Degradation of Malachite Green by Silver Doped TiO₂

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The present work reports the efficiency of Ag-doped and undoped TiO_2 for photocatalytic break down of malachite green colourant. The influence of various factors such as dye concentration, catalyst dose, pH, intensity of light *etc.*, on degradation of dye was observed. By changing the parameters optimum conditions (pH 9, dye concentration 5×10^{-6} mol/L, amount of nano catalyst used 0.12 g and intensity of light 60 mW cm^{-2}.) were obtained. It was observed that photocatalytic degradation was maximum *i.e.* 99.5 % by using Ag doped TiO_2 as compared to undoped TiO_2 which was found to be 75 %, respectively. Scavenger studies have been applied to confirm the contribution of OH free radical. Many harmful products were produced by mineralization of these coloured compounds. The experimental records proved that the reaction follows Langmuir Hinshelwood model and pseudo first order kinetics.

Keywords: Malachite, Degradation, Ag doped TiO₂, Kinetics.

INTRODUCTION

The purification of water and air resources is a big challenge faced by the world. Although the populace is appreciating the luxuries as well as advantages provided by the sciences *e.g.* from medications to pigments, polymer combinations to computer chips, *etc.* Meanwhile the society is also confronting the challenge of appropriate removal of countless products as well as various industrial by-products including dye industries [1]. The textile industry is polluting the environment by discharging the toxic chemicals along with large quantity of water which is used in dyeing and finishing processes in the textile industries. Our water resources are severely polluted by the release of these dyes [2]. Distinctive sorts of colourants are recycled in various industries for instance paint, textile, cosmetics, ink and plastics. Roughly 50 % of world-wide preparation of artificial textile colourants (700000 tons/year) are categorized as azo compounds which have the chromophore of -N=N- element in their molecular structure and above 15 % of the dyes used in textile industries are going down in surplus water stream throughout the dyeing procedures [3-5]. It is understood that azo dyes which are soluble, after assimilated in the body these azo dyes broke up to produce analogous aromatic amines by means of enzymes action in liver and gut flora, which may result in melanomain human. The fabric industry yields large amount of extremely coloured waste matter, which are mostly poisonous and resistant to demolition

by bioremediation. Consequently, it is obligatory to discover an effective technique to eradicate dyes from textile effluents [6,7]. Classical procedures that are yet in use to purify polluted water consist of adsorption [8], chlorination, coagulation [9], ion flotation [10], membrane process [11], sedimentation [12] and solvent extraction [13]. The resultants of these procedures are essential to be processed further for thorough decontamination. Advanced oxidation processes (AOPs) have been developed to encounter the intensifying need of an effective treatment of wastewater. Photo catalysis is the prominent method among advanced oxidation processes. In the process of photo catalysis, a photo catalyst generates influential oxidizing hydroxyl radicals that wipe out the pollutants from the waste water totally. The semiconductor photo catalyst TiO_2 has an extensive band gap *i.e.*, 3.2 eV and therefore efficaciously used as a photocatalyst in treating an organic as well as colouring contaminants [14]. A metal oxide semiconductor titanium dioxide has been found to be one of the most effective photocatalysts because of its high efficacy and stability. Titanium dioxide is white, inexpensive and nontoxic. It is one of the most widely used photocatalysts for disinfection [15-18]. The advancement of photocatalytic properties of TiO_2 by doping transition metal is the encouraging and eye-catching method because this possibly will improve the parting of electron-hole and surface modification (porous, surface area). The standard doping metals such as Sn, La, V, Cr, Ta, W, Fe, Cu, Ga, Tb, Ce, Co, *etc.* are noticed to be effective and the active site for

these gas species easy to be produced [19,20]. Inert metals such as Ag, Ni, Pt, Cu, Pd, Rh, have been considered and proved to be very effective for improvement of TiO_2 photocatalysis. These metals lessen the probability of recombination of electron-hole, inducing efficient charge separation and higher photo-catalytic reaction rates. Consequently, noble metals can help electron transfer with these properties, directing to advanced photocatalytic action. Various researches of inert metal deposition on TiO_2 have been concentrated on group VIII metals for UV-irradiated photocatalytic break down of organic contaminants and diverse dyes. Among a range of transitional metals, Fe^{3+} has been supposed to be an applicable nominee because of the point that the radius of Fe^{3+} ion (0.69 A) is analogous to that of Ti^{4+} (0.745 A), so Fe^{3+} can be effortlessly merged into the crystal lattice of TiO_2. In addition, ferric ion can specify a shallow trap for photo-generated electron and hole aimed at the reason that the level of the energy of Fe^{2+}/Fe^{3+} lies adjacent to that of Ti^{3+}/Ti^{4+}, give preference to the separation of photo-generated electron-hole pair and as a result lead to the progress of quantum yield [19].

Malachite green is 4-{[4-(dimethyl amino)phenyl]-(phenyl)methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride. Molar mass and molecular formula of the malachite green is 364.91 g/mol and $C_{23}H_{25}N_2Cl$, correspondingly. This dye is water soluble. Traditionally malachite green is utilized as a colourant. Malachite green is also active contrary to the *Oomycete saprolegnia* that contaminates fish eggs in commercial aquaculture. It is a very prevalent in treating the *Ichthyo phthirius* in freshwater aquaria. Malachite green also have parasiticidal and antibacterial ability [5].

EXPERIMENTAL

Titanium tetrachloride ($TiCl_4$, Aldrich, 97 %), silver nitrate ($AgNO_3$, Merck, 99.9 %), Absolute ethanol (Merck, 99.9 %), malachite green ($C_{23}H_{25}N_2Cl$, Merck, 85 %) and distilled water were used during the entire study.

Procedure: The solution of dye was prepared in 0.12 g of Ag doped TiO_2 and distilled water and the molarity of the solution was found to be 9.00×10^{-5} M. Subsequently as the solution attain homogeneity entire system was subjected to sunbeams for 6 h and stirred enthusiastically at room temperature. After each single hour, approximately 5 mL of suspension was taken out by means of syringe and centrifuged at 6000 rpm for 0.5 h and studied by ultraviolet visible spectrophotometer in the wavelength ranging from 200 to 800 nm. The pH of reaction mixture was modified to 7.5, after this, the solution was then exposed to a 200 W tungsten uplighter at 60 mW cm^{-2}.

Mechanism of photocatalysis: When doped photocatalyst is subjected to sunlight, then absorption of energy by the electrons of valance band takes place and transmit that energy to conduction band resulting in the production of an electron-hole pair. The hole in the valance band, h^+_{vb} reacts with H_2O to generate $OH^\bullet$ and electron in the excitation band, e^-_{eb} reacts with dissolved O_2 to produce O_2^-. The decomposition of dye takes place due to these active radicals [21,22]. At the point when a semiconductor, assimilates photons the valence band electrons are eager to the conduction band. For this to happen,

the vitality of photon must match or surpass the band gap vitality of the semiconductor. This excitation results in the development of an electronic vacancy or positive gap at the valence band edge. This positively charged hole attaches on the surface of dye and reacts with the adsorbed water molecules producing the radical $OH^\bullet$. This hydroxyl radical has great ability for oxidation of organic molecules (Fig. 1). The basic mechanism is as follows:
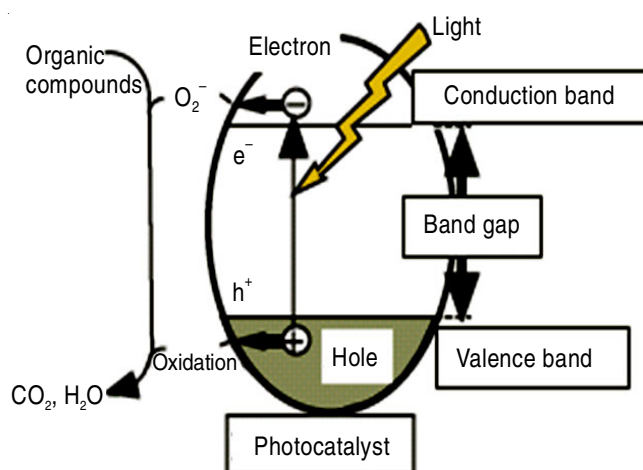
$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb}$$

$$H_2O + h^+_{vb} \longrightarrow OH^- + H^+$$

$$O_2 + e^-_{cb} \longrightarrow O_2^-$$

$$O_2^- + H^+ \longrightarrow HO_2^-$$

$$2HO_2^- \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \longrightarrow 2^\bullet OH$$
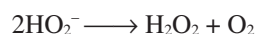
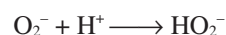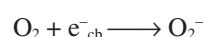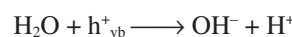$$^\bullet OH + Dye \longrightarrow CO_2 + H_2O$$

Fig. 1. Mechanism of photocatalysis

Once the reaction has initiated the molecules generated by the oxidation of the dye (*i.e.*, products) can be adsorbed on the catalyst and oxidized again due to the constant formation of $OH^\bullet$ during the irradiation period.

RESULTS AND DISCUSSION

The efficacy of dyes degradation has been studied by changing the concentration of dye and by determining the absorbance of these dyes. Effective degradation of the dyes is carried out in batch photo reactor by using TiO_2 doped catalyst. The photocatalytic investigation is done by using TiO_2 doped catalysts that are used for the applicable break down of dyes. There was established a format of variables in which the concentration of the dye, pH, time for exposing in the UV light and concentration of the catalyst were changed and finally applied to various solutions of the dyes. It was noticed that as time for exposure to UV light was increased, the absorbance of malachite green solution decreases (Fig. 2). A straight line graph between $1 + \log A$ *vs.* time was attained (Table-1), which shows that the pseudo-first order kinetics was followed by photocatalytic degradation of malachite green.
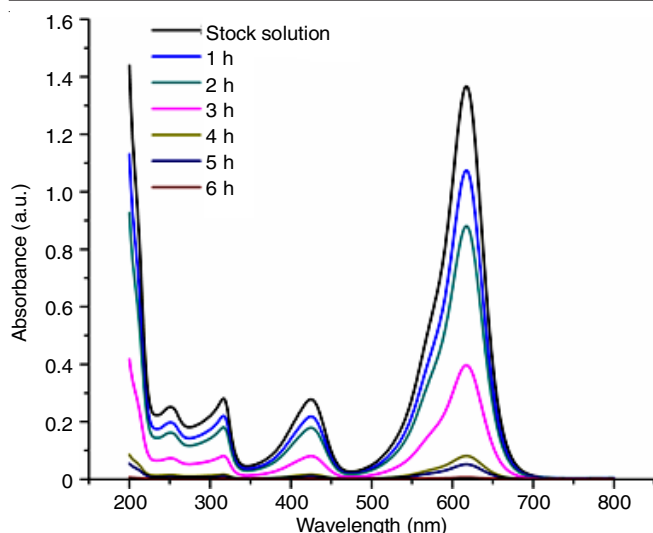
Fig. 2.   Effect of pH on photocatalytic degradation of malachite green (10 ppm) [TiO₂] = 10 mg/L, Irradiation time = 6 h

Fig. 3. Full scanning spectrum of malachite green (10 ppm) dye solution

TABLE-1
STANDARD RUN DATA. CONDITIONS; [MALACHITE GREEN] = 10 ppm; NANO-CATALYST USED = 10 mg/L, pH = 9

Time (min)	Absorbance (A)	1 + log A
0	0.60	0.78
5	0.52	0.71
10	0.45	0.66
15	0.38	0.57
20	0.35	0.52
25	0.29	0.47
30	0.25	0.40
35	0.21	0.37
40	0.19	0.28
45	0.16	0.20
50	0.14	0.15
55	0.12	0.08
60	0.10	0.21

For this reaction, the constant rate was determined by using the following equation k = 2.303 × slope.

Degradation of malachite green in UV irradiation

UV-visible spectra: During photo-radiation UV-visible spectrum of malachite green using TiO₂ doped catalyst is shown in Fig. 3. The absorption peaks of malachite green were observed at 313, 243 nm in UV region as well as 614, 427 nm in the visible region. The decolourization rate was documented according to the change in intensity of absorption peak at 614 nm. During the reaction peaks at 243, 313 and 427 nm reduced, which showed the discoloration of the dye. The degradation of malachite green in solar irradiation experiments were done in day time (between 9 am to 4 pm), to concentrate on the impact of sun based illumination on the photo catalytic degradation of malachite green. 100 mL of 50 mg/L dye solution was illuminated under sun oriented light. The effect of catalyst dosage and pH of the dye solution was additionally studied.

Effect of quantity of semiconductor: The dye degradation may influence by the quantity of semiconductor therefore, altered quantities of catalyst were used. It was noticed that on increasing the amount of nano catalyst the rate of reaction also increases. The optimal value of photo catalyst is at 0.12 g.
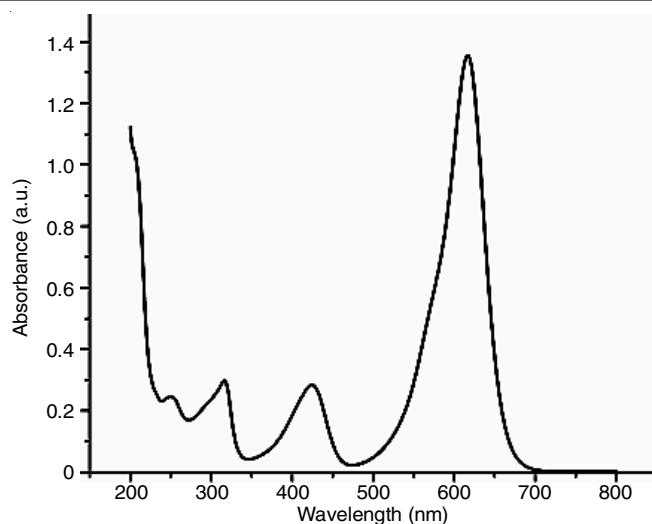
The reaction rate turns into nearly constant beyond 0.12 g. This can be elucidated on the grounds that on increasing the quantity of semiconductor, the visible surface area to the semiconductor was also raise (Table-2). On the other hand, subsequently a definite value (0.12 g), the raise in the semiconductor concentration results in enhance in the width of the layer of semiconductor but it will have no influence the subjected surface area. The above mentioned phenomena were approved by means of reaction vessels of dissimilar dimensions. It was viewed that as the level of vessel is increased, the saturation point moved to a greater value and *vice versa*.

TABLE-2
EFFECT OF AMOUNT OF SEMICONDUCTOR (Ag/TiO₂); CONDITIONS; [MALACHITE GREEN] = 10 ppm, pH = 9

Amount of Ag/TiO₂ (g)	Rate constant (k) × 10⁻⁴ s⁻¹	Amount of Ag/TiO₂ (g)	Rate constant (k) × 10⁻⁴ s⁻¹
0.01	2.39	0.10	4.49
0.03	3.06	0.12	4.83
0.05	3.56	0.14	4.82
0.07	4.22	0.16	4.84

Effect of dye concentration: The outcome of colourant concentration was noticed *via* acquiring changed concentrations of the malachite green dye. It was observed that as rise in the concentration of malachite green will activate photocatalytic break down rate of the colorant. It may be ascribed that by increasing the dye concentration the molecule of the dye increases. In this way more number of molecules are accessible for excitation and successive energy/electron transferral and therefore the rate of degradation was increased (Table-3). However, result was reversed as the concentration of dye will increase above the optimum value (9.00×10^{-5} M). The reason behind this fact is that when a specific concentration is attained after that the dye might act as an inner filter and this one will not further facilitate adequate amount of intensity of light that effect surface of the photo catalyst at the extremity of reaction vessel.

Influence of pH: The degradation of malachite green is also altered by changing the pH of solution. On the breakdown of malachite green the influence of pH was studied in the

TABLE-3
EFFECT OF MALACHITE GREEN CONCENTRATION;
CONDITIONS; pH = 7.5, Ag/TiO$_2$ = 0.12 g

Concentration of dye	Rate constant (k) × 10^4 (s^{-1})	Concentration of dye	Rate constant (k) × 10^4 (s^{-1})
0.60	2.77	1.10	3.89
0.70	3.26	1.20	3.41
0.80	4.08	1.30	2.97
0.90	4.83	1.40	2.00
1.00	4.22	1.50	1.61

pH range from 4.5 to 8.5. It has been observed that the rise in pH directly increases the degree of photocatalytic activity of malachite green (Table-4). It reached optimal value at pH 7.5. If pH is further increased, there was a decrease in reaction rate. This activity possibly will be described on the basis that with the increased pH, there is possibility of hydroxyl radical's formation. By the creation of additional •OH radicals, the photocatalytic degradation level of the colourant rises. Beyond pH 7.5, the positively charged form of malachite green is transformed to its neutral structure, which shows no affinity to those semi-conductors which have negatively charged surfaces because of adsorption of $^-$OH ions. Hence there will be a decline in the rate of breakdown of the dye.

TABLE-4
EFFECT OF pH ON RATE OF PHOTODEGRADATION.
CONDITIONS; [MALACHITE GREEN] = 10 ppm,
Ag/TiO$_2$ = 0.12 mg/L

pH	Rate constant (k) 10^4 (s^{-1})	pH	Rate constant (k) 10^4 (s^{-1})
4.5	1.32	7.5	4.61
5.5	1.47	8.0	4.68
6.0	2.22	8.5	4.73
6.5	3.73	9.0	4.83
7.0	4.24	9.5	4.02

Conclusion

On the basis of the reported investigations, this analysis emphases on the involvement of different operative factors on the photocatalytic degradation of several colorants and phenols and explains the key improvements. Titanium oxide has been recom-mended to be applicable for the mineralization and degradation of different contaminated organic waste product, *e.g.*, phenols and colorants in water in the existence of UV and visible light. There is an optimum value for the dopant concentration and photocatalyst loading at which the photo activity attains a maxima. As the concentration of the dopant is increased, photocatalytic activity is increased with the separation of electron-hole. Kinetic studies reveal that the photo degradation follow pseudo first order reaction. The conclusions also put forward that several operational parameters such as type of photocatalyst, different methods of preparation of photo catalyst, source of light, types of contaminant, primary concentration of contaminants, dopant concentration of the dopant and finally the loading of photo catalyst.

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