

# The Role of Inorganic Salts on the $\text{TiO}_2$ based Photocatalysis of Rodamin B (RB) in Aqueous Solutions

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## Abstract

The photo-catalytic bleaching of industrial dyes using  $\text{TiO}_2$  has appeared promising in laboratory studies, but little attention has been focused on whether other species might be found in wastewater have a harmful or useful effects on the photo-bleaching. This study highlights effects of some ionic species on the photo-bleaching of Rodamin B (RB) dye in the aqueous acidic and basic solutions. The rate of RB photo-catalytic oxidation was studied at different pH values. The effect of solvents on photo-degradation of RB was also investigated. Various metals doped titanium dioxide ( $\text{TiO}_2$ ) photocatalysis have been studied intensively for the photodegradation of dye in wastewater treatment. The Ag particles were photodeposited on  $\text{TiO}_2$  powder surface. Nanostructure Ag- $\text{TiO}_2$  nanoparticles were synthesized by photo reduction method. The X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy dispersive X-ray spectroscopy (EDXS), and photoluminescence (PL) spectrophotometry were applied to investigate the structure and morphologies of the samples. It was found that the loaded Ag particles have no effect on the XRD patterns. Photodegradation capacity of  $\text{TiO}_2$  nanoparticles was compared to Ag/ $\text{TiO}_2$  photoactivity. Above the optimum silver ion loading, the activity of Ag/ $\text{TiO}_2$  particles decreased. The use of electron acceptors, such as  $\text{S}_2\text{O}_8^{2-}$  in  $\text{TiO}_2$  system increased dye photo-degradation.

**Keywords:** Photo catalytic oxidation;  $\text{TiO}_2$ ; Rodamin B; Ionic species

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## Introduction

Rhodamine dyes (RB) are important class of xanthene dyes. They have high quantum yield of fluorescence and high absorption factors. They have been widely studied due to their properties and practical applications in dye lasers [1]. Furthermore, RB dyes have been used for some specific applications, such as biological stains, electrochemical luminescence sensitizer, water-tracing agents, molecular probes, chromo-ionophores in optical chemical sensors and solar collectors and many others devices so treatment extra dye in wastewater is very important [2]. Clearly, wastewater is full of different material with different range of the pH values. Photo-degradation efficiency of dyes is affected by pH of the solution in the presence of  $\text{TiO}_2$ .

Heterogeneous photo-catalysis is a processing which the irradiation of an oxide semi-conductor produces photo-excited electrons ( $e^-$ ) and positive charged holes ( $h^+$ ) to the form

hydroxyl radical and superoxide radical anion, that both of them play as the oxidizing species in the photo-catalytic oxidation method. The efficiency of photo-excitation of the semi-conductor is dependent on the energy state of the electrons valence band and conduction band. The extent of dye adsorption depends on several factors such as, dye nature of the dye, surface area of the used photo-catalyst, concentration and pH of the solution. The pH controls the surface charge of the photo-catalyst and dye. Adsorption of the dye is minimum when the pH of the solution is at the isoelectric point (point of zero charge). The surface of the photo-catalyst is positively charged below isoelectric point and carries a negative charge above that. As a result, the structure of dye is important to be found in due course, i.e., the efficiency of adsorption on the surface of a photo-catalyst can be low or high in acidic and basic media [3].

In  $\text{TiO}_2$ /UV system positive charged holes can be scavenged by the negatively charged anions and therefore depends on the

positive charged or negatively charged adsorption of dyes on the surface of  $\text{TiO}_2$  is considerably inhibited or promoted [4]. Previous studies indicated that inorganic anions can scavenge  $\bullet\text{OH}$  to form the corresponding anion radicals [5-7]. The anion radicals may themselves oxidize organic and inorganic compounds [5,8,9], which can also influence on the total rates of the photo-catalytic oxidation. It is also reported that competitive adsorption of the inorganic anions for active sites on the  $\text{TiO}_2$  surface may contribute to the photo-catalytic degradation of organic compounds [10-13]. For instance,  $\text{Cl}^-$  decreases the degradation rate of 2-chlorophenol and 2-nitrophenol at pH values lower than the  $\text{TiO}_2$  point of zero charge (pHpzc), while  $\text{Cl}^-$  had no inhibitory role at pH values greater than the pHpzc due to slight adsorption to the negatively charged  $\text{TiO}_2$  surface [12]. Inorganic anions can also change the rates of dye photo-catalytic oxidation in one of the following ways: (i)  $\bullet\text{OH}$  scavenging by inorganic anions, (ii) direct oxidation of dye by anion radicals, or (iii) adsorption of inorganic anions to the  $\text{TiO}_2$  surface [14,15].

The photo-catalytic activity of  $\text{TiO}_2$  for the oxidative degradation of (RB) may be enhanced by first, surface modification using metals, second, transition metal doping and third, coupled photo-catalysts. In this research Ag metals were used for increasing in photo-degradation of (RB) dyes. Improving the photocatalytic activity by Ag deposition may be associated to different mechanisms: (1) Ag nanoparticles deposited on  $\text{TiO}_2$  act as electron traps, enhancing the electron-hole separation and the later transfer of the trapped electron to the adsorbed  $\text{O}_2$  acting as an electron acceptor [1-3].

(2) self-photosensitization pathway, that means, extend the light absorption into the visible range and enhance surface electron excitation by plasmon resonances excited by visible light, injecting an electron into the conduction band of the  $\text{TiO}_2$  semiconductor, so, the injected electron on the  $\text{TiO}_2$  particle reacts with adsorbed oxidants to produce reactive oxygen radicals and dye is degraded by these oxygen radicals. Under visible light irradiation, the semiconductor  $\text{TiO}_2$  acts only as an electron-transfer mediator and

(3) modify the surface properties of photocatalyst [4-8]. Zakerhamidi and co-author studied solvent effects on the dipole moment and photophysical properties of rhodamine dyes. This study describes the effective parameters such as pH of the solution, type of solvent and cationic and anionic species on the photo-bleaching of (RB) in the presence of  $\text{TiO}_2$  nanoparticles [16,17]. The amount of degradation of RB were discussed in different circumstances. In this experience it was investigated the effects of pH and common salts and solvent on photo degradation of dye Rhodamine (RB).

## Materials and Methods

Titanium dioxide nanoparticles (purity >99.5 %, ) with average particle size 30 nm and specific surface of 50  $\text{m}^2/\text{g}$  was purchased from Degussa Corporation (USA).

Compounds of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2$  were

obtained from Fluka (Buchs, Switzerland) and used without further purification. The pH (2, 6 and 12) values of the solutions were adjusted using HCl (0.01 M) and KOH (0.01 M) solutions. RB dye ( $10^{-5}$  M) was prepared from Fluka (Buchs, Switzerland). The photo-catalyst was added to dye solution and the suspension was irradiated under UV-Vis light. Then fluorescence spectra of the dye solutions were recorded and de-colorization process was monitored in terms of change in intensity at  $\lambda_{\text{max}}$  excitation (550 nm) and  $\lambda_{\text{max}}$  emission (580 nm) of the dye after 0, 2, 5, 8, 10 minute irradiation.

Ag- $\text{TiO}_2$  was synthesized by photo-reduction of  $\text{AgNO}_3$ . In this way,  $\text{Ag}^+$  ions are deposited as Ag metal on the  $\text{TiO}_2$  surface by photo-reduction of  $\text{AgNO}_3$  under UV irradiation [8]. One gram of  $\text{TiO}_2$  was added into 250 mL of double-distilled water and then irradiated with UV-Vis light for 10 min to remove any impurities present on  $\text{TiO}_2$  surface. Then appropriate amount of  $\text{AgNO}_3$  was added into the suspension of  $\text{TiO}_2$  solution and the suspension adjusted to pH 3.5, finally it was irradiated using UV light for 40 min with continuous stirring under  $\text{N}_2$  atmosphere. The suspension was then filtered, washed, dried and then ground into a fine powder [9,10].

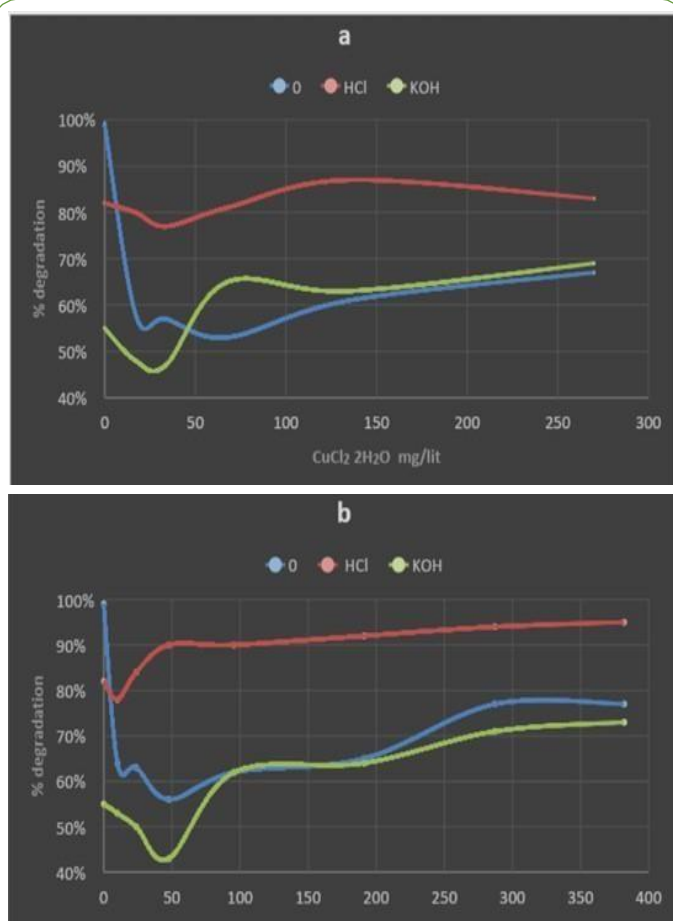
## General procedure

The photo-catalytic reaction was carried out in an inner irradiation type reactor. The photo-catalyst powder was dispersed by magnetic stirrer. A 300 W high-pressure mercury lamp from Oriol GMBH, Model 8500 (Cheltenham, England) was used as the light source and spectro-fluorimeter of Perkin-Elmer LS-3B Luminescence (USA) was used. The cell was made with Quartz (3 mL content) that it was put it in the close space in front of the light in reactor. Analysis of the crystalline structures was performed by XRD Diffractometer (GBC MMA made in Australia) with wavelength of Cu K $\alpha$  radiation in  $2\theta$  range from  $15^\circ$  to  $80^\circ$ , SEM analysis was performed by a VEGA TESCAN (USA) instrument.

## Results

### The effect of pH

To study the effect of pH on photo-degradation, several experiments were done using  $1.0 \times 10^{-5}$  M dye concentration and it was exposed under UV-Vis light in the presence of nanoparticles of  $\text{TiO}_2$ . **Figure 1** shows increasing of % degradation of RB in acidic (pH=2), normal (ca. pH=6) and basic medium (ca. pH=12) with increasing of anionic species, after ten minute UV-Vis irradiation in every experiments and in present of 0.1 g/L titanium dioxide. As can be seen acidic, normal and basic medium is significantly depended on the concentration of anions either  $\text{NO}_3^-$  or  $\text{Cl}^-$ . The behavior of dye degradation in acidic, normal and basic medium are nearly the same so that in higher concentration of anions the percentage of dye degradation as function of anion concentration is smooth (**Figure 1**).

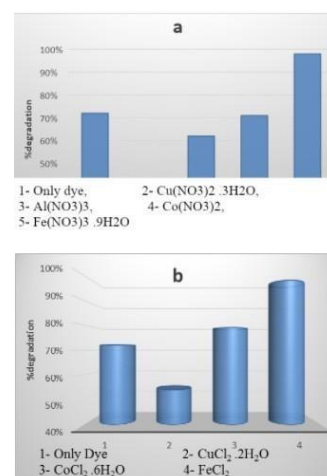


**Figure 1:** Effect of anions on the %degradation of RB under UV-Vis irradiation for 5 min at the present of 0.1 g/L titanium dioxide, in acidic (■), normal (♦) and basic (5) medium (a) Cl<sup>-</sup> and (b) NO<sub>3</sub><sup>-</sup>.

### Effect of cations on the titanium dioxide-based photo-catalytic oxidation of aqueous R

Wastewater is full of material, effect anion and cation for increase adsorption dye on catalyst was investigated in different pH, however the kind of cation is important. Salts of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> are very common. In a quartz cell, 3 mL of the solution containing 0.01 M of (a) NO<sub>3</sub><sup>-</sup> and (b) Cl<sup>-</sup> are exposed by UV-V irradiation for five minutes in the presence of 0.1 g/L titanium dioxide. Experiments were performed using 50 mL of solution with constant initial concentration of dye RB (10<sup>-5</sup> M) and in the present of salts nitrate and chloride. **Figure 2** shows the effect of cations on % degradation of RB in normal medium with increasing of anionic species. The counter ions are the same, i.e., (a) NO<sub>3</sub><sup>-</sup> and (b) Cl<sup>-</sup> for the cations of Al<sup>3+</sup>, Cu<sup>2+</sup> and Co<sup>2+</sup> and Fe<sup>3+</sup>. **Figure 2** illustrates the influence of the cations on the % degradation of RB. Results reveal that % degradation of RB is highly enhance in the presence of Fe<sup>2+</sup> and in contrast the degradation is very low in the presence of Cu<sup>2+</sup>. The other cations (Al<sup>3+</sup>, Co<sup>2+</sup>) are also have differences effects, in this case both cations of Al<sup>3+</sup>, Co<sup>2+</sup> have almost similar effect on the % degradation of RB so that % degradation almost have the nearly the same values. The order

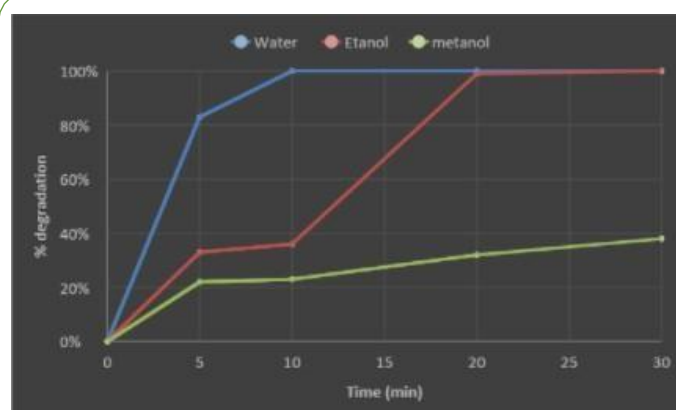
of % degradation for the cations are as follows Fe<sup>3+</sup> > Co<sup>2+</sup> > Al<sup>3+</sup> > Cu<sup>2+</sup> (**Figure 2**).



**Figure 2:** Effect of caions on the % degradation of RB under UV-Vis irradiation for 5 min at the present of 0.1 g/L titanium dioxide. (a) NO<sub>3</sub><sup>-</sup> and (b) Cl<sup>-</sup>.

### Effect of solvent

The percentage of dye degradation was also examined using different of solvents i.e., water, methanol and ethanol. **Figure 3** illustrate the effect of dye degradation in aqueous (water) and nonaqueous (alcoholic medium). Results indicated that rate of % degradation in water is the highest amount (**Figure 3**).



**Figure 3:** Effect of solvents on the %degradation of RB under UV-Vis irradiation for 5 min at the present of 0.1 g/L titanium dioxide, in ethanol (■), water (♦) and methanol (5) medium.

### Characterization of TiO<sub>2</sub> and Ag-TiO<sub>2</sub> nanoparticles

In order to investigate the changes in the crystal structure due to silver deposit, XRD measurements were taken in the range of 2θ 15-80 for pure TiO<sub>2</sub> and Ag-TiO<sub>2</sub> nanoparticles (**Figure 1**). It is seen that the XRD patterns of Ag-TiO<sub>2</sub> sample are almost the same as for pure TiO<sub>2</sub>, except for the intensities of the peaks. Also, the XRD patterns show no diffraction peaks due to silver deposition. This may be due to the fact that deposition alters the crystallinity but not the crystal structure of Ag-TiO<sub>2</sub> and thus suggest that the silver deposits are merely placed on the surface of the crystals. Diffractions that are attributable to anatase phase of TiO<sub>2</sub> crystals



are clearly detectable at  $2\theta$  25 [10, 11] (Figure 4).

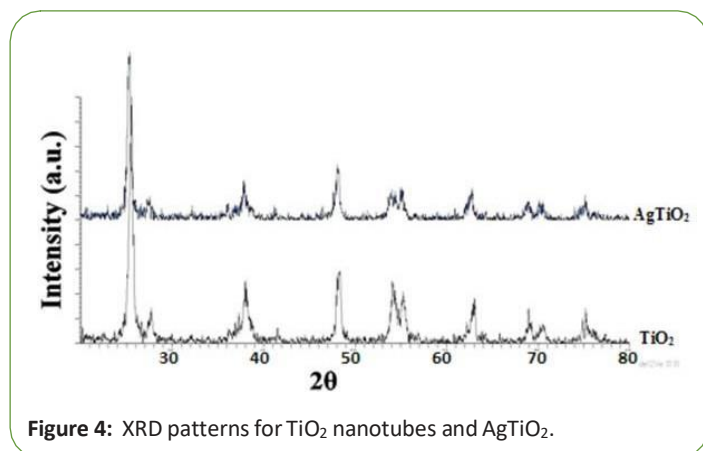


Figure 4: XRD patterns for TiO<sub>2</sub> nanotubes and AgTiO<sub>2</sub>.

Figure 2 shows the PL spectra of unloaded and loaded TiO<sub>2</sub> samples. The signal intensity of unloaded sample is very strong and shows evident characteristics of the radiative recombinations of electrons and holes. The PL peak at 367 nm arises from the band-to-band recombination which evidently decreases with the loaded Ag particles. Two factors affect the PL intensity after Ag deposition. One is the migration of the electrons from TiO<sub>2</sub> to Ag particles; the other is the Ag plasmon absorption. The PL band from 390 to 440 nm is from the recombination transition related to the surface structure, which also decreases with the loaded Ag, indicating the photo-deposited Ag has affected the surface structure of TiO<sub>2</sub>, leading to the decrease of surface recombination but if silver amount became above the optimum loading, silver particles can also act as recombination centers so the signal intensity of loaded sample is very strong [11, 12] (Figure 5).

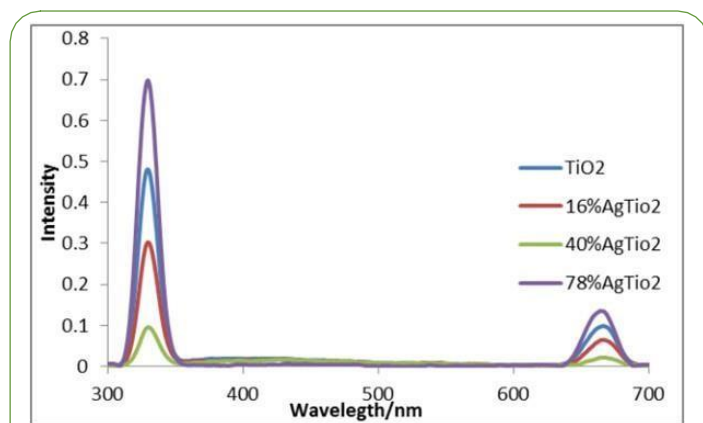


Figure 5: The PL spectra of unloaded and loaded TiO<sub>2</sub> samples.

Figure 2 shows SEM images of the AgTiO<sub>2</sub> composites. The general morphology of the AgTiO<sub>2</sub> can be clearly observed in these micrographs. TiO<sub>2</sub> particles were uniformly distributed. It can be considered that the better dispersion provides a larger number of active catalytic centers for the photocatalytic reaction (Figure 6).

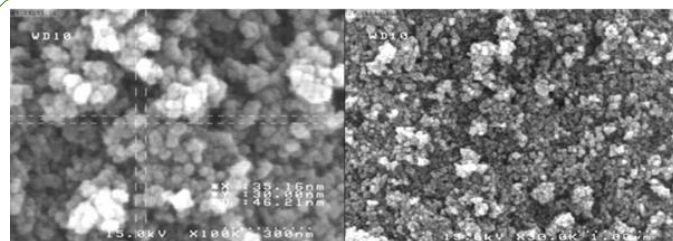


Figure 6: SEM images of AgTiO<sub>2</sub> composites.

Figure 4 shows the results of elemental analysis from the EDX spectra of AgTiO<sub>2</sub> with 23, 45 at % weight of Ag composites. These spectra show the presence of peaks from Ag and Ti. The elemental composition analysis of the composite series is listed in Tables. Ti was the major elements in the composite series. Figure 7a is 23 at % weight of Ag composites and Figure 7b is 45 at % weight of Ag composites. As expected, it was observed that the Ag content of the AgTiO<sub>2</sub> composites showed an increase with increasing the at % weight of Ag (Figure 7).

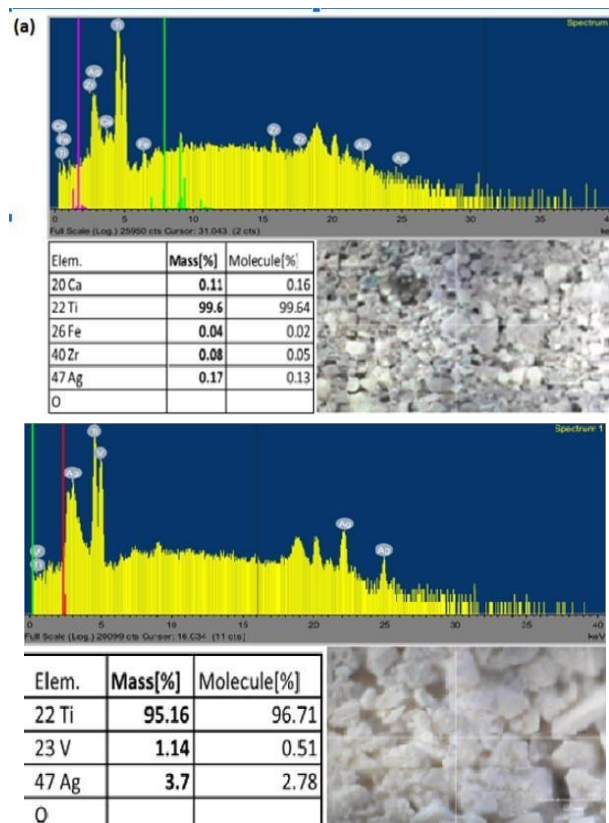
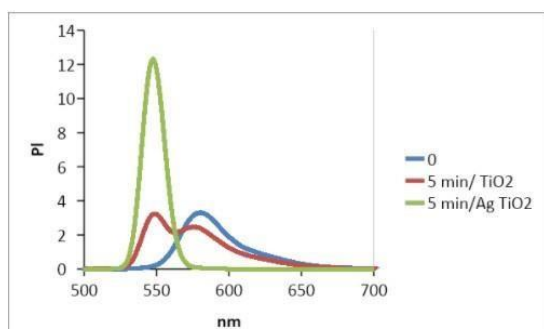


Figure 7: The results of elemental analysis from the EDX spectra of AgTiO<sub>2</sub> with (a) 23, and (b) 45 at% weight of Ag composites.

### Photo-catalytic degradation of RB

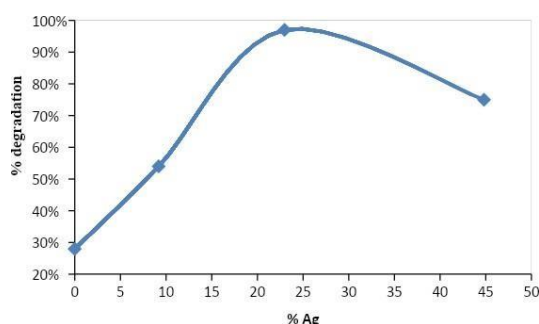
Figure 5 shows the change in the intensity of fluorescens spectra of RB ( $1.0 \times 10^5$  M) in the presence of the TiO<sub>2</sub> and Ag-TiO<sub>2</sub> nanoparticles (100 mg/L) as photo-catalyst. After irradiation with UV-Vis light, the intensity of spectra decreased due to decolouration of the dye. Figure 5 indicated that speed of decolouration, after 5 min irradiation in present of AgTiO<sub>2</sub> was faster than in present of TiO<sub>2</sub> (Figure 8).



**Figure 8:** Shows the change in the intensity of fluorescens spectra of RB ( $1.0 \times 10^{-5}$  M) in the presence of the  $\text{TiO}_2$  and Ag- $\text{TiO}_2$  nanoparticles (100 mg/L) as photo-catalyst.

### Effect of catalyst amount

The effect of Ag- $\text{TiO}_2$  amount on the photo-catalytic degradation of RB was studied at fixed concentration of RB M in aqueous solutions. **Figure 6** shows the photo-degradation efficiency of RB (% E) as a function of the amount of at % weight of Ag composites. An optimum silver ion loading of 23 at % weight of Ag was found. For all silver ion loadings used, Ag/ $\text{TiO}_2$  performed significantly better than bare  $\text{TiO}_2$ . Above the optimum silver ion loading, the activity of Ag/ $\text{TiO}_2$  particles decreased. There are several reasons for the existence of an optimum metal loading. It is also possible that above the optimum loading, silver particles can also act as recombination centres [5,6,13] (**Figure 9**).

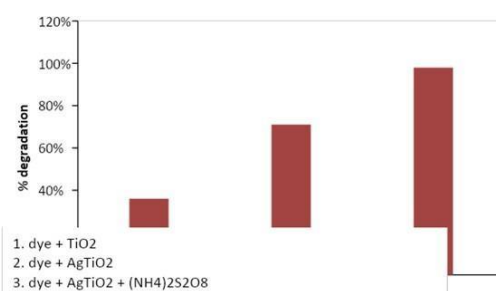


**Figure 9:** Shows the photo-degradation efficiency of RB (% E) as a function of the amount of at % weight of Ag composites.

### Effect of electron acceptors in dye photo-degradation

The use of inorganic oxidants, such as  $\text{S}_2\text{O}_8^{2-}$  in  $\text{TiO}_2$  system increased the quantum efficiencies either by inhibiting electron-hole pair recombination through scavenging conduction band electron at the surface of  $\text{TiO}_2$  or by offering additional oxygen atom as an electron acceptor to form the superoxide radical ion and along reaction electron acceptor with Ag $\text{TiO}_2$  due production of active radicals. **Figure 7** gives the effect of electron acceptors in photo-catalytic activity of Ag $\text{TiO}_2$ . Dye exposed under UV-Vis for 2 min, (a) in present only Ag $\text{TiO}_2$ =0.12 g/lit, (b) in present  $\text{TiO}_2$ =0.1

g/lit and in present of  $\text{S}_2\text{O}_8^{2-}=1 \times 10^{-3}$  M [10] (**Figure 10**).



**Figure 10:** The effect of electron acceptors in photo-catalytic activity of Ag $\text{TiO}_2$ . Dye exposed under UV - Vis for 2 min, (a) in present only Ag $\text{TiO}_2$  = 0.12 g/lit, (b) In present  $\text{TiO}_2$  = 0.1 g/lit and in present of  $\text{S}_2\text{O}_8^{2-} = 1 \times 10^{-3}$  M.

## Discussion

### The effect of pH

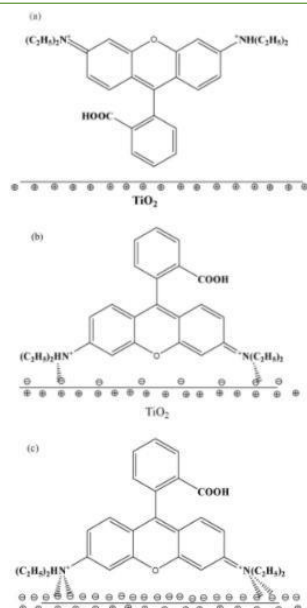
The pH of the solution is an important parameter which strongly influences the surface charge properties in aqueous dispersion. Generally, surface of the net  $\text{TiO}_2$  is positively charged in acid media and negatively charged in alkaline media with an isoelectric point of around pH 6~7 [18]. Therefore, adsorbates in the aqueous solution tend to adsorb on the surface of  $\text{TiO}_2$  by the negatively charged or electron abundant group in acidic solution and by positive charged in alkaline solution because of the electrostatic interaction [19]. The  $\zeta$ -potential of  $\text{TiO}_2$  with different pH amounts was investigated before. Photo-degradation efficiency of dyes is affected by pH of the solution in the presence of  $\text{TiO}_2$ . The amount of pH solution changes the surface charge of  $\text{TiO}_2$  particle [3]. As a result, the adsorption of dye on the surface is altered thus causing a change in the reaction rate. Under acidic or alkaline condition the surface of  $\text{TiO}_2$  can be protonated or deprotonated (Eq. 1 and 2) respectively according to the following reactions, therefore, the pH effect is often dependent on the nature of the dye. To study the effect of pH on photo-degradation, several experiments were done using  $1.0 \times 10^{-5}$  M dye concentration and it was exposed under UV-Vis light in the presence of nanoparticles of  $\text{TiO}_2$  [20]. **Figure 1** shows increasing of % degradation of RB in acidic (pH=2), normal (ca. pH=6) and basic medium (ca. pH=12) with increasing of anionic species, after ten minute UV-Vis irradiation in every experiments and in present of 0.1 g/lit Titanium dioxide. **Figure 1** shows the effect of anions (i.e.,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) on the % degradation of RB under UV-Vis irradiation (for 5 min) at the present of 0.1 g/L titanium dioxide in acidic, normal and basic medium. As can be seen acidic, normal and basic medium is significantly depended on the concentration of anions either  $\text{NO}_3^-$  or  $\text{Cl}^-$ ). The behavior of dye degradation in acidic, normal and basic medium are nearly the same so that in higher concentration of anions the percentage of dye degradation as function of anion concentration is smooth. It is pertinent to point out that in both normal and basic medium the concentration of anion at concentration of about 25 mg/L

has lowest value of degradation either in the presence of  $\text{NO}_3^-$  or  $\text{Cl}^-$ . Results also revealed that the % degradation of RB is hardly depends on the concentration of anion concentration in acidic media. As a result the % degradation of RB is depended on medium, i.e., acid, neutral and basic. This evidence can be attributed to the surface of nanoparticles as well as the chemical structure of the dye in question.



### Acidic medium

In acidic medium, the rationale behind this is that at low pH values, more  $\text{H}^+$  are available for adsorption to mask the surface of the catalyst thus inhibiting the photo-excitation of semiconductor particles, [3]. In addition, adsorption of dye on the surface positively charged of  $\text{TiO}_2$  is not favorite, results indicated that adsorption of RB on  $\text{TiO}_2$  is significantly increased in the presence of the anionic species in acidic medium and hence increasing RB % degradation. **Figure 11** shows theoretically suggestions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the anion species ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ) in acidic solution with  $10^{-2}$  molar of HCl with different concentrations of salt (**Figure 11**).

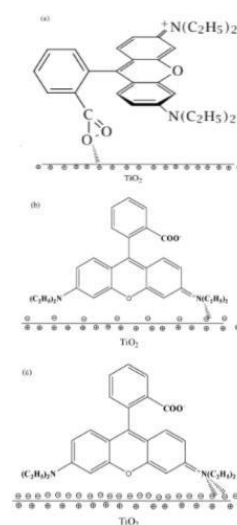


**Figure 11 :** Theoretically suggestions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the anion species ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ) in acidic solution, a no salt, b has moderate concentration and c with higher concentration than b.

### Neutral medium

In neutral solution, the pH value of the reaction solutions under the experiment conditions was controlled at about 6, in which the surface of  $\text{TiO}_2$  was positively charged. The acid dissociation constant of the carboxyl group of RB is about  $4.1 \pm 0.1$ . Thus, under the experimental conditions, most of the carboxyl group of RB was dissociated and negatively charged at  $-\text{COO}^-$  state and RB tends to adsorb on the surface positively charged of  $\text{TiO}_2$

by the negatively charged carboxyl group of RB [19]. So rate of photo degradation of dye (RB) without salt in neutral medium is the highest. Therefore, RB Dye is zwitter-ionic form when the solution pH is higher than the acid dissociation constant of RB [21]. Adsorption of RB molecules through the positively charged significantly increased in the presence of the anionic species in normal medium. **Figure 12** shows theoretically suggest ions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the anionic species ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ) in normal medium (**Figure 12**).

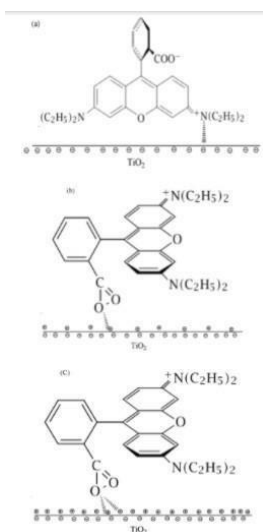


**Figure 12:** Theoretically suggestions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the anionic species ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ) in normal medium, a no salt, b has moderate concentration and c with higher concentration than b.

### Basic medium

In basic solution, RB is zwitter-ionic and the surface of  $\text{TiO}_2$  is negatively charged. As a result, adsorption of RB molecules through the positively charged is chosen on the surface negatively charged of  $\text{TiO}_2$ . Besides  $\text{H}_2\text{O}_2$  molecules that are formed during photo-degradation process could easily self-decomposed in basic medium. The species of  $\bullet\text{OOH}$  could also react with both  $\bullet\text{OH}$  radical as well as  $\text{H}_2\text{O}_2$  in the basic medium. Thus, it would decrease the concentration of  $\bullet\text{OH}$  radicals and affect degradation efficiency of RB. The degradation rate was found to increase with oxidation potential of  $\bullet\text{OH}$  radical in the acidic medium as reported by Wang additionally in the alkaline conditions there is a competitive adsorption between hydroxyl groups and the dye molecule [3,22,23].

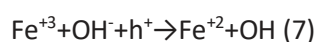
It is pertinent to point out that the adsorption of RB molecules through the negatively charged carboxyl group on the surface negatively charged of  $\text{TiO}_2$  was also significantly increased in the presence of the cationic species in basic medium. Results indicated that positively copper complex, leads to increase adsorption of RB on  $\text{TiO}_2$  and hence increasing color removal from the solution. **Figure 13** shows theoretically suggest ions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the cation species  $\text{Cu}^{+2}$  in basic medium using  $10^{-2}$  M of KOH with different concentrations of salt (**Figure 13**).



**Figure 13:** Theoretically suggestions for increasing adsorption of RB on  $\text{TiO}_2$  in the presence of the cation species  $\text{Cu}^{+2}$  in basic medium, a no salt, b has moderate concentration and c with higher concentration than b.

### Effect of cations on the titanium dioxide-based photo-catalytic oxidation of aqueous RB

It can be justified that suppression of  $\text{OH}^\bullet$  radicals takes place due to trapping of the conduction band electrons by the adsorbed metal ions and decreasing color removal might be expected [24]. Results indicated that significant decreasing in the initial degradation rate of photo-catalysis, is occurred in the presence of cations, among them  $\text{Cu}^{+2}$  has the largest effect (Figure 2). It can deduce that the retardation is due to  $\text{Cu}^{+2}$  ions, which it scavenges the electrons required for the formation of hydroxyl radicals. Results specified the Fe ions have an important role (increasing of % degradation) in the photo-degradation process which also has been reported by many researchers [25-27].  $\text{Fe}^{+3}$  ions can accelerate the decomposition of many organic compounds in water using hydroxyl radicals formed in the following process [28].



This effect could be attributed to the scavenging of OH radicals by solvents or solubility of electrons, which are vital for generating OH radicals. If latter is the reason, one can expect higher degradation in more polar solvents than in less polar solvents. The dielectric constants of methanol and ethanol are 32.6 and 24.3, respectively. Therefore the possibility of generation OH radical in protic solvent like methanol is much higher compared to that of ethanol and consequently increases the rate of the degradation [29].

This is not surprising since excited electrons are less solvated in organic solvents than in aqueous solution. It may be that as the organic portion of the reaction mixture is increased, free electrons becomes less easily solvated, and the possibility of recombination with the positive hole ( $\text{h}^+$ ) increases. Another possibility is that the acetonitrile (and the other solvents examined) scavenge surface holes, which might be expected to retard photo-oxidation

[30,31].

As a result, solvent also can play a significant role in photo-degradation process. These effects are closely related to the nature and degree of the solute dipole moment changes in the process of solute solvent interactions [32]. In organic solvents, free electrons are less solvated and hence recombination of electron with hole is increased. Dye (RB) is zwitterionic form in neutral medium. Results specified that the degradation of dye in methanol is less than the others, this probably due to more solvation of dye in methanol. Since solvation can inhibit adsorption of dye on the surface of nano particles since solvation of dye in ethanol is less and hence degradation of dye in ethanol is more than methanol. **Figure 3** presents the effect of solvents (Water, Ethanol and methanol) on the % degradation of RB by use  $\text{TiO}_2$  and in present of 0.1 g/lit Titanium dioxide.

In previous studies, the effect of parameters such as pH, adsorbent amount and initial dye concentration and the adsorption of (RB) dye were carried out using sodium montmorillonite [16]. Results obtained from the present work specified that using  $\text{TiO}_2$  nanoparticles, the photodegradation of RB is significantly.

## Conclusion

Photo-degradation of (RB) using nanoparticle  $\text{TiO}_2$  under UV light was investigated. The basis of reaction is photoredox process. Different parameters have important role in this process. Results showed that pH of the solution, type of solvent and the type of ions species can influence on dye degradation. The amount of pH solution changed the surface charge of  $\text{TiO}_2$  particle. As a result, the adsorption of dye on the surface is altered thus causing a change in the reaction rate. In neutral medium, the adsorption of dye on the surface positively charged of  $\text{TiO}_2$  is favourite, therefore % degradation of (RB) in this medium was the most amount. Adsorption of (RB) molecules on the surface of  $\text{TiO}_2$  significantly changed in the presence of more amounts of the ionics in the normal, acidic and basic solutions so was influenced on the photo-bleaching of (RB) dye. Plus, in the normal solutions and in presence of the same amount of different salts, kind of salt was very important. Results indicated that significant decreasing in the initial degradation rate of photo-catalysis, is occurred in the presence of various cations, among them  $\text{Cu}^{+2}$  has largest effect but  $\text{Fe}^{+2}$  increased photo degradation of (RB). Results indicated that, solvent also can play a significant role in variation of photo-physical properties in solutions, and results indicated that rate of % degradation in water is the highest amount between ethanol and methanol and water.

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