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Photocatalytic degradation of Crystal Violet (C.I. Basic Violet 3) on silver ion doped TiO_2

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Abstract

The photocatalytic degradation of Crystal Violet, a triphenyl methane dye (also known as Basic Violet 3) in aqueous solutions was investigated with Ag^+ doped TiO_2 under UV and simulated solar light. The dye degradation using untreated TiO_2 and Ag^+ doped TiO_2 was compared. It was found that Ag^+ doped TiO_2 is slightly more efficient. Ag^+ doping was done also to separate the photocatalyst easily from the treated effluent just by settling or centrifuging and decantation thus avoiding the costly filtration process. Measurements of COD were done at regular intervals to have an idea of mineralization of the dye. The effects of pH, catalyst loading, substrate concentration, interfering substances such as Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, Ca^{2+}, Fe^{3+} and humic acid on dye degradation were investigated. The degradation of the dye (20 ppm) was >97% on UV illumination for 105 min with TiO_2 and >99% with Ag^+ doped TiO_2. The dye (20 ppm) was found to degrade about 88% after illumination for 10 h by a simulated solar light source in the presence of Ag^+ doped TiO_2. The degradation kinetics fit well to Langmuir–Hinshelwood rate law.

Keywords: TiO_2; Ag^+ doped TiO_2; Photocatalytic degradation; Crystal Violet; UV-irradiation

1. Introduction

Various industries such as textiles, paint and varnishes, ink, plastics, pulp and paper and cosmetics use different types of organic dyes and dye intermediates. About 15% of the dyes produced throughout the world are lost during synthesis and processing with wastewater [1,2]. Such coloured dye effluents pose a major threat to the surrounding ecosystem. Some of the dyes are extremely toxic [3].

The increased public concern with these dyes and the stringent international environmental standards (ISO 14001) have prompted the need to develop novel treatment methods for converting these organic dyes to harmless compounds [4].

Dye effluents can be treated by biological methods, flocculation, reverse osmosis, adsorption on activated charcoal, chemical oxidation methods and advanced oxidation processes [5]. Biological methods have been proved to be ineffective [6–8]. Flocculation, reverse osmosis and adsorption methods transfer the pollutants to other media, thus causing secondary pollution [9,10]. Chemical oxidation methods are not cost effective [11].

Advanced oxidation processes have been used to treat various organic pollutants during the last two decades. Among these oxidation processes, heterogeneous photocatalytic methods are the most effective and attractive ones. They use atmospheric oxygen as oxidant and can be carried out under ambient conditions and may lead to total mineralization of organics to CO_2, water and low molecular weight fatty acids. Photocatalytic degradation of harmful dyes in the presence of the large band

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gap semiconductor (such as TiO_2 or ZnO) shows promise in becoming a viable commercial technology. This method uses environmentally benign photocatalysts (usually TiO_2), which are largely available, cheap, nontoxic and photo stable [12–14]. Separation of TiO_2 from effluent after dye degradation, however, is difficult due to its fine size. Hence, it needs a costly filtration process before disposal. To combat this difficulty TiO_2 is sometimes immobilized on transparent supports [15] or it is doped with either metal or metal ions [16].

Crystal Violet is a well-known dye and has been used for various purposes (such as a biological stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc.) [17,18]. It is also extensively used in textile dying and paper colouration. It is a mutagen and mitotic poison [18]. Therefore, there are both environmental and health concerns on this particular dye. In the present work photocatalytic degradation of Crystal Violet using UV light and silver ion doped TiO_2 has been studied. In order to improve the photocatalytic property of TiO_2 and to make it settleable, it is doped with silver ion. Silver ion doping is done by liquid impregnation method. Effects of various factors such as pH, concentration of dye, dose of photocatalyst etc. on the photo degradation of Crystal Violet have been found out. COD removal is studied to know the extent of mineralization. The photocatalytic activity of silver ion doped TiO_2 is compared with that of untreated TiO_2.

2. Materials and methods

2.1. Materials

Crystal Violet (99% pure) was purchased from B.D.H., Poole, England and was used without further purification. Titanium dioxide obtained from Merck India (mainly anatase, average particle size about 1 μm (from SEM), surface area 4.86 m^2/g) was used as photocatalyst. Double distilled water was used for all studies. Silver nitrate (99.9% pure) from S.D. Fine chem. was used for silver ion doping. Other chemicals used in the study such as NaOH, HNO_3, NaCl, KCl, Na_2SO_4, $NaNO_3$, Na_2HPO_4, $CaCl_2$ and $FeCl_3$ were obtained from Merck India. Humic acid was obtained from Aldrich.

2.2. Instrumentation

The instruments used for the study were Systronics spectrophotometer 106, UV fluorescent lamp (16W), Philips tungsten-halogen lamp (250 W) (solar light simulating) [19], JEOL JSM-5800 scanning electron microscope (SEM), Gallenkamp revolving centrifuge, Hach COD digester, Systronics digital pH meter and Remi magnetic stirrer.

2.3. Preparation of photocatalyst

Silver ion doped TiO_2 (1% molecular) was prepared using the following procedure. First 0.01 mol of $AgNO_3$ was dissolved in 100 ml of water in a porcelain bowl. Then 0.99 mol of TiO_2 was added to the solution and the solution was stirred well and was allowed to stand for 24 h. Water was then evaporated by heating it at 100 °C for 12 h in an incubator. The dried solids were ground in an agate mortar and calcined at 400 °C for 6 h in a muffle furnace [20].

2.4. Adsorption and direct photolysis

Adsorption studies were performed in the dark under stirring condition using 20 ppm dye solution (60 ml) with 1 g/l TiO_2 and 1 g/l silver ion doped TiO_2 separately. Aliquots were taken at regular time intervals and centrifuged. The remaining dye concentration was measured spectrophotometrically. Direct photolysis of dye was also studied by irradiation in the absence of photocatalyst.

2.5. Photocatalytic degradation

Stock solution of the dye (400 ppm) was prepared with double distilled water from which working solution (20 ppm) was prepared. The experimental setup [Fig. 1] consisted of a 500 ml borosil beaker placed on a magnetic stirrer above which an UV fluorescent tube (16 W) emitting UV light of wavelength ~365 nm was placed which served as the light source. The height and diameter of beaker were 12 cm and 8 cm, respectively. Sixty milliliters of the working solution of the dye

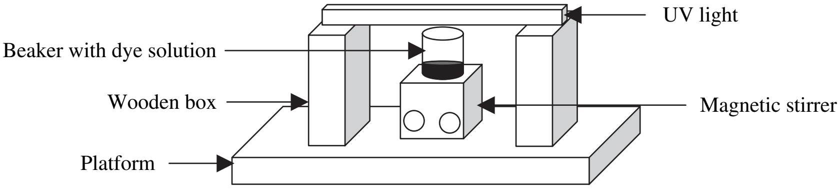


Fig. 1. Experimental setup for the photocatalytic dye degradation.

(20 ppm) was taken in the beaker and to it was added TiO_2 or Ag^+ doped TiO_2 at a dose of 1 g/l. The height 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 cm. The solution was stirred in the dark for 30 min to establish the adsorption equilibrium. The zero time reading was then taken and the solution was irradiated. Aliquots were taken at regular intervals, centrifuged and filtered through 0.45 µm membrane filter (in case of TiO_2 only) to analyze the percent degradation of the dye. The experiment was repeated with 40 ppm and 60 ppm dye solution. The experiment was also conducted with 20 ppm dye solution with both TiO_2 and Ag^+ doped TiO_2 under irradiation by simulated solar light source.

2.6. Analysis

The mineralization of the dye was monitored by measuring the COD using closed reflux titrimetric method. The dye degradation was monitored spectrophotometrically. The absorbance of the dye was followed at λ_{max}: 588 nm after 5 times dilution of the irradiated solution. The pH adjustment was done with 1 N HNO_3 and 1 N NaOH solutions. HNO_3 is used because the catalyst was doped with $AgNO_3$. The decolourized effluent was tested for the presence of silver ion by adding 1 N NaCl solution.

3. Results and discussion

3.1. Catalyst characterization

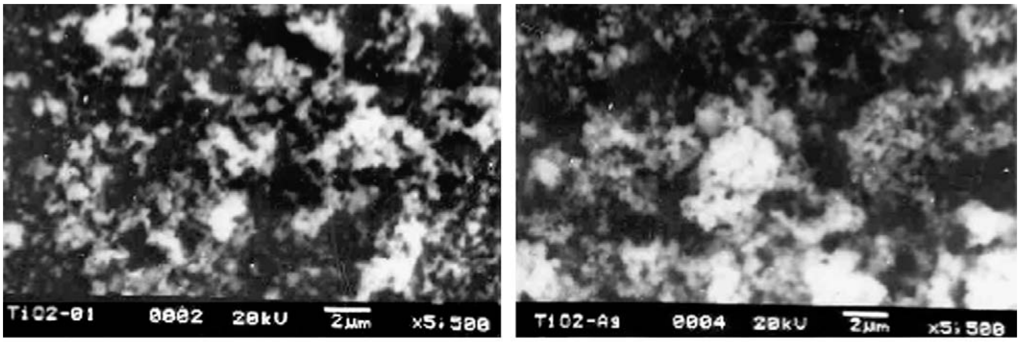
Both the photocatalysts TiO_2 and Ag^+ doped TiO_2 were characterized by the scanning electron microscope. The micrographs taken at 5500 times magnification are shown in Fig. 2a, b. The average particle size was found to be about 1 µm. The compositions of TiO_2 and Ag^+ doped TiO_2 were found to be as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

3.2. Photocatalytic degradation

The structure of Crystal Violet is shown in Fig. 3. It shows its maximum absorption at λ_{max}: 588 nm. The degradation of the Crystal Violet dye (20 ppm) after UV irradiation of aqueous solution in the presence of the photocatalyst TiO_2 (1 g/l) and Ag^+ doped TiO_2 (1 g/l) was found to be >97% and >99%, respectively, after irradiation for 105 min [Fig. 4a]. Ag^+ doped TiO_2 was found to be more efficient and it settled easily. Dye solutions, 40 ppm and 60 ppm, degraded by >88% and >56% under similar conditions with Ag^+ doped TiO_2 [Fig. 4b]. Dye solution (20 ppm) degraded by >88% on irradiation for 10 h by simulated solar light with Ag^+ doped TiO_2. At the start of the photocatalytic degradation the pH was measured and 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 surface of TiO_2 a valence band electron moves in to the conduction band thus forming a positively charged hole in the valence band. The conduction band electrons and the valence band holes then migrate to the oxide surface and react with chemisorbed O_2 and/or OH^-/H_2O molecules to generate reactive oxygen species such as $O_2^{\cdot -}$, $HOO^{\cdot}$, $OH^{\cdot}$ radicals, which attack dye molecules and lead to their degradation. Alternatively, the electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anion and subsequent reaction of the radical anion can lead to the degradation of the dye. The molecule of Crystal Violet is photochemically active [21]. Also the adsorbed dye molecules may be directly oxidised by the valence band holes to form dye radical cations which ultimately cause dye degradation [21]. The enhancing effect of Ag^+ may be explained by its ability to trap electrons. This



(a) (b)

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

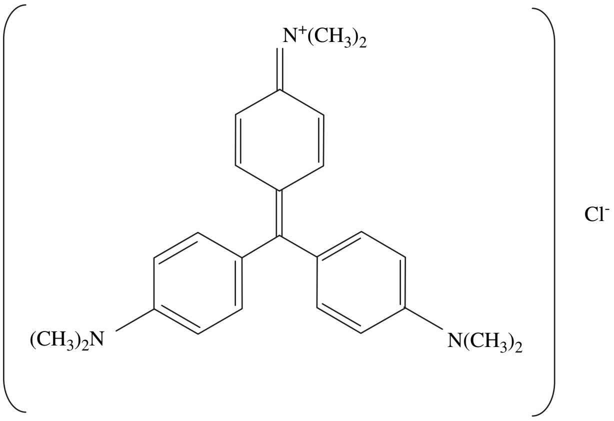


Fig. 3. Structure of Crystal Violet (C.I. Basic Violet 3).

process reduces the recombination of charges and favours oxidation of substrate. The reduction potential of silver ion is suitably positioned for the effective photocatalytic reduction $Ag^+ + e^- \rightarrow Ag^0$ producing metallic silver on TiO_2 surface. This is authenticated by the slight colour change of the catalyst to black [20].

3.3. Adsorption and direct photolysis

The results of adsorption studies of dye solution (20 ppm) with TiO_2 (1 g/l) and Ag^+ doped TiO_2 (1 g/l), respectively, in the dark are shown in Fig. 5. TiO_2 showed 26% adsorption whereas Ag^+ doped TiO_2 showed 31% adsorption after 105 min. Direct photolysis of dye solution by magnetic stirring and irradiation in the absence of the photocatalysts showed no observable degradation after 2 h.

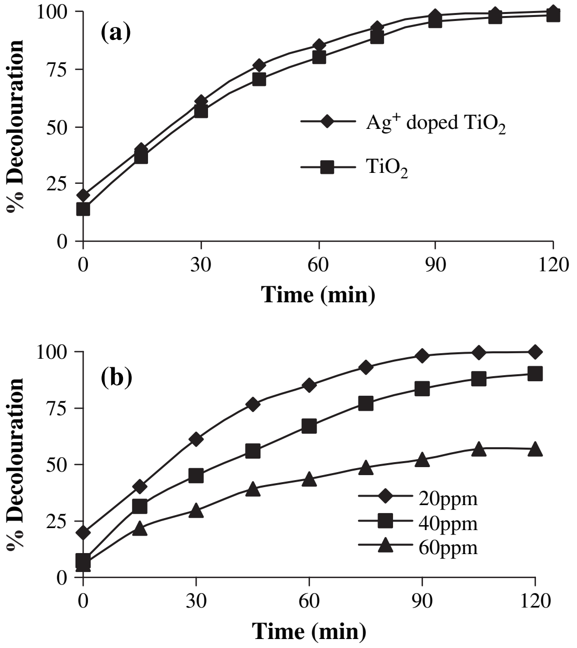


Fig. 4. Photo decolouration of dye using (a) Ag^+ doped TiO_2 and TiO_2 with dye concentration: 20 ppm, (b) Ag^+ doped TiO_2 with dye concentration: 20 ppm, 40 ppm and 60 ppm; pH: 6.4; temperature: 31 ± 2 °C; catalytic dose: 1 g/l.

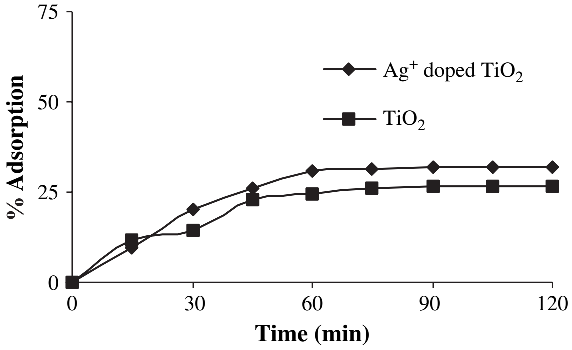


Fig. 5. Adsorption of dye using Ag^+ doped TiO_2 and TiO_2 with dye concentration: 20 ppm; pH: 6.4; temperature: 31 ± 2 °C; catalytic dose: 1 g/l.

3.4. Kinetic analysis

The dependencies of the rate of dye degradation on the concentration of dye have been described well by the Langmuir–Hinshelwood kinetic model [22].

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \tag{1}$$

Neglecting KC as compared to 1 in the denominator the above equation can be simplified to a pseudo first order equation

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t \tag{2}$$

where r is the rate of degradation (ppm/min), C_0 is the initial concentration of the dye (ppm), C is the concentration of the dye at time t (ppm), t is the irradiation time (min), k the reaction rate constant (min^{-1}), and K the adsorption coefficient of the dye onto the photocatalyst particle (l/mg). The kinetic curves in Fig. 6 were of pseudo first order as confirmed by the linear transform $\ln(C_0/C) = k_{app}t$. The apparent rate constants were as follows:

- With Ag^+ doped TiO_2: $k_{app} = 0.0408$, $R^2 = 0.86$.
- With TiO_2 (untreated): $k_{app} = 0.0302$, $R^2 = 0.97$.

3.5. COD measurements

To account for the extent of mineralization of the dye COD was measured at regular intervals [15]. The dye solutions with initial concentration of 20 ppm, 40 ppm and 60 ppm with 1 g/l Ag^+ doped TiO_2 were exposed

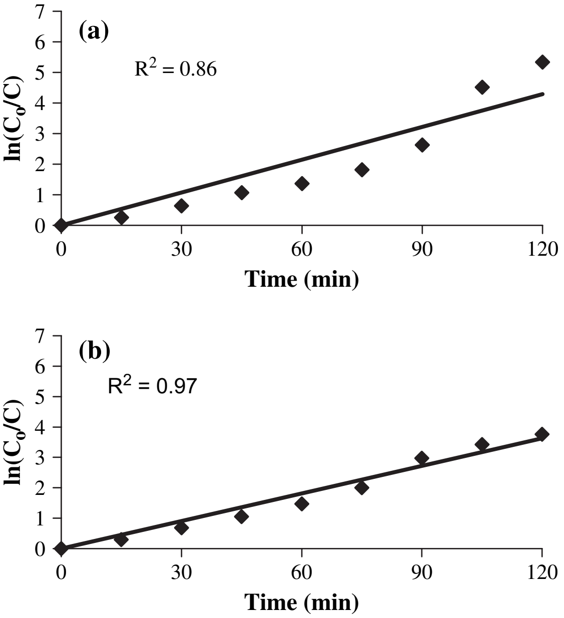


Fig. 6. Kinetic analysis with (a) Ag^+ doped TiO_2, (b) TiO_2; dye concentration: 20 ppm; pH: 6.4; temperature: 31 ± 2 °C; catalytic dose: 1 g/l.

separately to UV light, aliquots were taken at 15 min intervals and COD was measured using closed reflux titrimatric method [23]. The dye was found to have mineralized to the extent of 85%, 70%, and 46%, respectively, after being irradiated for 105 min. The plot of COD versus irradiation time is shown in Fig. 7. The experiment was continued for 30 min more during which there was practically no change of COD. Because ~85% mineralization has taken place, it is probable that the $-N(CH_3)_2$ is changed to NO_3^-, NH_3 and N_2 [24].

3.6. Effect of initial dye concentration

The effect of dye concentration on its degradation was studied. Fig. 8 shows the percent degradation at various initial dye concentrations. At higher concentration, the degradation was found to be less. This may be because as the concentration of dye increases the catalyst particles adsorb more and more dye. Hence, the UV light does not reach the catalyst surface. At higher concentration, the light travels up to a smaller distance [15].

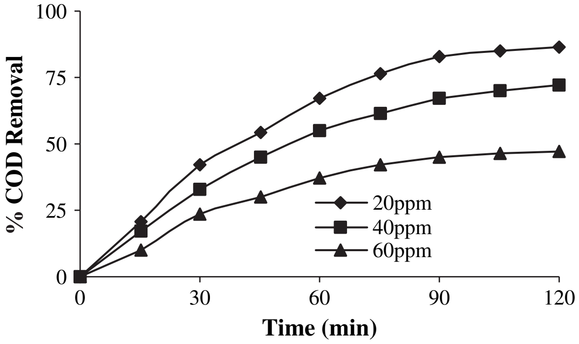


Fig. 7. COD removal on UV irradiation with time using various dye concentrations; pH: 6.4; temperature: 31 ± 2 °C; catalytic dose: 1 g/l.

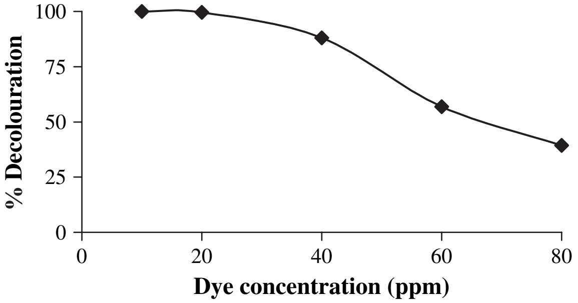


Fig. 8. Dye decolouration at different initial concentration, Ag^+ doped TiO_2: 1 g/l; irradiation time: 105 min; pH: 6.4; temperature: 31 ± 2 °C.

3.7. Effect of catalytic dose

The dye solution (20 ppm) was irradiated for 105 min with different catalytic doses (0.1 g/l, 0.5 g/l, 0.7 g/l, 1 g/l, 1.2 g/l). Fig. 9 shows a plot of percent degradation of dye versus catalytic dose. The degradation increases with increase in catalytic dose. At 0.7 g/l catalytic dose the dye was found to be almost completely decolourized on irradiation for 105 min. Hence, an optimum catalytic dose of 1 g/l was selected.

3.8. Effect of pH

The study on the effect of pH on the dye degradation was undertaken because the pH of textile effluent varies to a great extent. Also the pH of the dye solution decreases during the photo degradation. Degradation of the dye (20 ppm) was studied in the pH range between 3 and 13 after irradiation for 105 min. The initial pH was adjusted by adding 1 N HNO_3 or 1 N NaOH. The dye degradation was varied only within 2% by pH change.

3.9. Effects of interfering substances

Crystal Violet solutions (20 ppm) mixed separately with different interfering substances such as [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^{3+} (0–200 ppm), humic acid (25 ppm)] were irradiated for 105 min with 1 g/l Ag^+ doped TiO_2. It was found that in the described range of Cl^- and NO_3^- there was no effect on the degradation of the dye. On the other hand, SO_4^{2-} was found to favour the degradation to a very small extent while HPO_4^{2-}, Ca^{2+}, Fe^{3+} and humic acid were

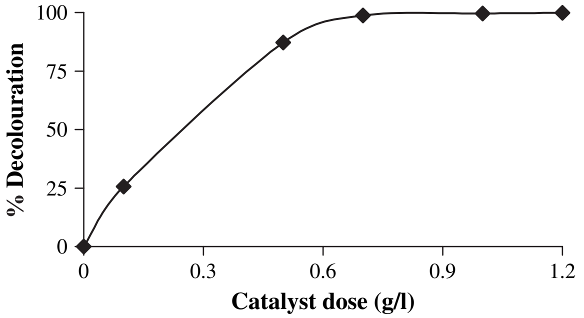


Fig. 9. Decolouration at different doses of Ag^+ doped TiO_2; dye concentration: 20 ppm; pH: 6.4; irradiation time: 105 min; temperature: 31 ± 2 °C.

found to inhibit the degradation to a great extent. Fig. 10a–f shows the degradation of dye in the presence of different doses of the interfering substances. The inhibiting effect of HPO_4^{2-} may be due to the reaction of the positive holes formed on the surface of TiO_2 with anions and those anions behaving like hole scavengers resulting in prolonged degradation [25,26]. At the normal pH, i.e. ~6.4, the TiO_2 surface is positively charged (pH_{ZPC} 6.6) and the pH decreases as the reaction proceeds. The increasing effect of SO_4^{2-} (although to a very little extent) may be due to its adsorption onto the positively charged TiO_2 surface making the TiO_2 surface less positive leading to the increased adsorption of the dye onto TiO_2 surface [3]. The inhibiting effect of the cations may be because Crystal Violet 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 photocatalyst, which may be the cause of inhibition [27]. The detrimental effect of high metal ion concentrations on the oxidation may be because the metallic species generally compete with oxygen for the conduction

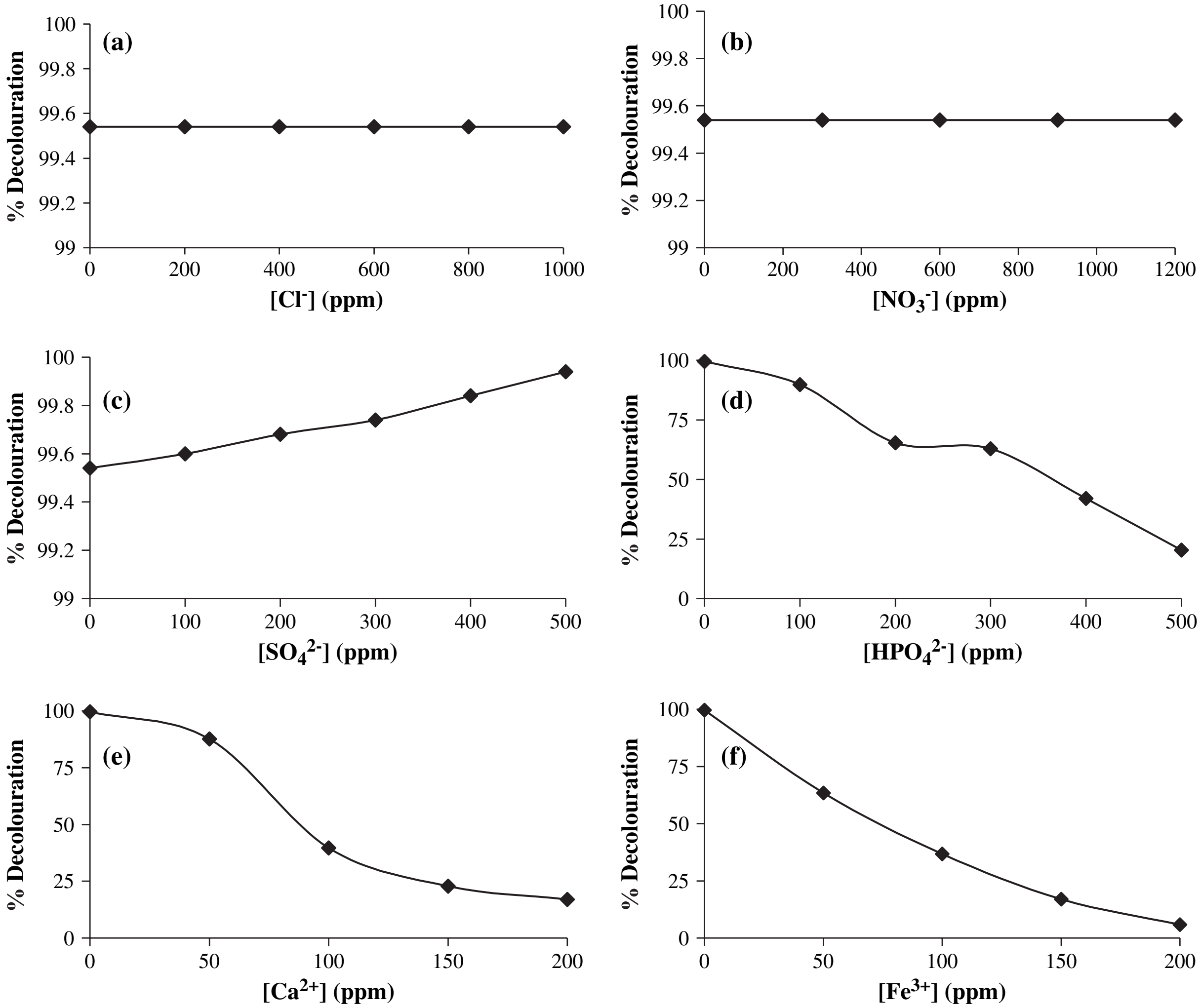


Fig. 10. Effect of interfering ions (a) Cl^-, (b) NO_3^-, (c) SO_4^{2-}, (d) HPO_4^{2-}, (e) Ca^{2+}, (f) Fe^{3+}; dye concentration: 20 ppm; pH: 6.4; temperature: 31 ± 2 °C, Dose of Ag^+ doped TiO_2: 1 g/l; irradiation time: 105 min.

band (cb) electrons thus reducing the generation of oxidising species [28]. There was not much effect in the degradation of Crystal Violet in the presence of humic acid. The dye was found to degrade by about 95% in the presence of humic acid (25 ppm).

3.10. Effect of O_2

The degradation was studied in the presence and absence of atmospheric O_2 by taking Crystal Violet solution (20 ppm) and irradiating for 105 min with and without magnetic stirring. The degradation at the end of 105 min irradiation was found to be less in the absence of O_2 indicating that O_2 is a prerequisite for the photocatalytic degradation process. However, the effect of oxygen 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 [15].

3.11. Detection of silver ion in the treated effluent

To detect the presence of silver ion in the effluent after dye degradation, 1 N NaCl solution was added to the solution of Crystal Violet (20 ppm) after irradiation for 105 min with 1 g/l of Ag^+ doped TiO_2 and centrifugation. Absence of white precipitate indicated the absence of silver ion in the effluent after treatment.

3.12. 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 also with 90% efficiency. The regeneration of the catalyst can be done in a very simple way. After the degradation of the dye, the dye 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 degradation with a fresh lot of dye solution (20 ppm). 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 Crystal Violet 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.

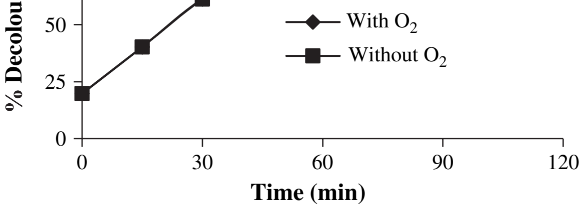


Fig. 11. Decolouration with and without O_2; dye concentration: 20 ppm; pH: 6.4; temperature: 31 ± 2 °C; dose of Ag^+ doped TiO_2: 1 g/l.

4. Conclusions

UV-irradiation of the dye Crystal Violet (CV) in the presence of Ag^+ doped TiO_2 and oxygen led to the degradation of the dye up to 99% in 105 min, and the mineralization could be achieved up to 85%. Doping of TiO_2 with Ag^+ increased the settlability of the catalyst. The reaction followed pseudo first order rate law. The degradation was favoured by the presence of SO_4^{2-} while HPO_4^{2-}, Ca^{2+}, Fe^{3+} and humic acid were found to inhibit the degradation to a great extent. The catalyst could be reused with little less efficiency.

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