Photocatalytic activity of sulfate modified titania 3: Decolorization of methylene blue in aqueous solution

P. Mohapatra, K.M. Parida *

Colloids & Materials Chemistry Cell Department, Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India

Abstract

The photocatalytic decolorization of methylene blue (MB) was studied under solar radiation over sulfate modified titania. The results obtained were compared with that of adsorption and under UV light. It was found that percentage of decolorization was the highest under solar radiation. The effects of pH, time, adsorbate concentration, catalyst dose, H_2O_2, potassium persulfate and sodium chloride were studied on the percentage of decolorization. The degradation rate followed first-order kinetics. The percentage of decolorization increased with increase in pH of the suspension. The presence of Cl^- ion decreased the rate of decolorization where that of potassium persulfate increased the rate. Addition of H_2O_2 facilitated the generation of $^\bullet OH$ radicals, which in turn increased the rate of decolorization. The catalyst could be regenerated for repeated use.
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1. Introduction

Photocatalysis has been an area of rapidly growing interest over last two decades. The use of semiconductor particles as photocatalyst for the initiation of redox chemical reactions continues to be an active area of investigation [1]. When semiconductor is illuminated with light of an appropriate wavelength it generates highly active oxidizing sites, which can potentially oxidize a large number of organic wastes such as dyes, pesticides, bacteria and herbicides [2,3]. Out of the total world production of dyes 15% is lost during the dying process and is released in textile effluents [4]. Wastewater generated by the textile industries are known to contain considerable amounts of non-fixed dyes, especially of azo-dyes, and huge amount of inorganic salts. It is well known that some azo-dyes and degradation products such as aromatic amines are highly carcinogenic [5]. Physical methods, such as adsorption [6], biological methods [7] and chemical methods [8] are the most frequently used for the treatment of these textile dyes. Unfortunately these processes have high operating cost and are of limited applicability. Photocatalytic decolorization of dyes has been proposed as an alterative method for removal of colour from the effluents of textile industries. Among the textile dyes methylene blue (MB) is a brightly coloured blue cationic thiazine dye with L_{max} at 665, 614, 292 nm. Methylene blue is used as an antidote for cyanide poisoning in humans, antiseptic in veterinary medicine and most commonly, in vitro diagnostic in biology, cytology, hematology and histology [9]. Methylene blue has various harmful effects on human being, on inhalation it can give rise to difficult breathing, while injection through mouth produces burning sensation, nausea, vomiting, diarrhoea and gasestrics, painful micturation and methemoglabinemia like syndromes [10]. From our earlier studies we have found that sulfated TiO_2 as an effective photocatalyst for degradation of 4-nitrophenol under solar radiation [11]. The present study reports the photocatlytic activity of sulfate modified TiO_2 for the decolorization of methylene blue in aqueous solution.

2. Experimental

2.1. Sample preparation

Hydrated titania was prepared at pH 3, 5, 7 and 9 by adding dilute ammonia to the stirred aqueous solution of titanium tetra-

* Corresponding author. Tel.: +91 674 2581636 305/425;
fax: +91 674 2581637.
E-mail addresses: kmparida@yahoo.com, kmparida@rrlbhu.res.in
(K.M. Parida).

chloride (Spectrochem, Bombay). Obtained gel was filtered and washed repeatedly to remove Cl⁻ (negative to AgNO₃ test), dried at 383 K for 10 h, powdered to 45–75 μm mesh size and kept for anion impregnation.

One series of sulfated titania samples with varying the weight percentage of SO_4^{2-} was prepared using $(NH_4)_2SO_4$ as the source of sulfate ions by solid–solid kneading method and the other series of samples was prepared by aqueous wetness impregnation method using dilute H_2SO_4 (strength = 1.0 M). The suspended mass was evaporated to dryness on a hot plate while stirring. The samples were then dried in an air oven at 383 K and subsequent activation (by calcination) at 573, 673, 773, 873, 973 and 1073 K at the heating rate of 283 K min⁻¹ in a muffle furnace for 3 h.

2.2. Characterisation

The XRD patterns of pure and modified TiO_2 samples were recorded on a Philips X-ray diffractometer. The FT-IR spectra of the samples were recorded with a Perkin-Elmer (model: Paragon 500) FT-IR spectrometer in the range of 4000–400 cm⁻¹ on KBr (spectrophotometric grade). The morphologies of the samples were examined using a Hitachi H-600 transmission electron microscope (TEM). Surface area (BET) was determined by the N_2 adsorption–desorption method at liquid nitrogen temperature using Quantasorb (Quantachrome, USA).

2.3. Photocatalytic reaction and adsorption

The decolorization of methylene blue was performed taking 25 mL of 100 ppm solution (guaranteed grade reagent, s.d. fine chemicals) in 100 mL pyrex flask and 1.6 g L⁻¹ of catalyst. The solutions were exposed to sunlight at room temperature (no extra cooling) and agitated with magnetic stirrer so that no appreciable amount of the catalyst remained on the bottom of the reaction vessel. All the experiments were performed in triplicate during the second half of March 2005 (sunny days), from 10.00 a.m. to 14.00 p.m. Similar experiments were performed under dark condition to know the amount of adsorption. Also decolorization was studied under UV-irradiation with 6 W low pressure Hg vapor lamp (90% of light is 254 nm) as a source (Quartz Emersion Well Photoreactor, SAIC, India). After reaction, the suspension was centrifuged to separate the catalyst and MB concentration was analysed quantitatively by measuring the absorption band at 665 nm using Cary-1E (Varian, Australia) spectrophotometer.

3. Results and discussions

3.1. Sample characterisation

From the TEM images it was found that TiO_2 sample prepared at pH 3 possesses uniform, finely distributed TiO_2 particles of size ≅12 nm and with sulfate loading the particle size sharply decreases to 2–3 nm. The XRD patterns revealed that the samples prepared at pH 3 possess mixture of anatase and rutile phases whereas at pH 5, 7 and 9 possess only anatase phases. It is also

found that sulfate ion stabilises the anatase phase of TiO_2 up to 973 K activation temperature. From surface area measurement, it is found that the presence of low amount of sulfate ion is responsible for the formation of porous network. From this observation it was concluded that samples prepared at pH 3 and impregnated with 2.5 wt% of sulfate have high surface area, low crystallite size and stable anatase phase of TiO_2 at high calcination temperature than compared to the samples prepared at high pH and also have better photocatalytic activity [11]. So we have studied the photocatalytic activity of 2.5 wt% sulfated titania for decolorization of methylene blue in this paper.

3.2. Photocatalytic decolorization of methylene blue

Methylene blue could be completely decolorized by using sulfate modified titania in aqueous solution under solar radiation. The reaction involves initial adsorption of the cationic functional group of MB molecule, which is probably adsorbed perpendicularly to the surface down to the final products [12].

There is no significant decrease in the concentration of MB under solar radiation and without the presence of catalyst. From Fig. 1 it was found that under solar radiation with increasing time the percentage of decolorization increases and maximum was observed at 4 h. For adsorption the decolorization percentage is only 17% and with increasing time it increases only up to
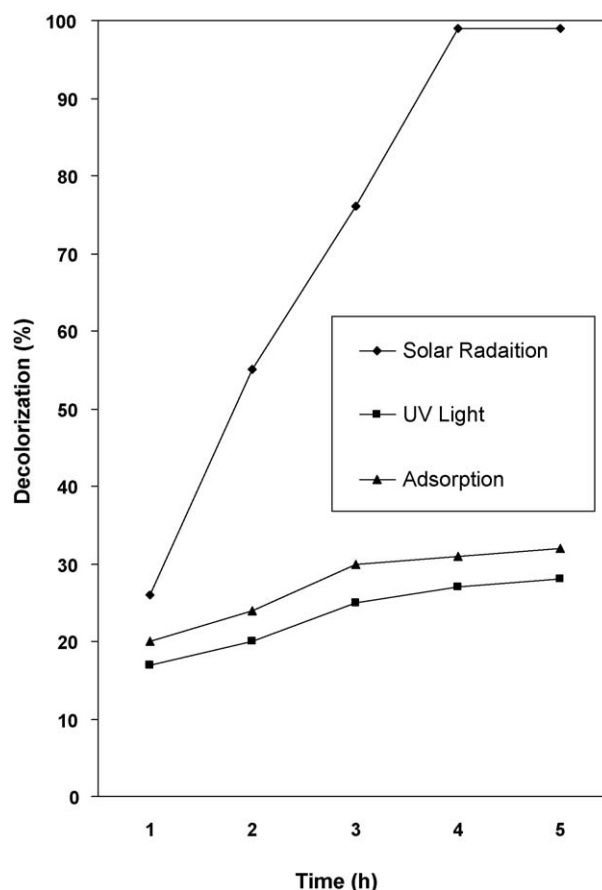

Fig. 1. Effect of time on percentage of decolorization of MB. [MB] = 100 ppm, catalyst = 1.6 g L⁻¹.

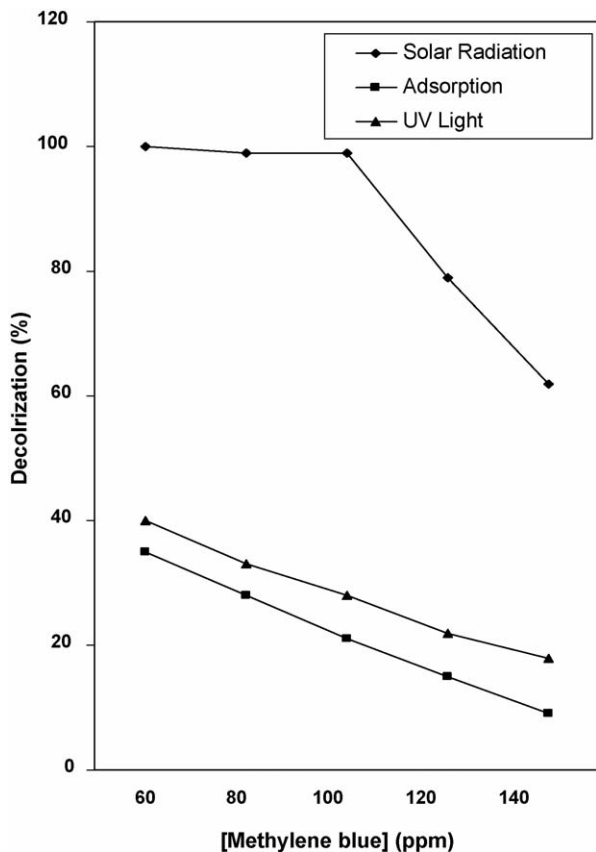Fig. 2. Effect of initial concentration of MB on the percentage of decolorization. Catalyst = 1.6 g L^{-1}, time = 4 h.

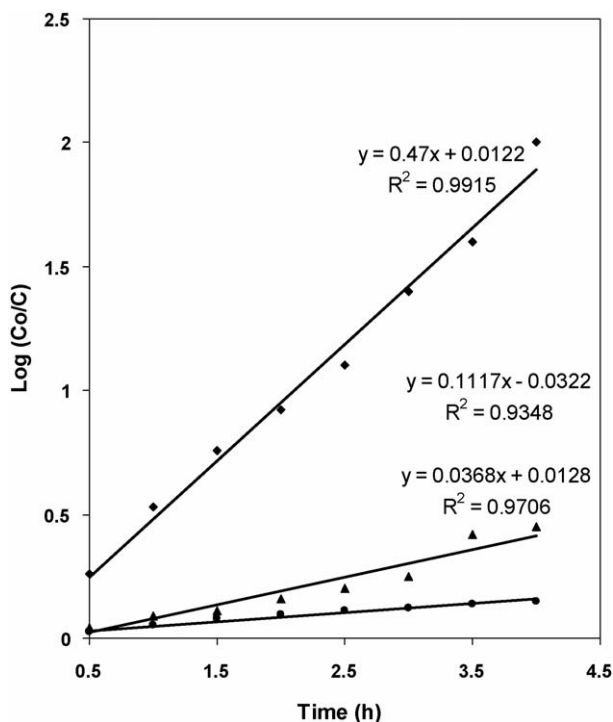28%. Also for UV radiation it increases from 20% to 32%. It may be concluded that MB decolorization is favored under solar radiation in comparison to adsorption and UV light.

The pollutant concentration is an important factor. Fig. 2 shows the effect of MB decolorization over the concentration range of 60–140 ppm. There is complete decolorization of MB under solar radiation for initial concentration up to 100 ppm and there after it decreases. This observation is comparable with that of adsorption and UV light. In all cases with increasing concentration the percentage of decolorization decreases. The concentration of MB has significant effect on the degradation rates and the rate of decrease in the MB concentration is faster when the initial concentration is less. The degradation rate is lower for higher initial concentration as the order decreases and therefore the Langmuir–Hinshelwood rate is proposed for this experimental data, the results agree with the observation made by Sivalingam et al. [13]. The variation of initial concentration of MB in the range of 100–140 ppm was studied under constant conditions of pH, catalyst weight. Photocatalytic decolorization of MB at low concentration followed first-order kinetics. A linear relationship was observed between MB concentration and irradiation time as shown in Fig. 3 (log C_0/C versus time, where C_0 is the initial concentration of MB and C is the concentration at time t). The calculated data for first-order rate constants "k"
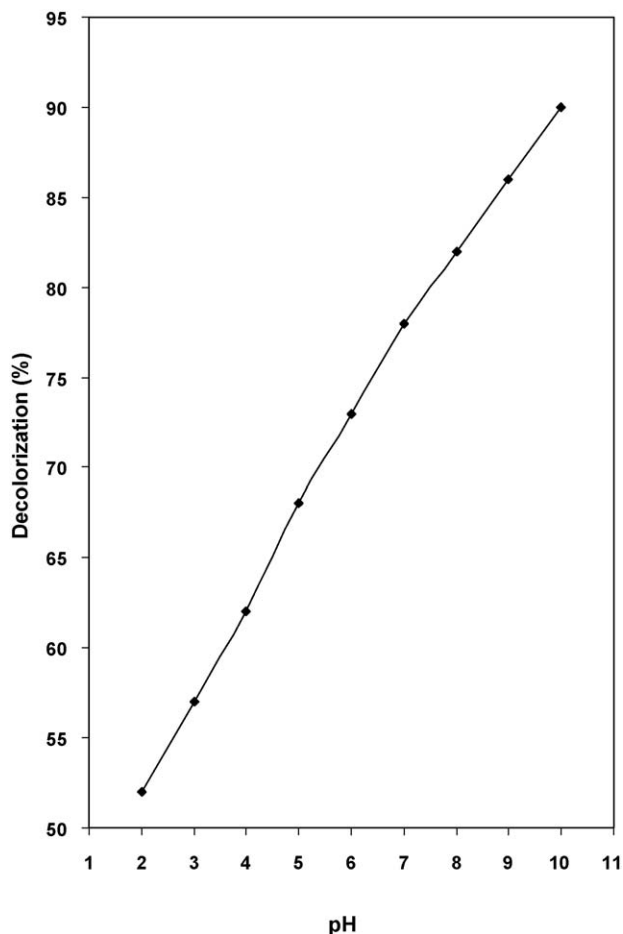

Fig. 3. Plot of log(C_0/C) vs. time (h), catalyst = 1.6 g L^{-1}.

Fig. 4. Effect of pH of the solution on the percentage of decolorization of MB. [MB] = 100 ppm, catalyst = 1.6 g L^{-1}, time = 4 h.

Table 1
Rate constants at different initial MB concentration

Concentration of MB (ppm)	Rate constant (h^{-1})
100	0.47
120	0.11
140	0.03

at different MB concentration were given in Table 1. The rate constant values were found to decrease with increase in the MB concentration.

The wastewater from textile industries usually has a wide range of pH values. Generally, pH plays an important role both in the characteristic of textile wastes and generation of hydroxyl radicals. Hence attempt has been made to study the influences of pH in the degradation of dye at pH values in the range of 2–9 (Fig. 4). With increasing the pH the percentage of decolorization increases. pH influences at the same time both the surface state of titania and the ionization state of ionizable organic molecule [14]. The pH effect can be explained on the basis of zero point charge of TiO_2. The pH_{pzc} of TiO_2 is 3.5–6.7 [15]. pH value

higher than pH_{pzc} the surface becomes negatively charged and it is opposite for pH value less than pH_{pzc}. Since MB is a cationic dye, it is conceivable that at high pH the adsorption is favored on a negatively charged surface. Since the adsorption is a requirement for reaction, the reaction is faster at basic pH.

The effect of catalyst dose on the percentage of decolorization of MB is shown in Fig. 5. It is observed that as with increase in the catalyst amount up to $1.6\,g\,L^{-1}$ the percentage of decolorization increases and there after it remains constant. The rate increased with an increase in the amount of catalyst and remained almost constant above certain level. It may be due to the reason that when the amount of catalyst is increased the number of photons adsorbed and the number of dye molecules adsorbed are increased owing to an increase in the number sulfated TiO_2 particles. Above a certain level the substrate molecules available are not sufficient for adsorption by the increased number of sulfated TiO_2 particles, i.e. although more area is available for a constant dye concentration the number of substrate molecules present in the solution is same. Hence the additional catalyst powder is not involved in the catalytic activity and the rate does not increase with an increase in the amount of catalyst beyond certain limit.

The photocatalytic degradation of organic substrates is significantly improved by the presence of H_2O_2 as the reactive $^{\bullet}OH$ radicals are easily generated by the breakdown of H_2O_2. Fig. 6 represents the effect of H_2O_2 on the percentage of decolorization. With increasing the H_2O_2 amount the percentage of decolorization increases, as reported earlier the addition of small
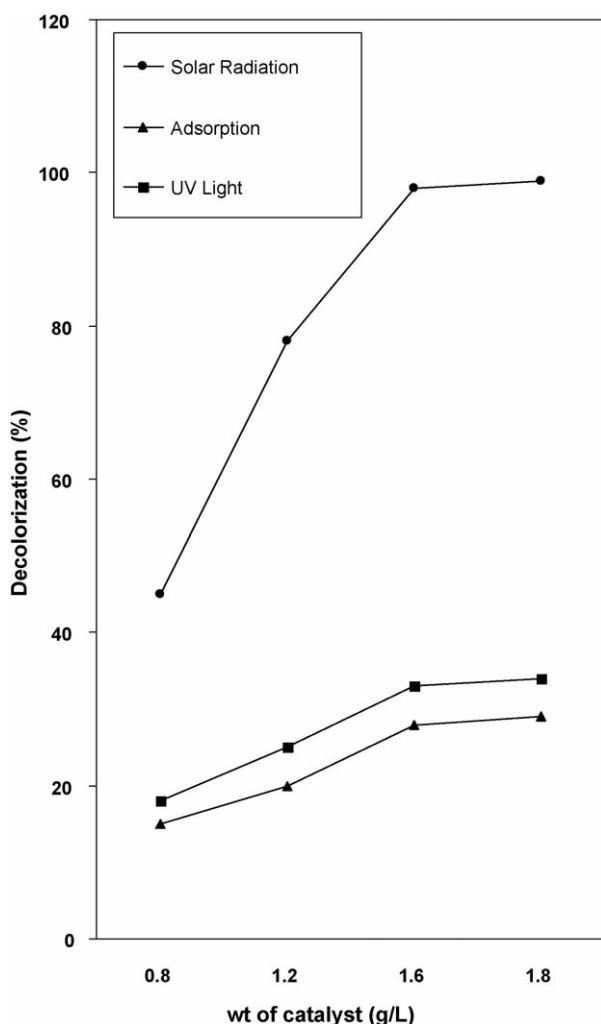

Fig. 5. Effect of catalyst dose on the percentage of decolorization of MB. [MB] = 100 ppm, time = 4 h.
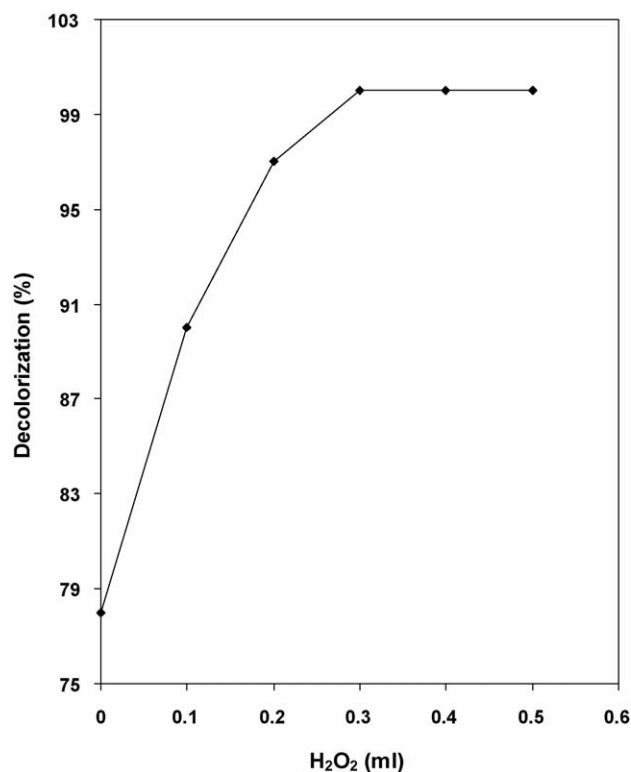

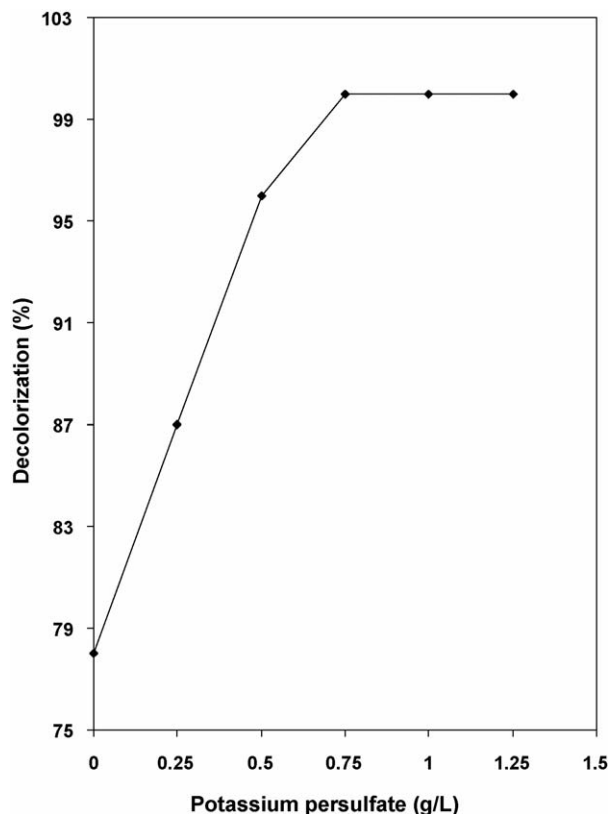Fig. 6. Effect of H_2O_2 on the percentage of decolorization MB. [MB] = 100 ppm, catalyst = $1.6\,g\,L^{-1}$, time = 3 h.

Fig. 7. Effect of potassium persulfate on percentage of decolorization MB. [MB] = 100 ppm, catalyst = 1.6 g L^{-1}, time = 3 h.

Fig. 8. Effect of sodium chloride on percentage of decolorization MB. [MB] = 100 ppm, catalyst = 1.6 g L^{-1}, time = 4 h.

amount of H_2O_2 greatly enhances the oxidation of organic pollutants [16]. The time for complete decolorization decreases to 3 h by adding only 0.3 mL of 30% H_2O_2 to the MB solution. This may be due to the reason that excess H_2O_2 scavenges the OH in the solution by forming H_2O and HO_2.

To study the effect of electron scavenger on the degradation process, potassium persulfate (0.012–1 g L^{-1}) was added to the MB solution (Fig. 7). It is observed that with increasing the amount of persulfate the decolorization percentage increases.
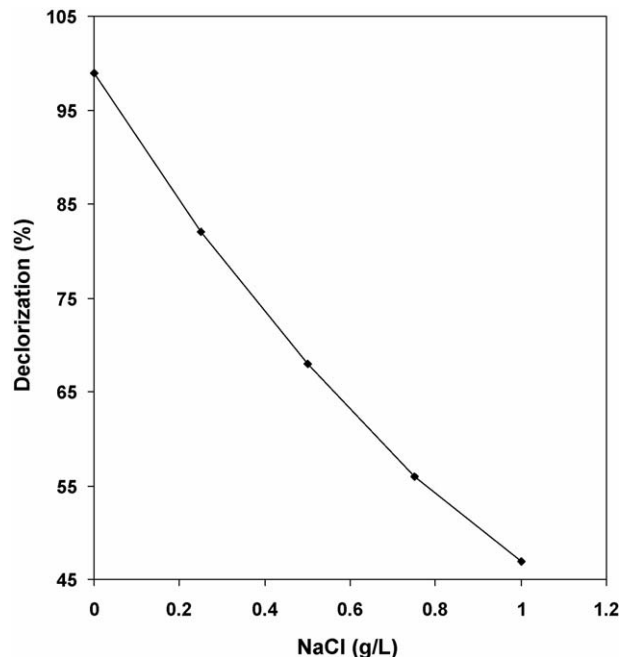
It may be due to the fact that sulfate radical is formed by taking the electron from the medium, which is a strong oxidant so the dye molecules degrade at faster rate [17]. Also it has been reported that potassium persulfate has more oxidizing impact than H_2O_2 for the dechloination of PVC over TiO_2 under solar radiation [18]. By adding 0.75 g L^{-1} of potassium persulfate to MB solution the time for complete decolorization decreases to 3 h.

Sodium chloride usually comes out in the effluent along with sectional wastes of textile mills. Fig. 8 reports the effect of sodium chloride on the photocatalytic decolorization of MB. With increasing the Cl$^-$ the decolorization percentage decreases may be due to Cl ion reacts with Cl radical formed at the vb to form Cl^{2-} for which the OH formation is decreased and the

Table 2
Comparison of different photocatalysts for MB decolorization

Catalyst	Light source	Concentration of MB (ppm)	Amount of catalyst	Time	Reference
TiO_2 and TiO_2 support	Photoreactor of Platform de Almeria (Spain)	30	0.5	2 h	[14]
P25 TiO_2	480 W xenon	10	0.1 wt% of suspension	–	[20]
Carbon coated TiO_2	20 W blue florescent light	90	0.52 g L^{-1}	4 h	[21]
TiO_2 mounted pumice	UV light of intensity 1.6 mW cm^{-2}	3	1.6 g (0.1 g of TiO_2	48 h	[22]
TiO_2 loaded on activated carbon	UV radiation from Black light (10 W)	20	–	30 h	[23]
TiO_2 thin film	12.8 W UVA Black light	3	–	10 min	[24]
$(Sr_{1-x} La_x) TiO_{3+\delta}$–$TiO_2$ composite	500 Xe	6	0.20	6 h	[25]
ZrO_2/TiO_2	UV light	9	1	–	[26]
Combustion synthesized TiO_2	125 W medium pressure mercury lamp	200	0.5 kg m^{-3}	2.6 h	[27]
	Solar radiation	100	1 kg cm^{-3}	3.6 h	
P25	High pressure 125 W mercury lamp	30	0.5 kg cm^{-3}	2 h	[28]
P25	–	20	1 kg cm^{-3}	5 h	[29]
TiO_2	125 W Philips	26	2.5 g L^{-1}	2 h	[30]
SO_4^{2-}/TiO_2	Solar radiation	100	1.6 g L^{-1}	4 h	This work

decolorization process is stoped [19]. Washing the catalyst with pure water carefully restore the catalytic activity when Cl^- are present in the wastewater.

To know the reusability of catalyst, after photocatalytic reaction the catalyst was separated from the solution and kept for further use. It was found the same catalyst can be used repeatedly and the activity remains almost same. After five times there is some decrease in activity which can be regenerated by heating it at 300 °C for 2 h.

To best of our knowledge there is no report found on the decolorization of methylene blue using sulfate modified titania. The present results can be directly compared with the data published earlier (Table 2). While optimising the photocatalytic reaction conditions, we found that 100 ppm of MB can be completely decolorized by $1.6\,g\,L^{-1}$ of sulfate modified TiO_2 in 4 h under solar radiation. These results found better than those reported earlier with respect to the concentration of MB, amount of catalyst, time and solar radiation.

4. Conclusion

 (i) Methylene blue (100 ppm) is completely decolorized using $1.6\,g\,L^{-1}$ of 2.5 wt% sulfated titania under solar radiation in 4 h.
 (ii) With increase in pH the decolorization percentage increases.
 (iii) Addition of H_2O_2 and potassium persulfate to the methylene blue solution the time for complete decolorization decreases.
 (iv) The catalyst can be regenerated by heating at 300 °C for 2 h for further use.

Acknowledgements

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