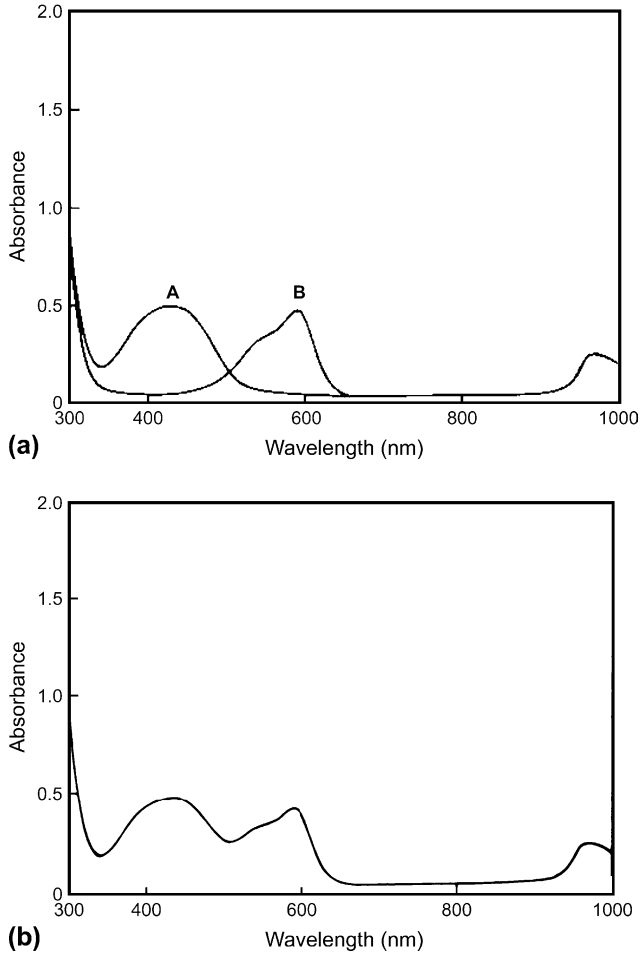


Fig. 3. Absorption spectra of: (a) MR (curve A) and CV (curve B) and (b) mixture of CV and MR.

3.3. Adsorption and direct photolysis

The mixtures prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the V/V ratios of 1:1, 1:5 and 1:10 did not undergo any observable adsorption on to the photocatalyst surface on stirring magnetically in the dark for 1 h. The mixture upon direct photolysis by stirring magnetically and UV irradiation in the absence of the photocatalyst showed no observable degradation after 2 h.

3.4. Photocatalytic degradation

All the solutions prepared by mixing CV and MR in different ratios (1:1, 1:5 and 1:10 V/V) degraded by >99% on 90 min UV irradiation with Ag^+ doped TiO_2 (1 g/l) (Fig. 4a–c). The photocatalyst completely settled on standing for 12 h. The degradation of the above mixture of dyes was also tested with untreated TiO_2 (1 g/l) and was found to be about 70% after 90 min. The mixture, 1:5 V/V, degraded by >85% on irradiation for 12 h by a simulated solar light source with Ag^+ doped TiO_2 (1 g/l). At the start of the photocatalytic degradation the pH was measured, it was ~6.4. But during the process of degradation the pH decreased and at the end it was measured to be ~5.3.

When a photon of UV light strikes the TiO_2 surface, an electron from its valence band jumps to its conduction band creating a positively charged hole in the valence band. The conduction band electrons and the valence band holes so formed then migrate to the surface of TiO_2 where they react with the chemisorbed O_2 and/or OH^-/H_2O molecules to form reactive oxygen species such as $O_2^{\cdot -}$, $HOO^{\cdot}$, and $OH^{\cdot}$ radicals, which attack dye molecules successively to cause their complete degradation and mineralization. Alternatively, the

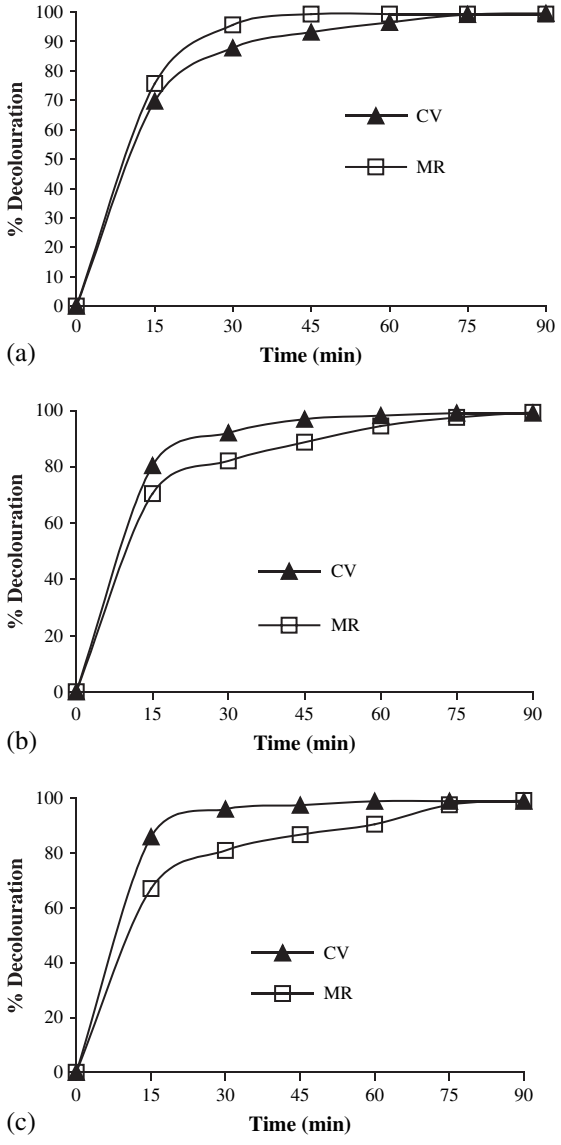


Fig. 4. Kinetic studies on the photocatalytic decolouration of mixtures prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the V/V ratio of: (a) 1:1, (b) 1:5 and (c) 1: 10; pH: 6.4; temperature: 30 ± 2 °C; Ag^+ doped TiO_2: 1 g/l.

electrons in the conduction band can be picked up by the adsorbed dye molecules, thus forming dye radical anions. Subsequent reaction of the above anions with the photocatalyst can lead to the degradation of the dye. The dye molecules are usually photoactive. Also the adsorbed dye molecules may be directly oxidised by the valance band holes to form dye radical cations, which ultimately cause dye degradation. The enhancing effect of Ag^+ may be explained by its ability to trap electrons. They act as electron scavengers. This process reduces the recombination of charges and favors oxidation of substrate by producing more $OH^{\cdot}$ [23]. The reduction potential of silver ion is suitable positioned for the effective photocatalytic reduction $Ag^+ + e^- \rightarrow Ag^0$ producing metallic silver on TiO_2 surface. Thus it was observed that the catalyst slightly darkens during the irradiation [20]. The enhancing effect may also be due to intermediate Fenton type reactions:

$$Ag^+ + H_2O_2 \rightarrow Ag^+ + OH^{\cdot} + OH^- \quad (1)$$

However, high concentration of metal decreases the photocatalytic property of TiO_2 due the filter effect.

3.5. Reaction mechanism

A semiconductor is characterized by an electronic band structure in which the highest occupied energy band of a semiconductor called valence band (vb), and the lowest empty band, called conduction band (cb), are separated by a band gap. Heterogeneous photocatalysis is a process in which a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle like TiO_2 promoting an electron from the vb to the cb with simultaneous generation of a hole (h^+) in the vb. The e^-_{cb} and the h^+_{vb} can recombine on the surface or in the bulk of the particle in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. Thereby, subsequent anodic and cathodic redox reactions can be initiated. Generally, A is dissolved O_2, which is transformed in to super oxide radical anion ($O_2^{\cdot -}$) and can lead to the additional formation of $OH^{\cdot}$. D is the adsorbed dye molecule or other organic contaminant. Great discussion exists nowadays about the oxidative pathway, which could be performed by direct hole attack or mediated by $OH^{\cdot}$ radicals, in their free or adsorbed form. The oxidative pathway leads, in many cases, to complete mineralization of an organic substrate to CO_2 and H_2O.

3.6. Kinetic analysis

The dependencies of the rate of dye degradation on its concentration as irradiation proceeds have been described well by the Langmuir–Hinshelwood kinetic model [24].

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (2)$$

As KC is very small as compared to 1, neglecting KC in the denominator and integrating with respect to time t, the above equation can be simplified to the pseudo first order kinetic equation

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t \quad (3)$$

where r = the rate of dye degradation (ppm/min); C_0 = the initial concentration of the dye (ppm); C = the concentration of the dye at time t (ppm); t = the irradiation time (min); k = the reaction rate constant (min^{-1}); K = the adsorption coefficient of the dye onto the photocatalyst particle (l/mg).

The kinetic curves for the degradation of the aqueous solution prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the V/V ratio of 1:5 with Ag^+ doped TiO_2 (1 g/l) shown in Fig. 5 follow pseudo first order kinetics with respect to both CV and MR as confirmed by the linear transform $\ln(C_0/C) = k_{app}t$. The apparent rate constants calculated from the above curves were as follows:

At λ_{max} 590 nm (for CV): $k_{app} = 0.0688\ min^{-1}$, $R^2 = 0.94$.
At λ_{max} 430 nm (for MR): $k_{app} = 0.0502\ min^{-1}$, $R^2 = 0.97$.

3.7. COD measurements

The COD of the remaining dye in the solution was measured at regular intervals to examine whether the dye was mineralized on photodegradation and to what extent. The aqueous solutions of a mixture of CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in

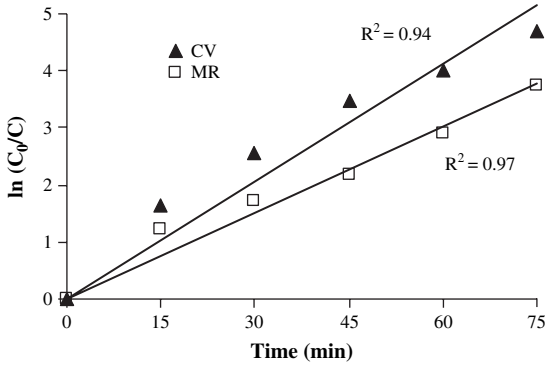


Fig. 5. Kinetic analysis at λ_{max} 590 nm (CV) and 430 nm (MR).

1:1, 1:5 and 1:10 V/V ratio were exposed separately to UV irradiation in the presence of Ag^+ doped TiO_2 at a dose of 1 g/l. Aliquots were taken at 15 min interval and COD was measured using closed reflux titrimatric method. All the mixtures of dyes were mineralized by >86% after irradiation for 90 min. The mineralization of 'N' present in both the dyes may yield either of NO_3^-, NH_3 or N_2, whereas those of 'C', 'H' and 'O' may yield CO_2 and H_2O [25]. The plot of percent COD removal versus irradiation time is shown in Fig. 6.

3.8. Effect of pH

The mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1:5 V/V, was subjected to photocatalytic degradation for 90 min with Ag^+ doped TiO_2 (1 g/l) in the pH range of 3–13 under UV irradiation. Fig. 7 shows the percent degradation of the mixture of dyes at different pH. The degradation was monitored at λ_{max} values of 590 nm and 430 nm for CV and MR, respectively. For CV there was no influence of pH on the degradation in the entire range. While in case of MR the degradation although not influenced up to pH 10, but after that there was a steep decrease in the percent degradation with increase in pH. The pH of the solution is an important parameter in the photocatalytic reactions taking place on the surface of the particles as it dictates the charge on the particle surface and the size of the aggregate it forms. The zero point charge (pH_{zpc}) of Ag^+ doped TiO_2 is at pH 6.6 [26]. Hence at acidic pH the particle surface is positively charged and vice versa [26]. The decrease in degradation at higher pH value (at λ_{max} 430 nm) may be because MR is an anionic dye and at high pH values its negative charge is more pronounced. Hence there may be repulsion between the dye molecules and the catalyst particles. The pH was adjusted by adding 1 N HNO_3 and 1 N NaOH.

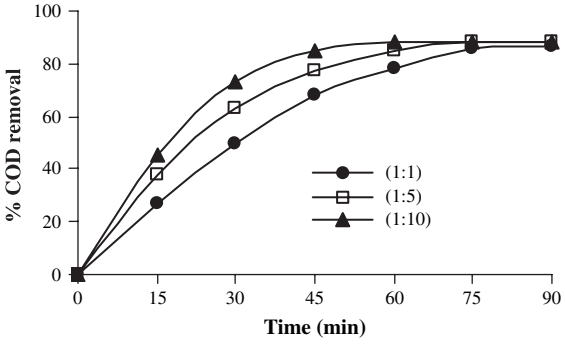


Fig. 6. COD removal on UV irradiation with time for the mixtures prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in 1:1, 1:5 and 1:10 V/V ratio; pH: 6.4; temperature: 30 ± 2 °C; Ag^+ doped TiO_2: 1 g/l.

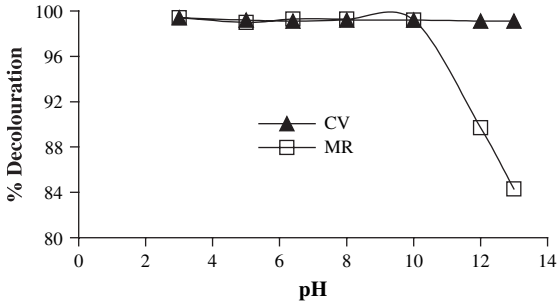


Fig. 7. Effect of pH on the photocatalytic decolouration of mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio 1:5 V/V; temperature: 30 ± 2 °C.

3.9. Effects of interfering substances

Aqueous solutions of the mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio 1:5 V/V, mixed separately with different interfering substances viz., Cl^- (0–1000 ppm), NO_3^- (0–1500 ppm), SO_4^{2-} (0–500 ppm), HPO_4^{2-} (0–500 ppm), Ca^{2+} (0–200 ppm), Fe^{2+} (0–200 ppm), humic acid (25 ppm) were subjected to photodegradation under UV irradiation for 90 min using Ag^+ doped TiO_2. The effects of these substances on the percent degradation of the two dyes in the mixture are shown separately in Fig. 8a–f. The dye degradations were monitored separately at their respective λ_{max} values of 590 nm and 430 nm. In the described range the degradation of CV was not affected by all the anions and humic acid while the cations inhibited it. But on the other hand Cl^-, Ca^{2+} and Fe^{2+} ions inhibited the degradation of MR while other ions did not influence it. In the presence of interfering ions the catalyst separated easily after degradation.

The inhibiting effect of Cl^- ion on the degradation of MR may be due to the reaction of the positive holes formed on the TiO_2 surface with the anions, which acts as hole scavengers resulting in prolonged degradation [27]. This may also be because of the fact that the adsorbed anions compete with dye for the photo-oxidising species on the surface of the catalyst thus preventing the degradation of the dye by oxidative species like $OH^{\cdot}$, $O_2^{\cdot -}$ [28,29]. The inhibiting effect of Cl^- only in case of MR but not in case of CV may be because it is an anionic dye whereas CV is a cationic dye. Degradation due to direct attack of hole is not possible in the case of cationic dye. The inhibiting effect of cations on the degradation of CV in the mixture may be because of the fact that CV is a cationic dye. It was noticed that during photocatalytic degradation in the presence of cations, the cationic dye did not colour the photocatalyst, although the phenomenon was observed during photocatalytic degradation without the cations. This means that addition of cations eliminates the possibility of the adsorption of dye on to the

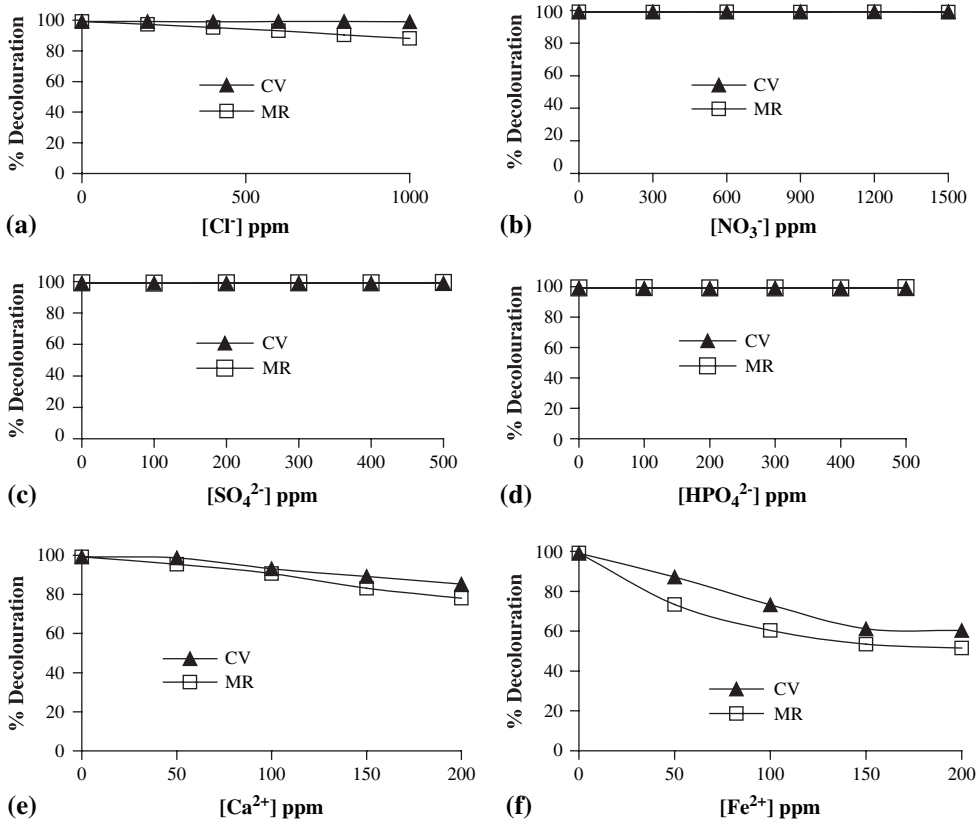


Fig. 8. Effect of: (a) Cl^-, (b) NO_3^-, (c) SO_4^{2-}, (d) HPO_4^{2-}, (e) Ca^{2+}, and (f) Fe^{2+} on the photocatalytic decolouration of mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1: 5 V/V; pH: 6.4; temperature: 30 ± 2 °C.

photocatalyst, which may be the cause of inhibition [30]. The anions did not affect the degradation of CV as it is a cationic dye and the positive charge on the catalyst surface is more pronounced at the reaction pH 6.4 (pH_{zpc} of Ag^+ doped $TiO_2 = 6.6$). The inhibiting effect of the cations on the degradation of MR may be either due to the competitive trapping of the oxidising species h^+ or $OH^{\cdot}$, or due to filter effect when salts significantly absorb UV light [30]. It may also be due to the formation of a coating of metal hydroxide on the surface of the photocatalyst [31]. To minimise the interference of the cations on the degradation of either of the dyes they were first masked by the addition of Na_2EDTA to the reaction mixture and then it was subjected to photocatalytic degradation for 90 min with 1 g/l of Ag^+ doped TiO_2. The masking was due to the complexation of cations with Na_2EDTA. In case of Ca^{2+} the interference was completely removed whereas in case of Fe^{2+} it was greatly reduced.

3.10. Effects of electron acceptors

Electron accepters such as H_2O_2 (300 ppm), $(NH_4)_2S_2O_8$ (300 ppm) and $KBrO_3$ (300 ppm) were added separately to the aqueous solutions of mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio 1:5 V/V ratio and they were subjected to photodegradation in the presence of Ag^+ doped TiO_2. The dye degradation in the presence of the above electron accepters after 15 min is shown in Fig. 9. It was observed that for CV H_2O_2 showed the maximum beneficial effect whereas for MR $KBrO_3$ showed the maximum beneficial effect. The photocatalysts did not have any effect on the two dyes under irradiation in the absence of Ag^+ titanium dioxide.

The enhanced degradation of CV in the presence of H_2O_2 could be due to the trapping of electrons by hydrogen peroxide thereby reducing the recombination of e^- and h^+ pairs and thus increasing the chances of formation of $O_2^{\cdot -}$, $HOO^{\cdot}$, and $OH^{\cdot}$ on the catalyst surface. The pronounced effect of bromate ion on MR degradation may be due to the change of reaction mechanism, since the reduction of bromate ions by electrons does not directly form hydroxyl radicals, but form other oxidising species like BrO_2^- and HOBr. Furthermore bromate ions by themselves can act as oxidising agents [32].

3.11. Photocatalytic degradation of synthetic textile effluent

Synthetic textile effluent was prepared by adding Cl^- (400 ppm), NO_3^- (600 ppm), SO_4^{2-} (100 ppm), HPO_4^{2-}

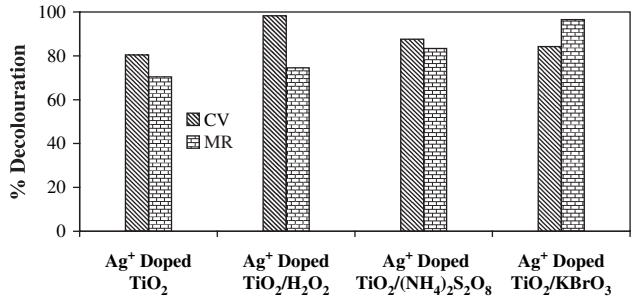


Fig. 9. Decolouration of mixture CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1: 5 V/V; pH: 6.4; temperature: 30 ± 2 °C; Ag^+ doped TiO_2: 1 g/l.

(100 ppm), Ca^{2+} (20 ppm) and Fe^{2+} (1 ppm) to a solution prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1:5 V/V. It was then subjected to UV irradiation in the presence of Ag^+ doped TiO_2 (1 g/l). The percent degradation for both CV and MR was studied (Fig. 10). The synthetic dye mixture degraded by >99% after UV irradiation for 150 min for both the dyes. The excess time taken may be due to the colour of iron interfering with the degradation. When iron was masked by adding Na_2EDTA solution in equimolar proportions, the degradation time reduced to 90 min. The photocatalyst settled easily after the degradation of synthetic wastewater. It may be due to the adsorption of ions on to the photocatalyst surface making it heavier.

3.12. Effect of oxygen

The degradation of both the dyes was studied individually at their respective λ_{max} under excess and limited supply of atmospheric O_2 by subjecting the mixture prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1:5 V/V to UV irradiation for 90 min with Ag^+ doped TiO_2 with and without magnetic stirring. The degradation was less under limited supply of O_2 indicating that O_2 is a prerequisite for the photocatalytic degradation process. The effect of oxygen, however, was moderate. This may be due to the fact that the doped Ag^+ substitutes the role of oxygen to some extent [20]. Fig. 11 shows the degradation in the presence and absence of O_2.

3.13. Detection of silver ion in the treated effluent

Various solutions prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1:1, 1:5 and 1:10 V/V were subjected to UV irradiation for 90 min with Ag^+ doped TiO_2 at a dosage of 1 g/l and centrifugation. Then 1 N NaCl solution was added in excess to these solutions. No white precipitate was formed which indicated the absence of silver ion in the effluent after treatment.

3.14. Reuse of the photocatalyst

The possibility of reusing the photocatalyst was examined to see the cost effectiveness of the method. It was observed that the used catalyst could be used for the second time with 90% efficiency. The regeneration of the catalyst could be done in a very simple way. After the degradation of the dye the solution was kept standing for 12 h and then the supernatant was decanted. The photocatalyst was then thoroughly washed with distilled water and reused for the degradation of dye with a fresh lot of dye solution prepared by mixing CV (5×10^{-5} mol dm^{-3}) and MR (7.5×10^{-5} mol dm^{-3}) in the ratio of 1:5 V/V. Further use of the catalyst is also possible with lesser efficiency. The drop in the photocatalytic activity of reused Ag^+ doped TiO_2 may be due to the fact that during the photocatalytic degradation of dyes some of the Ag^+ ions are converted into Ag^0. Since it is the silver ion that catalyses the reaction, if the same photocatalyst is reused the whole of the doped Ag^+ is not available. Efficiency of the used catalyst increased when 10% of unused catalyst was added to it.

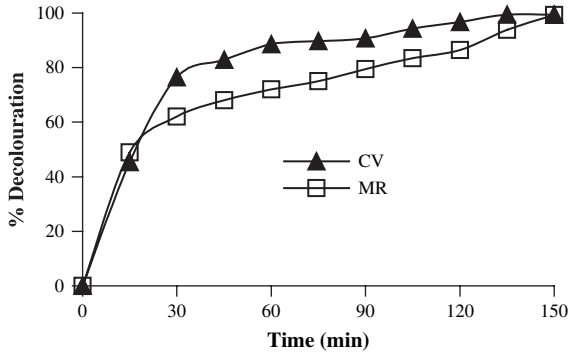


Fig. 10. Photocatalytic decolouration of synthetic textile wastewater; pH: 7.5; temperature: 30 ± 2 °C; Ag^+ doped TiO_2: 1 g/l.

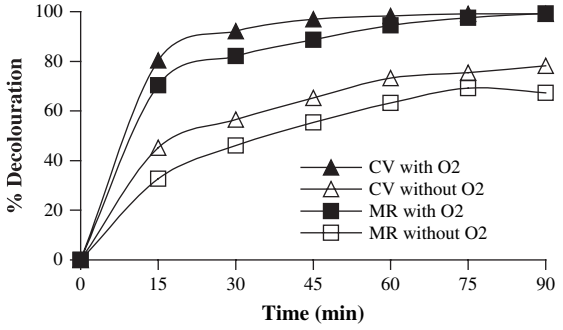


Fig. 11. Effect of oxygen on the photocatalytic decolouration of the mixture of dyes.

4. Conclusions

Under UV irradiation the photocatalytic degradation of mixture of two dyes Crystal Violet (CV) and Methyl Red (MR) in various proportions was achieved up to 99% in 90 min using Ag^+ doped TiO_2. The degradation followed Langmuir–Hinselwood pseudo first order rate law. COD measurement at regular interval showed that the dyes were mineralized by >86% on irradiation for 90 min. Electron acceptor such as H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ increased the percentage of degradation of both the dyes. H_2O_2 has the maximum beneficial effect on CV, while $KBrO_3$ has the maximum beneficial effect on MR degradation. Above pH 10 the percentage degradation of MR was decreased. The degradation of CV remains unaltered in the entire pH range of 3–13. Doping of Ag^+ on the TiO_2 made the separation of the catalyst easier and at the same time it also increased the degradation of the dyes. The catalyst could be reused for dye degradation with slightly less efficiency. Studies on the interference due to various ion/substances showed that Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, humic acid do not interfere the degradation of CV whereas Ca^{+2} and Fe^{+2} interfere. On the other hand, Cl^-, Ca^{+2}, Fe^{+2} interfered the degradation of MR but NO_3^-, SO_4^{2-} and HPO_4^{2-} did not affect it. Finally it is concluded that the mixture of the two dyes can be degraded effectively using Ag^+ doped TiO_2 under UV irradiation in presence of different interfering substances. This investigation was undertaken because the real dyes originating from various industries consist of mixture of dyes along with some interfering substances.

References

[1] Da Silva CG, Faria JL. J Photochem Photobiol A Chem 2003;155:133–43.
[2] Bruggen BV, Vreese ID, Vandecasteele C. Ind Eng Chem Res 2001;40:3973–8.
[3] Sharma KK, Rao BSM, Mohan H, Mittal JP, Oakes J, O'Neill P. A radiation chemistry study. J Phys Chem A 2002;106:2915–23.
[4] Fu Y, Viraraghavan T. Adv Env Res 2002;7:239–47.
[5] Stylidi M, Kondarides DI, Verykios XE. Appl Catal B Environ 2004;47:189–201.
[6] Cisneros RL, Espinoza AG, Litter MI. Chemosphere 2002;49: 393–9.
[7] Chen Y, Wang K, Lou L. J Photochem Photobiol A Chem 2004;163:281–7.
[8] Chang JS, Lin YC. Bitechnol Prog 2000;16:979–85.
[9] Mccallum JEB, Madison SA, Alkan S, Depinto RL, Rojas Wahl RU. Environ Sci Technol 2000;34:5157–64.
[10] Lucarelli L, Nadtochenka V, Kiwi J. Langmuir 2000;16:1102–8.
[11] Annadurai G, Juang RS, Yen PS, Lee DJ. Adv Environ Res 2003;7:739–44.
[12] Wong YC, Szeto YS, Cheung WH, McKay G. Langmuir 2003;19:7888–94.
[13] Xu Y, Langford CH. Langmuir 2001;17:897–902.
[14] Haque SA, Tachibana Y, Willis RL, Moser JE, Gratzel M, Klug DR, et al. J Phys Chem B 2000;104:538–47.
[15] Stock NL, Peller J, Vinodgopal K, Kamat PV. Environ Sci Technol 2000;34:1747–50.
[16] Sokmen M, Allen DW, Akkas F, Kartal N, Acar F. Water Air Soil Pollut 2001;132:153–63.
[17] Li J, Chen C, Zhao J, Zhu H, Orthman J. Appl Catal B Environ 2002;37:331–8.
[18] Chao HE, Yun YU, Xingfang HU, Larbot A. J Eur Ceramic Soc 2003;23:1457–64.
[19] Safarik I, Safankova M. Water Res 2002;36:196–200.
[20] Subba Rao KV, Lavedrine B, Boule P. J Photochem Photobiol A Chem 2003;154:189–93.
[21] Clesceri LS, Greenberg AE, Trussell RR. Standard methods for the examination of water and wastewater. 17th ed. American Public Health Association; 1987.
[22] Sahoo C, Gupta AK, Pal Anjali. Dyes Pigments 2005;66: 189–96.
[23] Subramanium V, Wolf E, Kamat PV. J Phys Chem B 2001;105:11434–46.
[24] Ozkan A, Ozkan MH, Gurkan R, Akcay M, Sokmen M. J Photochem Photobiol A Chem 2004;163:29–35.
[25] Hu C, Yu JC, Hao Z, Wong PK. Appl Catal B Environ 2003;42:47–55.
[26] Zeilinska B, Grzechulska J, Kalenczuk RJ, Morawski AW. Appl Catal B Environ 2003;45:293–300.
[27] Sokmen M, Ozokan A. J Photochem Photobiol A Chem 2002;147:77–81.
[28] Hu C, Yu JC, Huo Z, Wong PK. Appl Catal B Environ 2003;46(1):35–47.
[29] Vohra MS, Tanaka K. Environ Sci Technol 2001;35:411–5.
[30] Baran W, Makowski A, Wandas W. Chemosphere 2003;53: 87–95.
[31] Litter MI. Appl Catal B Environ 1999;23:89–114.
[32] Saquib M, Muneer M. J Environ Sci Health 2003;A38(11): 2581–98.