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Photocatalytic Decoloration Efficiencies of ZnO and TiO_2: A Comparative Study

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ABSTRACT

The photocatalytic process employing semiconductor photocatalysts are the most powerful technology for the mineralization and decoloration of organic pollutants such as dyes, phenols, etc. The photocatalytic decoloration of an azonium dye namely, Saffranin O dye by TiO_2 and ZnO was investigated under UV light illumination. The effects of initial concentration of dye, pH, TiO_2 and ZnO and the illumination time were experimented and the optimized conditions for maximum removal of the dye were determined and compared. The kinetic was studied with Langmuir- Hinshelwood mechanism. Among the two catalysts, TiO_2 exhibited more removal efficiency than ZnO in this study.

1. Introduction

Water is the most significant and necessary component for the living beings on the earth crust. Due to the tremendous growth of population and industrialization, the quality of water resources is deteriorating continuously and water pollution has become a series problem now-a-days [1]. All kinds of pollutants such as inorganic, organic and biological pollutants are present in waste water. Many organic pollutants such as dyes, pesticides, fertilizers, herbicides, surfactants, hydrocarbons, carboxylic acids, etc., have been detected in waste water coming from industries. These pollutants cause adverse effects on human beings and the aquatic organisms. Hence, the removal of such pollutants from the contaminated water is of great need. Among all these pollutants dyes impart color to the water. The presence of color reduces the penetration of sun light and results in eutrophication.

Dyes are a group of complex organic compounds which enter into the environment from various industries like tanning, paper, paint, inks and textile industries. Some of these dyes are of highly toxic [2]. Dyes in waste water can be treated by different methods. The traditional methods such as adsorption on waste materials, adsorption on activated carbons, precipitation, air stripping, flocculation, reverse osmosis and ultra-filtration can be used for the removal of dyes [3]. These methods are phase transferring methods and require further treatment for disposal [4]. The biological treatment of waste water is better to some extent over the above methods. But they are time consuming and produce large quantity of sludge which could not be recycled [5]. Also, many colorful waste waters are highly resistant to biodegradation.

Thus all the above methods are ineffective for removing the synthetic dyes that enter into water from various industries. A cost effective, simple and promising method to do complete mineralization of dyes into CO_2 and H_2O is the advanced oxidation process [6]. Among the various advanced oxidation processes, heterogeneous photocatalysis has emerged as powerful technique for the total mineralization of almost all the organic pollutants including the dyes [7]. Some metal oxide semiconductors like ZnO, WO_3, $SrTiO_3$ and hematite are also proven to be photoactive like TiO_2 [8]. Titanium dioxide is proven to be the best photocatalyst for the removal of dyes in waste water. However, the separation of TiO_2 after photocatalytic reaction is very difficult due to its fine size [9]. ZnO, an n-type semiconductor whose band gap is comparable to that of TiO_2 (~3.2 eV) is also a promising candidate in the field of photocatalysis. Removal of zinc oxide after photocatalytic reaction is quite simple as it settles down at the bottom of the photocatalytic reaction vessel quickly.

In the present work, we aimed to compare the photocatalytic activities of two semiconductors *viz*., ZnO and TiO_2 on the basis of photodecolouration efficiencies under UV light for the dye Saffranin O. Saffranin O is an azonium dye. It is widely used in textiles and biological laboratory as a staining agent. It is also used to dye wool, silk, tannin, mordant cotton, leather and paper. Effects of various parameters such as initial concentration of dye, dose of the photocatalysts and pH have been investigated.

2. Experimental Methods

2.1 Materials

Saffranin O (SO) dye was purchased from Himedia and was used without further purification. ZnO and TiO_2 were obtained from Merck and used as photocatalysts. All other chemicals used in this study were also obtained from Merck.

2.2 Characterization of Catalysts

To define the crystalline phase composition of TiO_2 and ZnO, X-Ray diffraction measurements were carried out at room temperature using X'PERT diffractometer with Cu K_α radiation. The average particle sizes were calculated using Debye Scherer's equation. Diffused Reflectance Spectra were recorded with UV-visible spectrophotometer [Model: Schimadzu, UV 2400 series]. PL spectra were taken from Luminescence spectrometer [Model: Perkin Elmer, LS 45 Luminescence spectrometer]. SEM images were recorded on VEGA3 TESCAN.

2.3 Photocatalytic Reactors and Degradation

The photocatalytic reactions were carried out in Heber Multilamp photoreactor [Model: HMP 88]. The photoreactor consists of eight numbers of 8 W Mercury lamps (Sankyo, Denki, Japan) as UV light source (λmax = 365 nm) and highly polished anodized aluminum reactor.

A sample of either ZnO or TiO_2 was suspended in 50 mL of the aqueous SO dye solutions. The suspension was stirred in dark for 30 minutes to attain adsorption-desorption equilibrium. During illumination, the contents of the reaction tubes were stirred continuously with magnetic stirrer which is inbuilt in the photoreactor. The tubes were withdrawn from the reactor at different intervals of time and the contents were

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centrifuged to remove the suspended catalyst particles. The supernatant dye solutions were analyzed by UV-visible spectrophotometer for the determination of concentration of the remaining dye. Absorbances of the dye solutions were measured at the λ_{max} of SO dye *i.e.,* at 519 nm. From the values of absorbance, the concentration of dyes was calculated from the standard calibration curve.

3. Results and Discussion

3.1Characterization of ZnO and TiO_2

In Fig. 1 (a), the entire nine diffraction peaks were indexed as hexagonal wurtzite structure of ZnO (JCPDS Card no: 36-1451) [10]. The analysis of the XRD pattern in Fig. 1 (b) revealed that TiO_2 exhibited the single phase of anatase (JCPDS card no: 21-1272). Similarly the peaks at different 2θ values were all well-defined and could be assigned to anatase crystalline form of TiO_2 (JCPDS Card no: 21-1272) [11]. The particle sizes of ZnO and TiO_2 were determined by applying the Debye-Scherrer's formula and are found to be 126.7 nm and 127.4 nm respectively.

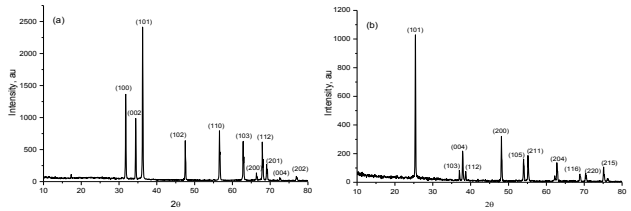

Fig. 1 X-ray powder diffraction patterns of (a) ZnO and (b) TiO_2

The band gap energies were calculated using UV-Visible Diffused Reflectance Spectra. Fig. 2 shows the plot of absorbance *vs* wavelength. The values of the band gap energies of ZnO and TiO_2 were calculated to be 3.28 eV and 3.52 eV respectively.

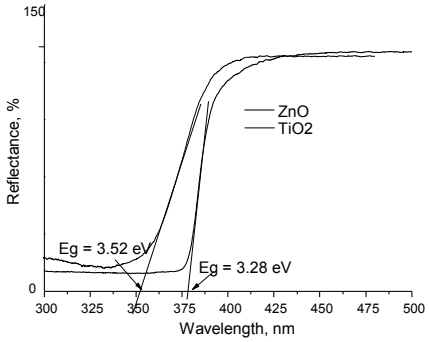

Fig. 2 UV- Visible Diffused Reflectance Spectra of ZnO and TiO_2

The photoluminescent (PL) properties of materials provide valuable information about their purity, quality, charge trapping, electron–hole recombination and so the photocatalytic efficiencies of semiconductors. Hence, PL properties of ZnO and TiO_2 were intensively studied. The room temperature PL spectra of samples were given in Fig. 3. From the PL spectra of ZnO and TiO_2, it was seen that UV-PL intensity is greatly reduced in TiO_2 than ZnO [12]. Therefore, TiO_2 is expected to show more photocatalytic efficiency towards the decoloration of SO dye.

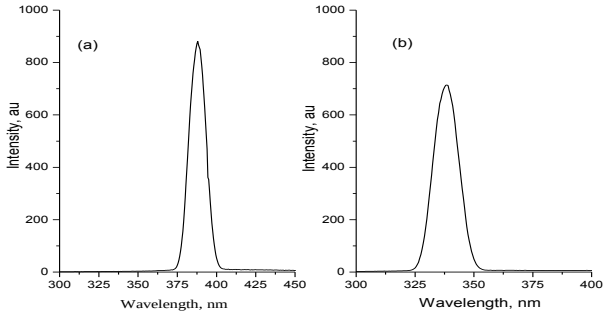

Fig. 3 Photoluminescence Spectra of ZnO and TiO_2 showing the NBE Peaks and their PL Intensity

3.2 Photodegradation of Saffranin O under UV light

3.2.1 Effect of Initial Concentration of SO Dye

The influence of increasing the concentration of SO dye in the photocatalytic decoloration efficiencies of ZnO and TiO_2 was studied by conducting experiments by varying the concentration of SO dye in the range of 5 ppm to 30 ppm for both ZnO and TiO_2 at its natural pH 9.4. The doses of ZnO and TiO_2 were 0.8 gL^{-1} and 0.4 gL^{-1} respectively. The percentage of decoloration of SO dye was decreased with increase in initial concentration of the dye for both ZnO and TiO_2 photocatalysts (Fig. 4). It could be explained on the basis of the following reasons: As the initial concentration of the dye increases, the hydroxyl radicals generated are insufficient to attack the dye molecules and hence resulted in lower percentage of decoloration. Another reason is that, with increase in initial concentration of the dye, the path length of the photons reaching the surface of the catalyst is decreased due to impermeability at the dye solution. Due to this, the relative number of hydroxyl radicals and O^{2-} species produced may be reduced even though the illumination time and amount of photocatalyst are being kept constant [13-15].

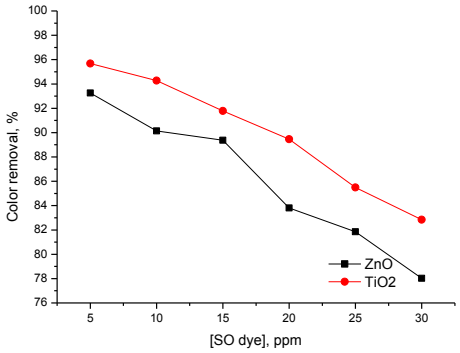

Fig. 4 Percentage of color removal of SO dye as a function of initial concentration of dye; ZnO-loading = 0.8 gL^{-1}, TiO_2- loading = 0.4 gL^{-1}, volume of the reaction solution = 50 mL, UV- light irradiation time = 60 min.

3.2.2 Effect of Catalyst Loading

In order to avoid the use of excess catalysts, it is necessary to find an optimum loading of catalysts for efficient removal of color from the SO dye. Hence, experiments were carried out in the range 0.2 gL^{-1} to 1.2 gL^{-1} of ZnO and 0.1 gL^{-1} to 0.6 gL^{-1} of TiO_2 for 50 mL of 15 ppm SO dye solution. As the weight of photocatalysts was increased, the percentage of decoloration was increased upto a certain loading and then decreased on further loading of photocatalysts. It could be attributed to the following two reasons: The increase in catalyst loading may lead to particle aggregation and reduced the catalytic activity [16]. Secondly, the increased loading of catalyst may cause opaqueness due to scattering of the photons and led to reduced percentage of removal [17].

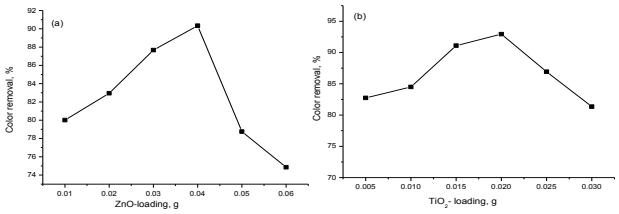

Fig. 5 Percentage of color removal of SO dye at different (a) ZnO-loading and (b) TiO_2-loading; [SO dye] = 15 ppm, volume of the reaction solution = 50 mL, UV- light irradiation time = 60 min.

3.2.3 Effect of pH

Since the effluents discharged from various industries have different pHs, the influence of pH on the percentage removal of the dye is most significant. The decoloration of SO dye was studied with ZnO and TiO_2 at different pHs varying from 3 to 11 (Fig. 6). As a result of Pzc, at acidic pHs, the catalyst's surfaces were positively charged and so the Cl^- ions were attracted more towards the surface of catalyst than the dye cation. This resulted in lower percentage of decoloration. The percentage of removal showed an increase with increase in pH value and reached their maximum value in the alkaline pHs. The surfaces of the catalysts were negatively charged in alkaline medium so that the dye cations were electrostatically attracted more towards the catalyst surface and thus decoloration of SO dye was enhanced. Another reason for this observation was due to the increased generation of OH^- radicals under alkaline conditions [18].

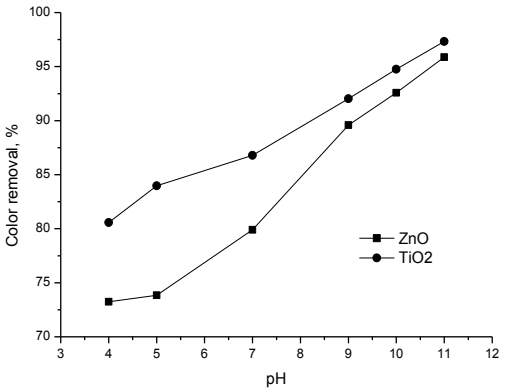

Fig. 6 Influence of pH on the percentage of color removal of SO dye; [SO dye] = 15 ppm, ZnO-loading = 0.8 gL^{-1}, TiO_2- loading = 0.4 gL^{-1}, volume of the reaction solution = 50 mL, UV- light irradiation time = 60 min.

3.2.4 Effect of Illumination Time and Kinetic Analysis

The decoloration of SO dye (50 mL of 15 ppm) was investigated under UV light irradiation in presence of 0.8 $gL^{-1}$of ZnO and 0.4 gL^{-1} TiO_2. The reaction tubes were withdrawn at regular time intervals of 10 minutes and were analyzed using UV-visible spectrophotometer for the concentration of remaining dye. The gradual decrease in the absorbance of SO dye with increase in illumination time was shown in Fig. 7. It was seen that absorption intensity of peaks at λ_{max} of 519 nm decreases gradually. Moreover, the absorbance of the peak at λ_{max} = 275 nm get decreased continuously and finally disappeared in both the cases and confirmed the photocatalytic degradation of SO dye with illumination time.

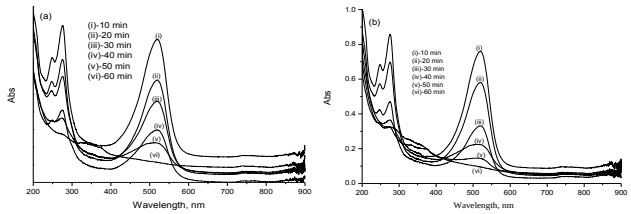

Fig. 7 UV-light induced decoloration of SO dye with (a) ZnO and (b) TiO_2: UV-visible spectra of reaction solution at 10, 20, 30, 40, 50, 60 min; [SO dye] = 15 ppm, ZnO-loading = 0.8 gL^{-1}, TiO_2- loading = 0.4 gL^{-1}, volume of the reaction solution = 50 mL.

The decoloration process of SO dye by both ZnO and TiO_2 was followed by pseudo -first order kinetics [19]. The plots were shown in Fig. 8. The rate constants for the decoloration of SO dye by ZnO and TiO_2 were 0.0151 min^{-1} and 0.0182 min^{-1} respectively. Thus, on comparing the rate constants of decoloration by ZnO and TiO_2, it was found that, TiO_2 showed the highest photocatalytic activity than ZnO. With the intension of determining the best color removal performance and the most efficient photocatalysts for the SO dye in aqueous solution, we carried out similar photocatalytic processes with 0.4 gL^{-1} ZnO. Kinetic rate constant for the photodecoloration processes with 0.4 gL^{-1} of ZnO was 0.0099. It was observed that the rate constant for TiO_2 mediated photodecoloration was 1.84 times higher than that of ZnO. Thus the most effective decoloration rate was achieved with TiO_2 and so, the ranking is in the order TiO_2 > ZnO.

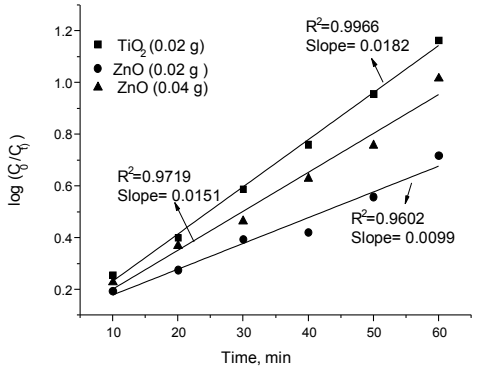

Fig. 8 Langmuir-Hinshelwood kinetics for decoloration of SO dye; [SO dye] = 15 ppm, ZnO-loading = 0.8 gL^{-1} and 0.4 gL^{-1}, TiO_2- loading = 0.4 gL^{-1}, volume of the reaction solution = 50 mL.

3.2.5 Adsorption and Photolysis of SO Dye

The property of adsorption on to the surface of ZnO and TiO_2 and photolysis of SO dye were studied. The results were depicted in Fig. 9. It was found that the decoloration of SO dye require both the photocatalysts and UV light illumination.

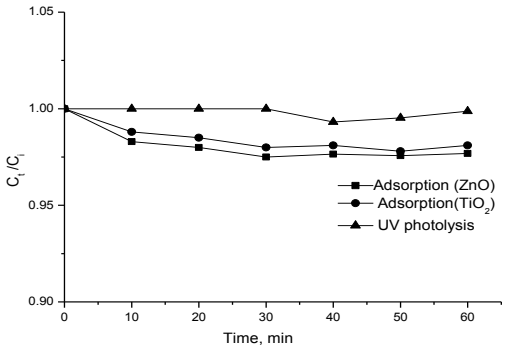

Fig. 9 Extent of color removal of SO dye under different experimental conditions; [SO dye] = 15 ppm, ZnO- loading = 0.6 gL^{-1}, TiO_2- loading =0.3 gL^{-1}, volume of the reaction solution = 50 mL.

4. Conclusion

In this work, we assessed the efficiencies of ZnO and TiO_2 for the photocatalytic decoloration of SO dyes. The results of our studies indicated that the photocatalytic decoloration of SO dye was affected by doses of the ZnO and TiO_2, initial concentrations of SO dye, initial pHs and irradiation time. We obtained the optimum amount of photocatalysts for the decoloration 15 ppm of SO dye as 0.8 gL^{-1} of ZnO and 0.4 gL^{-1} of TiO_2 under 60 minutes of UV light illumination. The highest percentage of decoloration was obtained in basic conditions with pH 11 for both the photocatalysts *viz.,* ZnO and TiO_2.

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