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# Photocatalytic Degradation of Quinol and Blue FFS Acid Using $TiO_2$ and Doped $TiO_2$

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## Abstract

The photodegradation of the model compounds Quinol, an aromatic organic compound and Acid blue FFS, an acid dye of chemical class Triphenylmethane was studied by using illumination with UV lamp of light intensity 250 W. $TiO_2$ and $TiO_2$ doped with Boron and Nitrogen was used as catalyst. The sol-gel method was followed with titanium isopropoxide as precursor and doping was done using Boron and Nitrogen. In photocatalytic degradation, $TiO_2$ and doped $TiO_2$ dosage, UV illumination time and initial concentration of the compounds were changed and examined in order to determine the optimal experimental conditions. Operational time was optimized for 360 min. The optimum dosage of $TiO_2$ and BN doped $TiO_2$ was obtained to be 2 $mgL^{-1}$ and 2.5 $mgL^{-1}$ respectively. Maximum degradation % for quinol and Blue FFS acid dye was 78 and 95 respectively, at the optimum dosage of BN-doped $TiO_2$ catalyst. It was 10 and 4% higher than when undoped $TiO_2$ catalyst was used.

***Keywords :*** *Photodegradation, Quinol, Blue FFS acid, Boron doping*

## 1. Introduction

Advanced oxidation process in the presence of semiconductor catalyst is an effective method to degrade lot of organic, inorganic, dyeing compounds in mild condition of temperature, pressure, in the presence of UV radiation and in the presence or absence of catalyst. The photomechanism in simple, can be explained as that under the influence of UV, electron is promoted from valence band to conduction band of semiconductor oxides, thus generating a hole in valence band. The activated electron can react with oxidizing agent yielding a reduced product and the generated hole can react with reductant to produce an oxidized product [1].

Photocatalytic degradation uses usually $TiO_2$ as slurry or immobilized or doped with metal/non-metals. Titanium di oxide has been widely utilized as a photocatalyst for generating electrons ($e^-$) and holes ($h^+$), thereby inducing reductive and oxidative reactions, respectively. The electrons and holes can be excited through UV light irradiation to overcome the band gap energy. Accordingly $O_2^-$ and $OH^-$ radical ions are produced and mineralize pollutants [2]. In order to lower the band gap energy, the structure of the catalyst is modified. Modification could be done by doping, immobilization, structure modification and sensitization. Previous works have been done by doping with metals and non-metal dopants. First non-metal doped $TiO_2$ was described in 1986 by Sato, *et al.* [3]. Nitrogen and Boron have been used for doping [4-6].

An organic compound which can be degraded using this mechanism is quinol. Quinol is used in the electronic industry for washing purposes and also a major component in photographic developers. They are also used as skin whitening agents in dermatological preparations. The effluents from textile industry are also the major pollutants for several decades. Blue FFS acid dye which is used in textile industry for dying of silk is a pollutant. It has been estimated that approximately 15% of textile dyes are lost in waste streams during manufacturing and processing operations. Many organic compounds are decomposed in aqueous solution in the presence of titanium dioxide powder illuminated with UV light. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete color removal and degradation of organics and dyes Other conventional methods of color removal from an aqueous medium include techniques like coagulation, filtration, adsorption by activated carbon and treatment with ozone. These techniques require downstream processing units which add to the cost of degradation process.

The aim of the study is to examine the decomposition of Quinol and Blue FFS acid dye by photodegradation in the presence of UV light using suspended $TiO_2$ with and without Boron-Nitrogen doping in an annular photocatalytic reactor with UV source of 250 W. Many authors have studied the performance of the metal doped catalyst under visible light [6]; hence experiments have been done to understand the decomposition under UV illumination. Industrial waste streams can be discharged with wide range of concentration and since photocatalysis is a surface phenomenon, the photocatalyst performance can be highly predisposed by the concentration of the stream, the nature of the compound, and its ability to absorb onto the photocatalyst surface. In acidic or caustic conditions, the surface of $TiO_2$ can respectively become positively or negatively charged. This property is typically influenced by the compound concentration and photocatalytic reaction times. Hence the operational parameters like concentration of the compound, time of irradiation have also been optimized.

## 2. Materials and Methods

### *2.1. Chemical reagents*

All the chemicals used were of analytical grade and the water used was distilled water. Quinol (CDH), $TiO_2$(CDH), 4-amino antipyrine (Ranbaxy fine chemicals limited), Potassium ferricyanide (CDH), Ammonium chloride (CDH), Ammonia solution (SRL), Blue FFS acid,Triton x-100 (SRL), Titanium isopropoxide (SRL), Boric acid (SRL), Urea (Ranbaxy fine chemicals limited )were used.

Quinol is also known as hydroquinone or p-benzenediol. It has the chemical formula of $C_6H_6O_2$. It is an off-white powder or needle-like crystals with melting point of 172°C. Blue FFS acid is generally referred to as Acid blue 15 with chemical formula $C_{42}H_{46}N_3NaO_6S_2$ and molecular weight of 775.95. Commercially with CI number 42665, Acid blue 15 is also referred to as Colocid Brilliant Blue FF, Dinacid Brilliant Blue B, Lecotan Blue AL, Monacid Coomassie Blue FF, Raviramine Blue BS whose chemical structure is given in Fig. 1.

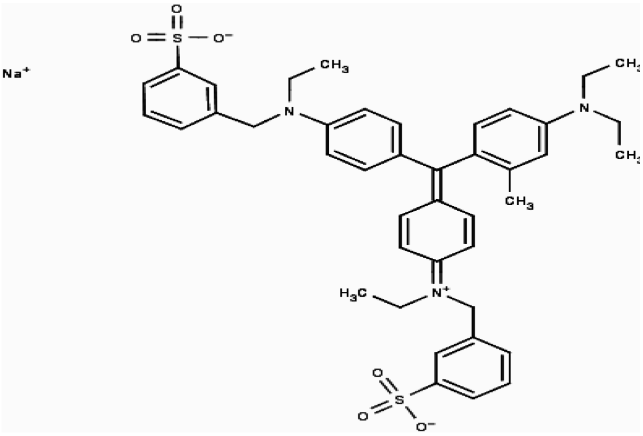

**Fig. 1.** Chemical structure of Acid Blue 15.

### *2.2. Photocatalytic degradation*

For experiments under UV light, stock solutions of the dye and quinol with desired concentration were prepared with distilled water. An immersion well photoreactor made of pyrex glass was used as a batch reactor. The UV fluorescent tube, which acts as light source was placed in the middle of the reactor vessel around which the cooling water was supplied continuously. UV light source of 250 W UV lamp was used. Samples were collected at regular intervals and centrifuged at 3000 rpm for 15 min. In the case of quinol, photodegradation was monitored by forming a complex compound using 4–amino antipyrine and measuring the absorbance at 460 nm by using UV- Vis spectrophotometer. In the case of Blue FFS acid, photodegradation was monitored by measuring the absorbance at 562 nm by using UV- Vis spectrophotometer. Then the percentage of quinol and Blue FFS acid degradation was calculated by using the Eq. (1)

$$\text{Degradation percentage} = (C_0 - C)/C_0 * 100 \quad (1)$$

where,

$C_0$ – Initial Concentration, $mgL^{-1}$
$C$ – Variable Concentration at time t, $mgL^{-1}$

### *2.3. Preparation of B-N codoped $TiO_2$*

B-N codoped $TiO_2$ was prepared by hydrothermal synthesis. 3.4 g $Ti(OBu)_4$ and 0.72 g Triton x- 100 were added to 20 mL of ethanol under stirring. Then a solution of 3 ml saturated urea solution containing 0.12 g boric acid was added drop wise. After stirring for an hour, the mixture was autoclaved at 120°C for 14 h and left to stand for cooling naturally. It was then washed with ethanol and then dried at 75°C for 1 h and calcined at 450°C for 1 h.

## 3. Results and Discussion

### *3.1. Effect of contact time*

The effect of time was analyzed for quinol with different initial concentrations 100 to 500 $mgL^{-1}$. The effect of time was analyzed for Blue FFS acid with different initial concentrations 20 to 100 $mgL^{-1}$. Catalyst used was 2 $gL^{-1}$ of $TiO_2$. The natural pH was maintained for all the concentration and the UV light intensity was kept constant at 250 W. Fig. 2 and Fig. 3 show that in the case of quinol and Blue FFS acid, the percentage degradation increases with increase in contact time. The $OH^-$ formed on the surface of $TiO_2$ is constant, the relative number of $OH^-$ attacking the compound increases, and thus the photodegradation efficiency increases with time [7].

### *3.2 Effect of initial concentration*

The effect of initial concentration of quinol on the

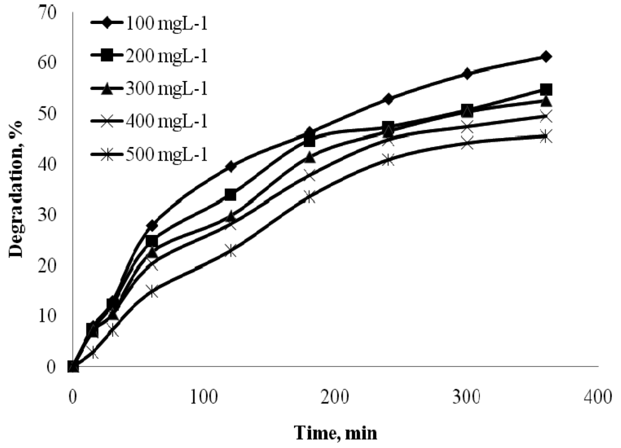

**Fig. 2.** Effect of contact time on photodegradation of quinol (UV 250 W, room temperature and natural pH, quinol concentration 100 to 500 mgL$^{-1}$).

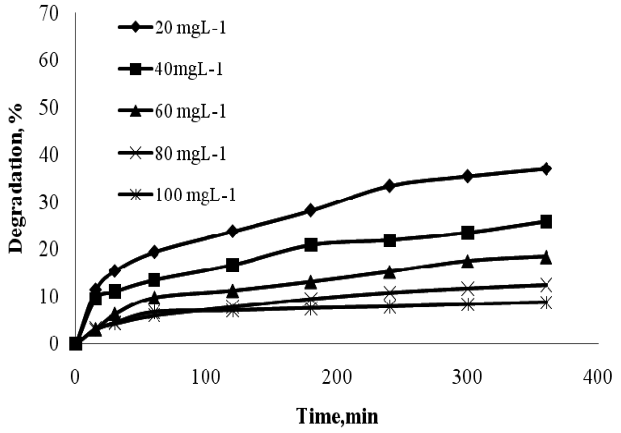

**Fig. 3.** Effect of contact time on photodegradation of Blue FFS acid dye (UV 250 W, room temperature and natural pH, concentration 20 to 100 mgL$^{-1}$).

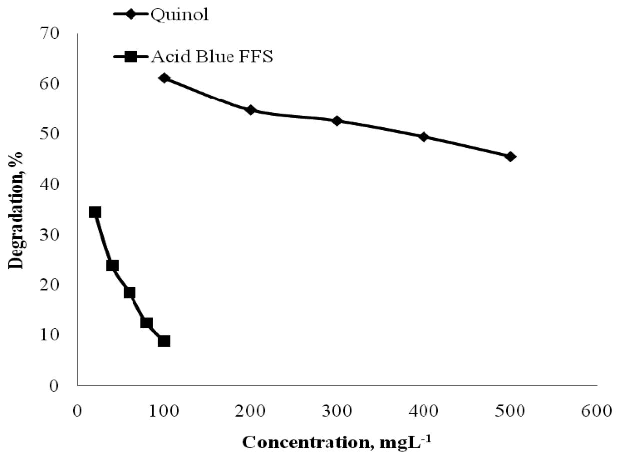

**Fig. 4.** Effect of initial concentration on photodegradation of quinol and Acid Blue FFS (UV 250 W, room temperature and natural pH).

photodegradation rate was analysed by varying the initial concentration from 100 to 500 mgL$^{-1}$. The effect of initial concentration of Blue FFS acid dye on the photodegradation rate was analysed by varying the initial concentration from 20 to 100 mgL$^{-1}$. Catalyst used was 2 gL$^{-1}$ of $TiO_2$. Fig. 4 shows that percentage degradation decreases as the initial concentration of quinol and Blue FFS dye increases. As the concentration increases, the number of photons that reaches the catalyst surface decreases. Hence, the number of catalyst molecules that is excited reduced. The rate of formation of holes, hydroxyl radicals and supra oxide ions which greatly depends on the excitation of the catalyst molecules decreases and hence there is decrease in the photodegradation rate. The amount of the molecules that attached to the active sites of the catalyst also gets limited because the catalyst surface area remains the same for all concentration of the compounds. At higher concentration a competition for the molecules to get attached to the surface increases and hence degradation decreases with increase in concentration [8].

### *3.3. Effect of Doped and undoped catalyst*

The effect of doped and undoped catalyst on the photocatalytic degradation of quinol and Blue ffs acid was studied by varying the amount of doped $TiO_2$ and undoped $TiO_2$ from 0 to 3 gL$^{-1}$ and the degradation profile is shown in Fig. 5 and Fig. 6. From the figure, it is vivid that the percentage degradation by using B-N codoped $TiO_2$ is higher than by using undoped $TiO_2$ for both quinol and Blue FFS acid dye. The series of experiments performed by varying the amount of $TiO_2$ from 0 to 3 gL$^{-1}$ shows that the percentage degradation of quinol is found to increase linearly upto 2 gL$^{-1}$ above this amount, increased turbidity of the solution reduced the light transmission through the

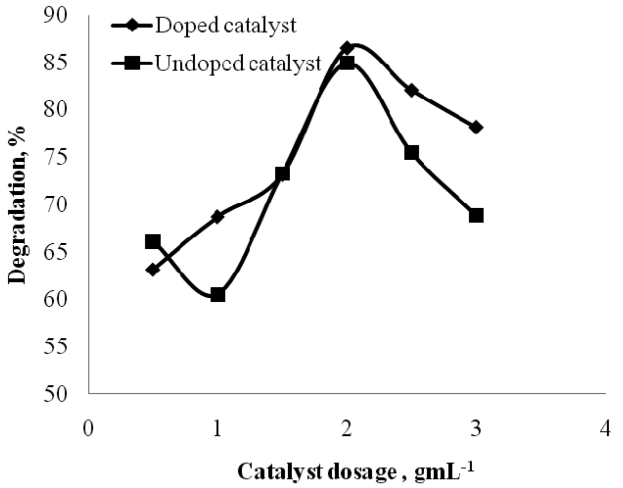

**Fig. 5.** Effect of catalyst and catalyst concentration on the photodegradation of quinol (concentration 300 mgL$^{-1}$), Time = 6 h (UV).

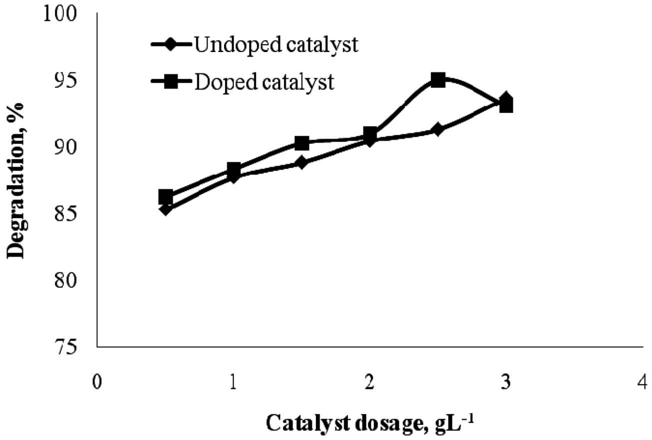

**Fig. 6.** Effect of catalyst and catalyst concentration on the photodegradation of Blue FFS acid (concentration 100 $mgL^{-1}$, time = 6 h).

solution, while below this level, it is assumed that the catalyst surface and the absorption of light by $TiO_2$ were limiting. The observed enhancement in the degradation is probably due to the increased number of catalytic sites on $TiO_2$. A further increase in the amount of $TiO_2$ decreases the percentage degradation of quinol. In the case of Blue FFS acid dye the percentage degradation is found to increase significantly in the presence of catalyst [6]. The percentage degradation of Blue FFS acid dye is found to increase constantly from 0.5 to 3 $gL^{-1}$.

The doped catalyst has better performance over the undoped catalyst. The possible reasons could be, in a Boron-Nitrogen doped catalyst, there is reduction in band gap energy, irradiation with UV light excites electrons in both the valence band and the impurity energy levels and finally, nitrogen may be doped in the oxygen deficient sites which help in blocking re-oxidation [9,10].

## 4. Conclusion

The photodegradation of quinol and Blue FFS acid was studied for various parameters like time, initial concentration, dosage of catalyst, dosage of doped catalyst . From the experimental data the following conclusions are made. The photodegradation of quinol and Blue FFS acid increases with increase in time. The photodegradation of quinol and Blue FFS acid decreases with increase in initial concentration. The present work illustrates that photocatalysis is an effective and sustainable method for the decomposition of organic compounds and dyes. The degradation effiency using photocatalyst is higher compared to that of photolysis. The B-N- codoped $TiO_2$ showed higher photodegradation effiency than undoped $TiO_2$.

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