

Synthesis of dye sensitized monometallic-TiO₂ photocatalyst and phenol degradation

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Abstract

Light both in visible and UV ranges are employed in Photo-catalytic processes to excite semiconductor materials to produce electron/hole pair which ultimately detoxifies the pollutants present in water. TiO₂ is one of the most promising photo-catalysts used in wastewater treatment. However, it shows poor activity in visible light irradiation. In this work, Ag-doped TiO₂ photo-catalyst was synthesized using UV photo-reduction method to narrow down the band gap energy. TiO₂ was suspended in a deaerated solution and dispersed by sonication. The solution containing 16.8 g TiO₂ and Ag (220: 1 w/w) in 100 mL solution water and ethanol (90:10 v/v). The solution pH was adjusted to 4 before the reaction. The suspension was continuously agitated and irradiated under high pressure Hg lamp for Ag⁺ photo-reduction to Ag⁰. In addition of this, Eriochrome cyanine red, an anionic dye, was employed to sensitize Ag/TiO₂ catalyst by expanding its photo-response to visible range. Catalyst characterizations were performed in terms of solid UV-spectroscopy, X-ray diffraction, zeta potential analysis and by measuring the specific surface area using chemisorption technique. The performance of dye sensitized Ag-doped TiO₂ catalyst was tested through oxidative degradation of a model effluent laden with phenol.

Keywords: Photo-catalyst; Photo-reduction; Dye-sensitization; Phenol, Eriochrome cyanine red, TiO₂.

1. Introduction

Photo-catalysis is a well-known recognized approach where light energy is employed to excite the semiconductor materials to produce electron/hole pair which ultimately detoxifies the target contaminants.[1] (Chowdhury et al., 2012). TiO₂ has been used extensively for treating different type of pollutants. However, degradation of pollutants using TiO₂ is proven to be an effective method under UV light .[2] (Ni et al., 2007) The main drawback of UV light is its narrow wavelength ranges and high cost of artificial UV light source. About 5% of solar spectrum is available for the band gap of TiO₂. Typically .04% of solar photon is effective in TiO₂ photo-catalysis process against the solar collector efficiency of 75 % and catalyst efficiency of 1%.

Efforts have been made to improve the photo-catalytic activity of TiO₂ and its response in the visible light range. [3] (Arsana et al., 2012) Modification of TiO₂ semiconductor to broaden its photo-response to visible region can be done by dye-sensitization. Dye-sensitization, [5]Chen et al., 2010) is a method where TiO₂ (with large band gap energy) is sensitized to the visible region with the help of a pre-adsorbed dye onto the catalyst. [4] (E. Pulido Melian et al., 2012) There are 2 significant impediments in dye-sensitization process i.e rapid recombination of electron/ hole pairs and poor activation of semiconductor catalyst. In this study, Ag- doped TiO₂ was synthesized by photo-reduction method to shorten the band gap of TiO₂ . Furthermore, the spectral sensitization of Ag/ TiO₂ photo-catalyst was performed using Eriochrome cyanine red (ECR) , an anionic dye.

The performance of ECR-Ag/TiO₂ was carried out through decomposition of phenol from model effluent.

2. Materials and Methods

2.1. Reagents

All chemicals and reagents were procured from M/s Loba Chemie Pvt Ltd, India. AgNO₃ was procured from M/s Merck, India. Deionized water (DI) (M/s Millipore, filtration unit, USA model: Elix-3) was used for the preparation of solution and reagents. NaOH and H₂SO₄ (0.1 N) were used to adjust the solution pH. The details of Eriochrome cyanine red R is listed in Table 1.

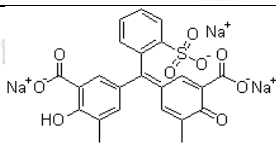
MolWt, g/mol	Molecular formula	Structure	Λ_{\max} , nm
536.4	C ₂₃ H ₁₅ Na ₃ O ₉ S		440 nm

Table 1. Structural details of Eriochrome cyanine red R

2.2. Analytical techniques

Phenol concentration was determined using a UV-Vis Spectrophotometer (model: UV 2300) of M/s Thermo Scientific, India. The XRD patterns were recorded between the 2 θ angle from 10 to 80°. X-ray diffractometer (model: D8 Advance) of Bruker (Germany) was employed for this work. Variation of zeta-potential of fabricated catalyst was measured using Zeta potential analyser (model: Delsa nano particle analyser C) of M/s Beckman Coulter (Switzerland). The spectral absorbance of catalyst was acquired using solid UV-Visible spectroscopy (M/s Shimadzu, Japan; model: Solid Spec 3700/3700DUV).

2.3. Experimental procedure

2.3.1. Synthesis of ECR-Ag/TiO₂ photo-catalyst

Silver was loaded on TiO₂ surface by photo-deposition method. 16.68 g of TiO₂ was stirred in an aqueous ethanol solution (ethanol/water=10/90 v/v) with 0.158 g of AgNO₃ to get a silver loading of 1% (w/w). The catalyst suspension was dispersed for 30 min in an ultrasonic bath (model:UC-02,50 Hz) of M/s Jeitech Instruments, Korea. pH of the suspension was adjusted to 4 using 0.1 N H₂SO₄/NaOH. The suspension was left for 12 h in dark and then irradiated under a 160 W high pressure mercury lamp for 3 h with gentle stirring at 50 rpm. Photo-reduction of Ag⁺ occurred and Ag⁰ particles were deposited on TiO₂ surface [6] (Abe et al., 2004). It was then filtered in a research centrifuge (R-23) of M/s Remi, (Mumbai) at 4700 rpm

for 30 min and washed with deionized water. Ag/TiO₂ was dried for 12 h at 100 °C in a hot air oven (M/s Navyug, India, ISO-9001-2000).

200 mL solution of 100 mg/L of ECR dye was adsorbed onto Ag/TiO₂ by stirring 16 g of catalyst powder at room temperature for 12 h in dark. After that it was filtered and washed with anhydrous ethanol so that loosely adsorbed dye comes out. Sample was dried at 100 °C for 12 h. ECR-Ag/TiO₂ sample obtained was kept in dark to avoid catalyst de-activation [7] (Chowdhary et al., 2011).

2.3.2. Photo-catalytic phenol degradation

A cylindrical borosilicate glass vessel (1 L) was used as a batch reactor. Experiment was carried out with 400 mL solution of phenol solution containing 0.5 g/L ECR-Ag/TiO₂. pH was adjusted to 7 using 0.1 N H₂SO₄/NaOH. Solution pH was measured using a pH meter (model: pH/ion 510) of M/s Eutech Instruments, Malaysia. The catalyst suspension was dispersed in an ultrasonic bath for 10 min, and then it was kept in dark for 60 min to achieve adsorption equilibrium of phenol adsorption. A sample of about 5 mL was taken to determine the initial phenol concentration prior to illumination following filtration with 0.2µm filter. A Visible lamp of 200 W equipped on the top of the reactor was used for reaction. The solution was agitated at 100 rpm using a magnetic stirrer (stirrer bar: length 40 mm, Ø 0.8 mm) of M/s Tarsons, India (model: Spinnot). The temperature was maintained at 25 °C. Samples were collected at every 30 min interval and analyzed for residual phenol [8] (Chatterjee et al., 2001).

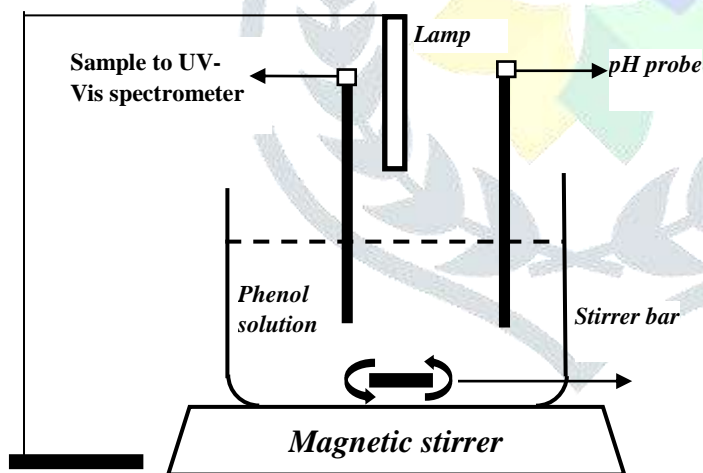


Figure 1: Schematic diagram of experimental setup.

3. Results and Discussion

3.1. Catalyst characterization

The variation of zeta potential as a function of pH is shown in figure 3. The point of zero charge was found as 3.9. Therefore, the adsorption of phenoxide ions is expected to be favourable below pH Zpc. Neutral pH was selected to find out the potential of ECR-Ag/TiO₂ where adsorption of phenol is less favourable.

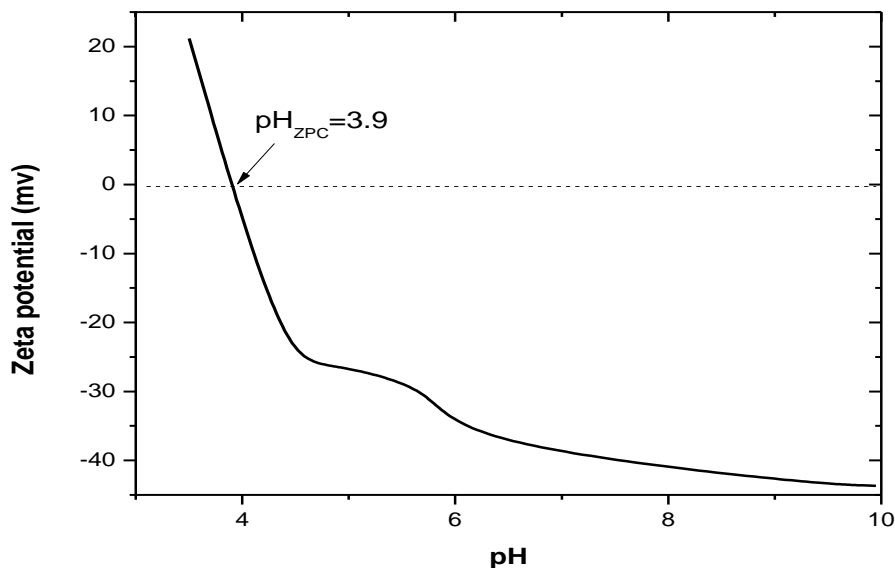


Figure 2: Zeta potential vs pH of ECR-Ag/TiO₂

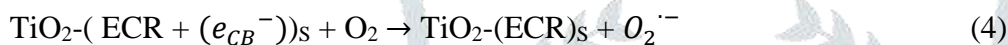
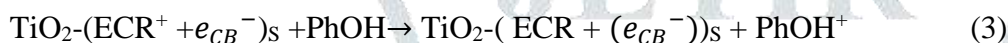
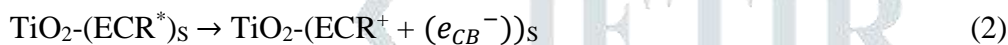
The XRD pattern of TiO₂ and ECR-Ag/TiO₂ were investigated to identify the crystalline phases of the sample. The XRD pattern was similar to the standard crystal structure of TiO₂, with no diffraction peaks associated with the Ag metal in the ECR-Ag/TiO₂ sample. This suggests that silver loading process did not produce separate impurity. However, the intensities of peaks in ECR-Ag/TiO₂ reduced a bit. The spectral absorption of ECR-Ag/TiO₂ indicates that there is a new peak in the visible region ($\lambda_{\text{max}} = 465 \text{ nm}$). It corresponds to ECR dye onto ECR-Ag/TiO₂. The maximum absorption aqueous ECR occurred at 440 nm. A pictorial view of dye- sensitized Ag/TiO₂ is shown in figure 3.



Figure 3: Visual appearance of ECR-Ag/TiO₂.

3.2. Phenol degradation under UV and visible light irradiation

The performance of synthesized ECR-Ag/TiO₂ for phenol decomposition is shown in Figure 4. The test was conducted under illumination of both visible and UV light. It was found that phenol degradation was 70.6 % and 51.6% under visible and UV light illuminations respectively. Greater phenol degradation can be attributed to dye sensitized photo-catalysis reactions under visible light. The process involves electron transfer to the conduction band of TiO₂ initiated by ECR dye sensitization under visible light. The photo-generated electrons have a high oxidation potential and produce superoxide ions ($O_2^{\cdot-}$) followed by OH^{\cdot} , which ultimately proceeds to complete mineralization of phenol. The reactions involves in dye sensitized can be expressed as (Eqs. (1)-(6)). Furthermore, Ag doping also improved the activity of TiO₂ in the visible range.



There was a decrease in pH of the solution during adsorption of phenol on TiO₂. This can be explained with the dissociation of phenol that takes place prior to the adsorption of phenolate ion (PhO^-) onto TiO₂ surface.



This explains the decrease of phenol adsorption with decreasing pH, which inhibits the dissociation process. The oxidation of phenol by OH^{\cdot} also account for pH decrement during illumination.

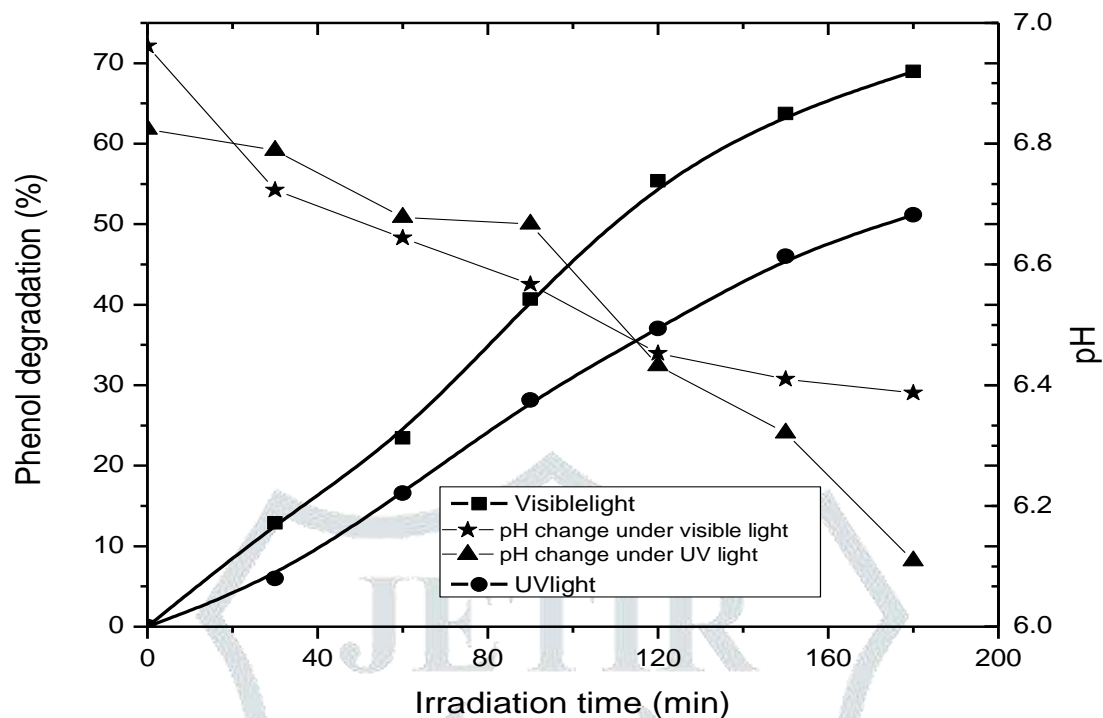


Figure 4: Phenol degradation under UV (160 W) and visible light (200 W).

3.3. Kinetic model of phenol decomposing

The kinetics of phenol decomposition using photo-catalyst can be expressed by pseudo first order [9]. The kinetic model (Eq.(7)) fitted to the experimental data is illustrated in Figure 5. The best fitted parameters are summarized in Table 2. Phenol degradation using both visible and UV light essentially followed pseudo-first order kinetics. The rate constant in visible light assisted phenol decomposition was about 1.6 times higher than the same in UV light [10].

$$C_{Phenol} = C_{Phenol}^0 \exp(-kt) \tag{7}$$

Table 2: Kinetic parameters for photochemical degradation of phenol using ECR-Ag/TiO₂.

Light source	<i>k</i> (min ⁻¹)	R ²
Visible	6.4 × 10 ⁻³	0.99
UV	3.9 × 10 ⁻³	0.99

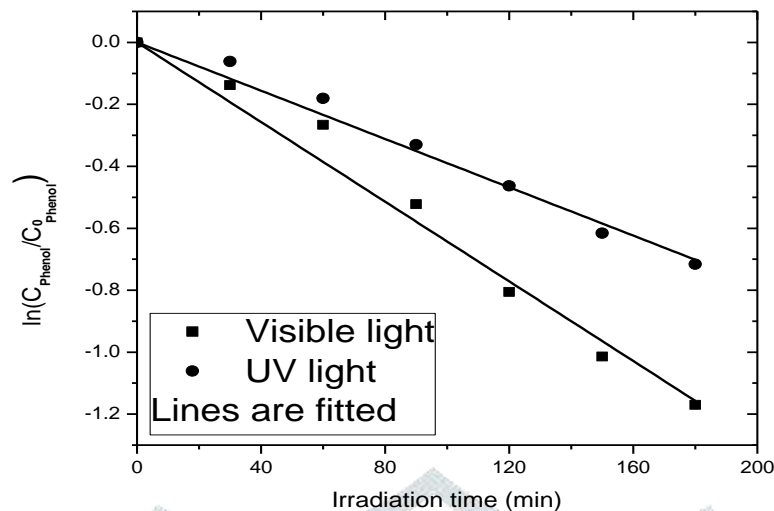


Figure 5: Kinetics of phenol degradation.

4. Conclusions

The following major conclusions are drawn based on the outcome of the present work.

- ECR red sensitized Ag/TiO₂ photo-catalyst was successfully synthesized. A broad spectral band was noted at 465 nm. pH_{ZPC} was found to be at around 3.9. No diffraction peak corresponded to Ag onto Ag/TiO₂.
- ECR-Ag/TiO₂ photo-catalysis was more effective in phenol degradation in the visible region. It gave around 19% more phenol decomposition over UV irradiation.
- Phenol decomposition by ECR-Ag/TiO₂ photo-catalyst both in visible and UV regions of light followed pseudo-first order kinetics with resonantly high regression coefficients.

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