

# Photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide

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## Abstract

In this paper, photocatalytic degradation studies of a hazardous water soluble xanthene dye cyanosine in aqueous suspensions of titanium dioxide under a variety of conditions, viz., catalyst concentration, substrate concentration, pH, temperature and electron acceptor hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) have been reported. It was observed that photocatalytic degradation by  $\text{TiO}_2$  is an effective, economic and faster mode of removing cyanosine from aqueous solution. The optimum conditions for the degradation of the dye was dye concentration  $1 \times 10^{-4}$  M, pH 8, catalyst concentration 0.04 g/L and temperature  $\pm 30^\circ\text{C}$ . Chemical oxygen demand and dye absorbance of the photodegraded dye solution substantially decreased.  
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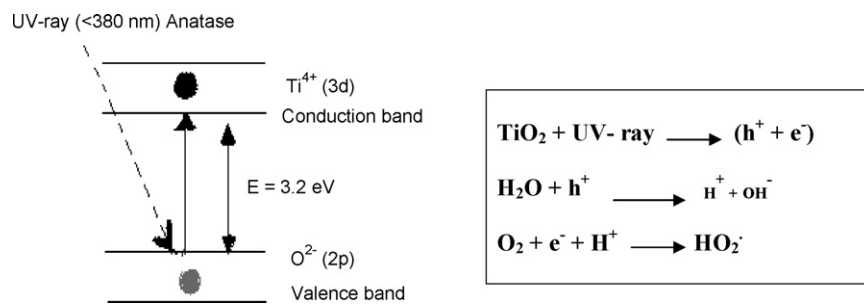
**Keywords:** Cyanosine; Photocatalytic degradation; UV light; Titanium dioxide; Kinetics

## 1. Introduction

Dyes are extensively used in the textile industry. The colour which dyes impart to water bodies is very undesirable to the water user for aesthetic reasons [1]. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, their discharges into rivers are harmful to the aquatic life [2,3]. They are the copious source of coloured organics emanating as a waste from the textile dyeing process [4]. The focus of the present work is to study the photocatalytic degradation of cyanosine dye using titanium dioxide and UV illumination. Cyanosine is a red, (xanthene group) dye, which is used for colouring all kind of natural fibers like wool, cotton and silk. It is also used in paints, inks, plastics, leather and cosmetics. However it may cause eye irritation, skin irritation, irritation of the digestive tract and may be harmful if swallowed [5]. The conventional biological treatment methods are ineffective for the complete colour removal and degradation of organics and dyes [6,7]. Other conventional methods of colour removal from an aqueous medium include techniques like coagulation, filtration, and adsorption by activated carbon and treatment with ozone [8]. Several workers have also tried water

treatment of dyes by adsorption over low cost materials [9–16]. Each method has its own advantages and disadvantages. For example, the use of charcoal is technically easy but has a high waste disposal cost. While in filtration, low-molar-mass dyes can pass through the filter system. Coagulation, using alum, ferric salts or lime is a low cost process. However, the disposal of toxic sludge is a severe drawback in all the above methods. The ozone treatment suffers from high cost. Advanced oxidation processes particularly based on photocatalytic degradation are of ample interest currently for the effective oxidation of a wide variety of organics and dyes [17,18]. The ability of the photocatalytic technique to completely degrade organics in to water and  $\text{CO}_2$ , without generating any harmful byproducts, has popularized its role as a wastewater purifier. The technique has been widely employed for the photomineralization of a large number of dyes such as methylene blue, direct and acid dyes, azo dyes and reactive black [19]. Amongst them, top priority goes to semiconductor assisted photocatalytic degradation. Most of the photocatalytic studies use either synthetic or commercial  $\text{TiO}_2$  as the photocatalyst [20,21]. During the past two decades, the photoassisted catalytic decomposition of organic pollutants in water and wastewater employing semiconductors as photocatalysts has been a promising technique [22–30]. Many photocatalysts have been attempted for the degradation of pollutants in wastewater. Among the semiconductors employed, anatase phase of  $\text{TiO}_2$  is the most preferable material for the photocatalytic process due

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Scheme 1. Energy band gap created on anatase pigment.

to its high photosensitivity, non-toxic nature, large band gap and stability [31,32].

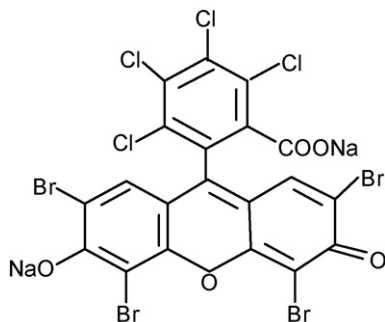
### 1.1. Mechanism

In heterogeneous photocatalysis, photocatalysts capture photons with energies greater than the band gap energy (3.2 eV) of the semiconductor to create electron–hole pairs [33], subsequently, the charge carriers interact with water and oxygen to produce oxidizing intermediates as hydroxyl radicals ( $\text{OH}^\bullet$ ) or  $\text{OH}_2^\bullet$ ,  $\text{O}_2^\bullet$ , which have the ability to oxidize pollutants to an inorganic compound (Scheme 1). After successive free radical attack and fragmentation most organics are mineralized to water, carbon dioxide and mineral acids [34].

## 2. Materials and methods

For the present investigation water soluble cyanosine (2,4,5,7-tetra bromo-4,5,6,7-tetra chloro fluoresceine disodium salt, molecular formula  $\text{C}_{20}\text{H}_2\text{Br}_4\text{Cl}_4\text{Na}_2\text{O}_5$  and molecular weight 829.66 g) was selected (Scheme 2). Anatase titanium dioxide 325 mesh, >99% was used as such without further treatment.

0.01 M stock solution of cyanosine was prepared in 100 mL of distilled water. All chemicals were of analytical grade and used without further purification. In 100 mL of dye solution of desired concentration, different catalyst dose was added and irradiated with UV lamp to provide energy to excite  $\text{TiO}_2$  loading. To ensure efficient mixing of  $\text{TiO}_2$  catalyst in the reactor, 7 mg/L oxygen was bubbled from the side of the reactor continuously throughout the reaction. At specific time intervals



Scheme 2. Structure of cyanosine dye.

suitable aliquot of the sample was withdrawn and analyzed after centrifugation. The concentration of dye was determined on Spectronic 20D+ thermospectronic spectrophotometer at  $\lambda_{\text{max}}$  538 nm. All the experiments were carried out at room temperature ( $30 \pm 0.1^\circ\text{C}$ ).

### 2.1. Instrumentation

Photocatalytic degradation studies were conducted in a photocatalytic reactor. Immersion well type photochemical reactor was used in photomineralisation studies. The reactor consist of an irradiation lamp, immersion well and reaction flask. Irradiation was carried out using a 6 W UV lamp placed inside the well of quartz glass reactor of 150 mL capacity. The reactor set up was covered with black colour wooden box to prevent UV radiation leakage. The lamp emits predominantly UV radiation of  $10 \text{ mW}/\text{cm}^2$  at wavelength of 254 nm.

pH metric measurements were made on Decibel DB 1011 digital pH meter fitted with a glass electrode, which was previously standardized with buffers of known pH in acidic and alkaline medium. For carrying out the COD experiments, reagents were prepared as per standard methods [35]. Usual 2 h open reflux method was applied for the COD determination. Chemical oxygen demand (COD) of coloured and photocatalysed solutions was recorded using COD digestion apparatus (Spectra lab-2015-S).

## 3. Results and discussions

The photocatalytic degradation of cyanosine was studied at  $\lambda_{\text{max}}$  538 nm. The optimum conditions for the removal of dye are conc.  $1.0 \times 10^{-4}$  M, pH 8,  $\text{TiO}_2$  0.04 g/L and temperature ( $30 \pm 0.1^\circ\text{C}$ ). The rate of reaction ( $k$ ) was determined using the following expression:

$$\text{rate } (k) = 2.303 \times \text{slope} \quad (1)$$

### 3.1. Preliminary observation

Preliminary photocatalytic studies were carried out by the  $\text{TiO}_2$  containing solution in the dark. Decrease in absorbance of dye in absence of UV light was very slow. Presence of  $\text{TiO}_2$  only does not catalyze the degradation of the dye. Only a minor loss of the dye on to the  $\text{TiO}_2$  surface could be observed due to the initial degradation of dye on  $\text{TiO}_2$  surface. The photochemical

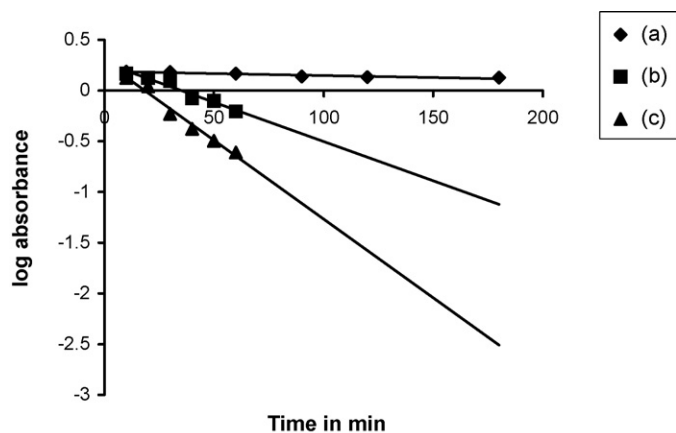


Fig. 1. Photocatalytic degradation of  $1.0 \times 10^{-4}$  M cyanosine under different conditions (pH 8 and temperature  $30 \pm 0.1$  °C). (a) Photodegradation of cyanosine in the absence of UV light. (b) Photodegradation of cyanosine in the presence of UV light but in absence of  $\text{TiO}_2$ . (c) Photodegradation of cyanosine in the presence of UV light, oxygen and  $\text{TiO}_2$ .

degradation of dye in absence and presence of both  $\text{TiO}_2$  and  $\text{O}_2$  was also investigated. It was found that only a minor loss of the dye adsorption was observed in the absence of both  $\text{TiO}_2$  and  $\text{O}_2$ , while better results were observed when small amount of  $\text{TiO}_2$  is added to the solution in the presence of  $\text{O}_2$  and UV light (Fig. 1).

### 3.2. Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of cyanosine was investigated employing different concentrations of the anatase  $\text{TiO}_2$  varying from 0.01 to 0.08 g/L (Fig. 2). Photodegradation of cyanosine increases rapidly with increasing the amount of  $\text{TiO}_2$  from 0.01 g/L to 0.08 g/L for dye concentration  $1.0 \times 10^{-4}$  M [36]. The increase in the amount of catalyst increases the number of active sites on the  $\text{TiO}_2$  surface which in turn increases the number of OH and  $\text{O}_2^-$  radicals. It was observed that 0.04 g/L of  $\text{TiO}_2$  is the optimum dose for efficient degradation of cyanosine dye.

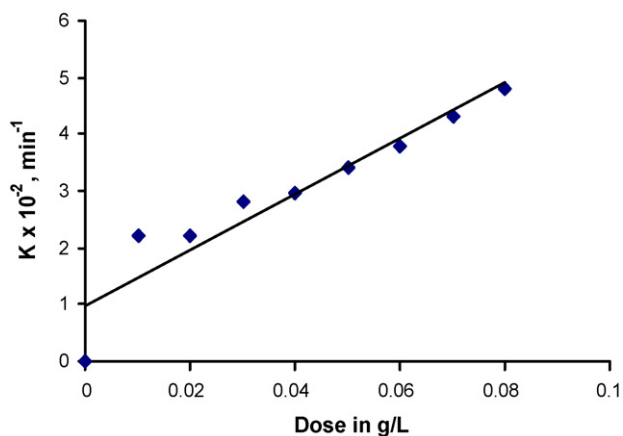


Fig. 2. Amount of  $\text{TiO}_2$  vs. rate constant graph for the photocatalytic degradation of  $1.0 \times 10^{-4}$  M cyanosine (pH 8 and temperature  $30 \pm 0.1$  °C).

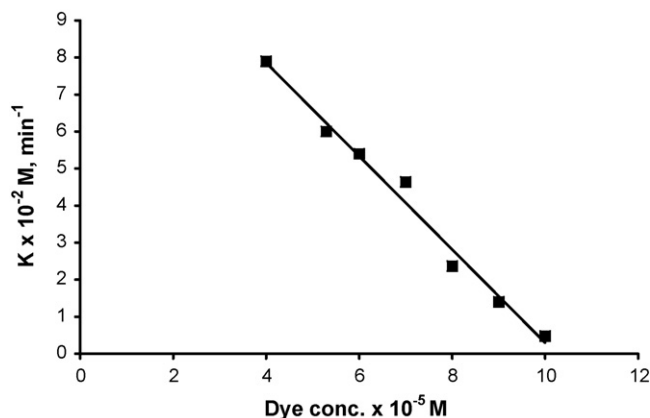


Fig. 3. Substrate concentration vs. rate constant graph for the photocatalytic degradation of cyanosine (amount of  $\text{TiO}_2$  0.04 g/L, pH 8 and temperature  $30 \pm 0.1$  °C).

### 3.3. Effect of substrate concentration

The photocatalytic degradation of different concentrations of cyanosine has been investigated in aqueous suspension of  $\text{TiO}_2$  as a function of irradiation time (Fig. 3). The rate of photodegradation of cyanosine dye was studied by varying the substrate concentrations from  $4.0 \times 10^{-5}$  M to  $1.0 \times 10^{-4}$  M. The experiment was carried out at fixed pH 8 and catalyst concentration 0.04 g/L. It was found that photocatalytic degradation decreases from  $4.0 \times 10^{-5}$  M to  $1.0 \times 10^{-4}$  M, because for a fixed catalyst concentration active sites remaining the same, the number of substrate ions accommodated in the inter layer space increases so that the degradation decreases. This may be due to the fact that with increase in initial concentration of the dye, more dye molecules are adsorbed on the surface of  $\text{TiO}_2$ . Thus, increase in the number of substrate ions accommodating in inter layer spacing inhibit the action of catalyst, which thereby decreases the reactive  $\text{OH}^\bullet$  and  $\text{O}_2^{\bullet-}$  free radicals attacking the dye molecules and photodegradation efficiency [37].

### 3.4. Effect of pH

The photocatalytic degradation of dye was studied at different pH values as it is an important parameter for reaction taking place on the particulate surface. The role of pH on the rate of photocatalytic degradation of cyanosine was studied in the pH range 3.7–10.2 at dye conc.  $1.0 \times 10^{-4}$  M and  $\text{TiO}_2$  conc. 0.04 g/L. It was observed that the degradation rate increased with an increase in pH. Similar results were reported earlier for the acid blue 40 dye degradation [38]. This effect may be attributed to more efficient generation of hydroxyl radicals by  $\text{TiO}_2$  with an increasing concentration of hydroxide ion (Fig. 4). It is apparent that the rate of degradation of cyanosine with increase in the pH values upto 10.2 and beyond this the rate of photodegradation becomes constant. This may be due to the fact that as the pH increases onwards 10.2 the repulsion of the dye anion by negatively charged  $\text{TiO}_2$  surface would result in reduction in efficiency of photodegradation of cyanosine dye.

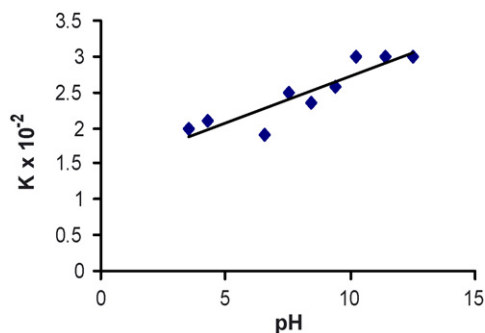
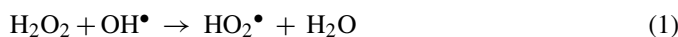


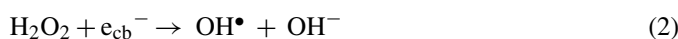
Fig. 4. Plot of pH vs. rate constant for the photocatalytic degradation of  $1.0 \times 10^{-4}$  M cyanosine (amount of  $\text{TiO}_2$  0.04 g/L and temperature  $30 \pm 0.1$  °C).

### 3.5. Effect of electron acceptor

It is observed that molar  $\text{H}_2\text{O}_2$  concentration is a key factor that can significantly influence the degradation of cyanosine because  $\text{H}_2\text{O}_2$  concentration is directly related to the number of  $\text{OH}^\bullet$  radicals generated in the photoassisted reaction. The degradation rate of cyanosine increases as the  $\text{H}_2\text{O}_2$  concentration increases until a critical  $\text{H}_2\text{O}_2$  concentration is achieved. When using a higher  $\text{H}_2\text{O}_2$  molar concentration, the further generation of  $\text{OH}^\bullet$  radical in aqueous solution is expressed by the following equation [39].



Thus, experiments were conducted with different amounts of  $\text{H}_2\text{O}_2$  ranging from 0.2 mM to 1.4 mM at fixed pH 8, dye conc.  $1.0 \times 10^{-4}$  M, catalyst dose 0.04 g/L. It is apparent from Fig. 5, that the rate of degradation is markedly enhanced in the presence of  $\text{H}_2\text{O}_2$  additive.  $\text{H}_2\text{O}_2$  is not only known to inhibit the electron–hole recombination process, but also it generates hydroxyl radicals on abstraction of an electron from the conduction band [40].



It was found that the critical  $\text{H}_2\text{O}_2$  molar concentration for the degradation of cyanosine is 1.2 mM. Further increase of  $\text{H}_2\text{O}_2$

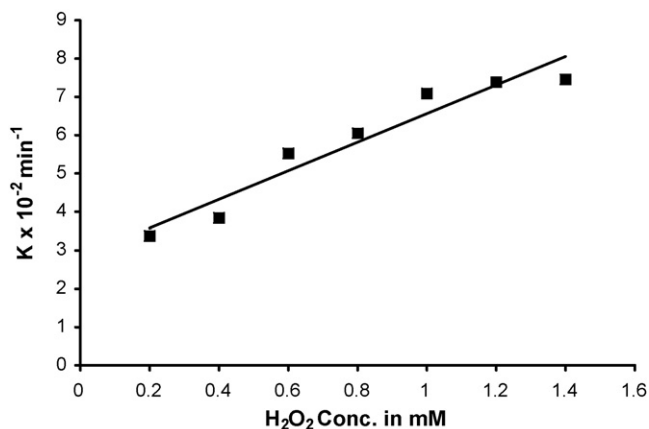


Fig. 5. Amount of  $\text{H}_2\text{O}_2$  vs. rate constant graph for the photocatalytic degradation of  $1.0 \times 10^{-4}$  M cyanosine (amount of  $\text{TiO}_2$  0.04 g/L, pH 8 and temperature  $30 \pm 0.1$  °C).

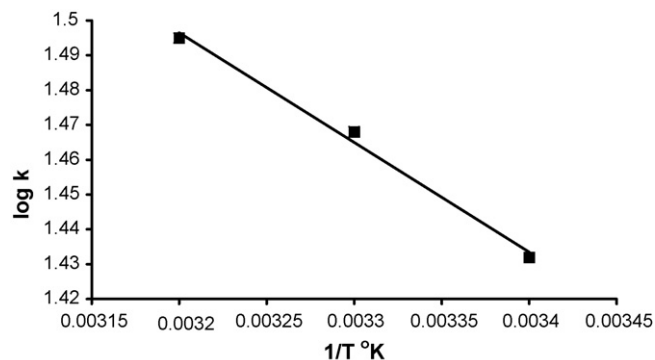
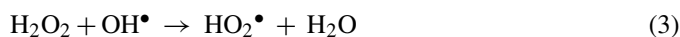


Fig. 6. Plot of temperature variations for the photocatalytic degradation of  $1.0 \times 10^{-4}$  M cyanosine (amount of  $\text{TiO}_2$  0.04 g/L and pH 8).

from 1.2 to 1.4 mM, the degradation efficiency remains constant. This is due to hydroxyl radical scavenging effect of  $\text{H}_2\text{O}_2$  [41].



### 3.6. Effect of temperature

The photocatalytic degradation was studied at various temperatures at range 293–313 K and rate constant  $k$  was determined from the first order plots. An increase in temperature helps the reaction to compete more efficiently with  $e^-/h^+$  recombination [4]. The energy of activation  $E_a$ , was calculated from the Arrhenius plot of  $\log k$  versus  $1/T$  K (Fig. 6). From the figure, the calculated activation energy ' $E_a$ ' is 6 kJ/mol.

## 4. Chemical oxygen demand (COD)

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to  $\text{CO}_2$  and water. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the feasibility of the photochemical process for the degradation of cyanosine dye solution. In photocatalytic experiments, cyanosine dye (100 mL) and the catalyst dose (0.04 g/L) were taken in a photochemical reactor and exposed to UV light for 40 min. Dye samples of about 2–3 mL were taken out at a regular interval from the test solution, centrifuged for 15–20 min and their absorbance were recorded at 538 nm. Comparison of the COD value of the initial dye solution with photocatalysed solution indicates the COD value is substantially reduced. It is observed that the COD value shows a significant decrease from 1345 to 236 mg/L indicating good potential of employing photocatalytic technique. The photodegradation efficiency was found to be 82.45%.

## 5. Conclusion

Photocatalytic oxidation using  $\text{TiO}_2$  and UV light was successfully applied for the degradation and mineralization of

cyanosine dye. The degradation rate was increased significantly by increasing the amount of catalyst, while on increasing substrate concentration decolourisation decreases. Alkaline pH conditions were found to significantly affect the dye degradation. The maximum degradation efficiency of dye was achieved with the combination of UV + H<sub>2</sub>O<sub>2</sub> + TiO<sub>2</sub>. The photodegradation efficiency of cyanosine dye is 82.45% and after elution the concentration of dye is  $0.164 \times 10^{-5}$  M.

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