ZnO/UV induced photocatalytic degradation of textile dye

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Abstract
The degradation of textile dye effluent is essential aspect in terms of environmental protection. In this present study, the medium of aqueous suspension laboratory synthesized ZnO has been used in the photocatalytic degradation of textile dye under various experimental conditions through UV irradiation. The performance of the textile dye degradation is studied by monitoring the change in dye concentration and other variables using UV Visible spectroscopic technique.

The effects of key operation parameters such as initial dye concentration, amount of catalyst loading, size of photocatalyst as well as light intensity on the decolorization extents are studied. The decolorization of the organic molecule followed the mechanism of pseudo first order kinetics and it proved the optimum result of 80% degradation.

Keywords: Textile dye removal, photo degradation, ZnO, decolorization, wastewater treatment.

Introduction
Textile industry is inevitable one in the developments of society which shows various challenges to environmental conditions in terms of soil pollution and water pollution. Textile industry involves bleaching and dyeing operations. Organic dyes are one of the largest groups of pollutants in effluent and most of them are produced from the textile industry in terms of bleaching and dyeing operations which use them in conjunction with a wide range of auxiliary chemicals for various dyeing and finishing process.

It is estimated that approximately 25% of dyes are lost annually during manufacturing and the processing operations. The discharge of these colored aqueous solutions in the ecosystem without treatment can cause serious problems due to the toxic nature of some of the dyes to the aquatic life and soil texture and in turn damaging to the aesthetic nature of the environment[1].

In general practice, several techniques of micro, nano, ultra-filtration and reverse osmosis are widely used in commercial operations but alternate to the above by looking to the activated carbon and other adsorbents[2-6] gathered to solve the problems caused by the toxic substances contained in these colored effluents. However, all of these treatments mentioned have a major disadvantage of simple transferring the pollutants from one phase to another phase rather than destroying them, which consequently leads to secondary pollution. Semiconductor photocatalytic oxidation is a famous modern effluent treatment technology. It has many advantages such as high efficiency, low energy-consumption, moderate condition, extensive applicability and decrease in secondary pollution. It can be used as catalyst and photocatalyst under the ultraviolet radiation (<368 nm) to resist bacteria, eliminate odor, disinfect, refine and protect the environment. Therefore, ZnO/TiO_2 will play an important role in the treatment of contamination[7].

In the recent years, many research groups have paid attention to the degradation of this colored effluent treatment through conventional and nonconventional form[8-11].

The photocatalytic mechanism of AOP's employing ZnO is investigated in details elsewhere. Briefly, when aqueous ZnO suspension is irradiated in light energy greater than the band gap energy of the semiconductor (Eg>3.2 eV), conduction band electrons (e^-) and valance band holes (h^-) are generated. If charge separation is maintained, the electrons and holes may migrate to the catalyst surface where they participate in redox reaction with the adsorbed species.

The photogenerated electrons react with the adsorbed molecule O_2 on the Zn (II) site and reduce it to superoxide radial anion (O_2^-), while the photogenerated holes can oxidize the H_2O or OH^- ions adsorbed at the ZnO surface to OH radicals.

These radicals together with other highly oxidant species (e.g. peroxide radicals) will act as strong oxidizing agent than can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus resulting in their complete degradation into small inorganic species. The dye derivative Rhodamine B (RhB) has been widely used in textile industry such as printing and dyeing in textile, paper, paints, leathers etc. and its structure is presented in fig. 1.

There is considerable effort made to investigate the treatment of textile dye based effluent by using various treatment techniques. In the present work, the photocatalytic degradation of RhB dye with ZnO and the effects of operational parameters such as the initial concentration of dye, mass of catalyst loading and light intensity on the decolorization are studied to optimize the process for maximum degradation.
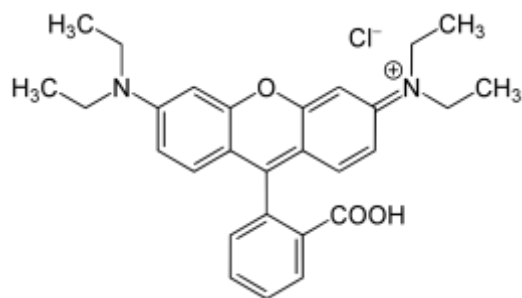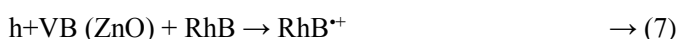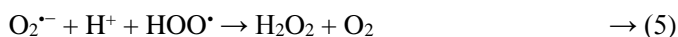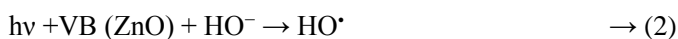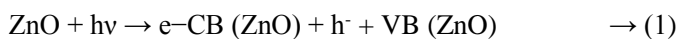
Fig. 1: Structure of Rhodamine B

Mechanism of dye degradation: In a photo-degradation process, when ZnO is irradiated by light with energy greater than or equal to its band gap, an electron in the valence band can be excited to the conduction band with the simultaneous generation of hole in the valence band (Eq. 3). These photogenerated electron-hole pair can interact separately with other molecules. The holes in the valence band can react with water on the surface of ZnO to form highly reactive hydroxyl radicals, while electrons are accepted by adsorbed oxygen to form superoxide radical anion. This radical anion further forms hydroxyl radicals which powerful oxidizing agent and attack the dye molecule to give the oxidized product. The reactions are summarized in eqs. (1-8)[15,21]:

$$ZnO + h\nu \rightarrow e{-}CB\ (ZnO) + h^- + VB\ (ZnO) \qquad \rightarrow (1)$$

$$h\nu + VB\ (ZnO) + HO^- \rightarrow HO^\bullet \qquad \rightarrow (2)$$

$$e{-}CB\ (ZnO) + O_2 \rightarrow O_2^{\bullet-} \qquad \rightarrow (3)$$

$$O_2^{\bullet-} + H^+ \rightarrow HOO^\bullet \qquad \rightarrow (4)$$

$$O_2^{\bullet-} + H^+ + HOO^\bullet \rightarrow H_2O_2 + O_2 \qquad \rightarrow (5)$$

$$HO^\bullet + RhB \rightarrow RhB^{\bullet+} \qquad \rightarrow (6)$$

$$h+VB\ (ZnO) + RhB \rightarrow RhB^{\bullet+} \qquad \rightarrow (7)$$

$$RhB^{\bullet+} \rightarrow Oxidative\ products \qquad \rightarrow (8)$$

Material and Methods
Chemicals/Materials: Laboratory synthesized smallest size of 10 nm ZnO nanoparticles were prepared by chemical deposition method and 200 nm size and 50 nm size ZnO powders prepared by thermal evaporation method. RhB dye is supplied by Indo Chem Industries Company, India. All other chemicals used in this study are of analytical grade and used directly without further purification.

Photocatalytic experiments: The photocatalytic activity of the 50 nm ZnO photo catalyst is evaluated by the degradation of RhB dye effluent. In this study, all experiments are carried out in a photo-reaction vessel of 500 mL capacity. A 125 W high pressure mercury lamp with the strongest emission at 365 nm is used as a light source. The beakers are put under the UV light maintaining the distance between the light source and the surface of the solution is controlled by using UVA-meter (German make). Prior to each test, the lamp is turned on and warmed up for about 10 - 15 min in order to get a constant output.

Batch tests are performed as per the following procedure 0.25 g ZnO catalyst was added into 100 mL dyes solutions, the mixture is stirred in dark for 45 min to allow the physical adsorption of dye molecules on catalyst particles reaching the equilibrium. In turn, the sample mixture is poured into the photo reactor and then start the photocatalytic degradation tests. Air diffuser is used to mix the reaction solution which is placed at the bottom of the reactor to uniformly disperse air into the solution with a flow rate of 0.1 – 0.2 mL/min.

The test samples are collected at regular intervals and are immediately centrifuged to remove particles for analysis. The concentration of RhB is determined by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 510$ nm by using a UV–Vis spectrophotometer (Shimadzu, Japan) with a 1 cm path length spectrometric quartz cell and then calculated from calibration curve.

The effect of various operational parameters such as amount of catalyst (0.5-2.5 g L^{-1}), light intensity (1.92-6.64 mW cm^{-2}) and concentration of dye (100-500 mg L^{-1}) on the photodegradation efficiency is studied. The percentage removal of photocatalytic degradation of RhB dye and apparent first order rate constant is calculated using the following relationships:

Degradation Efficiency (DE, %)= 100 x (Ci-Ct)/Ci

where Ci and Ct are the initial and time bounded photolyzed concentration (mg/L) respectively.

Results and Discussion
Effect of changes in the size of photocatalyst: A series of experiments are conducted by various the photocatalyst size of 10, 50, 100 and 200 nm with 500 mg/L dye concentration, reaction temperature of 30ºC, Time duration is of 60 min to investigate the effect of changes in the size of photo catalyst such as ZnO on the final degradation efficiency. The behavior of photocatalytic degradation is illustrated in fig. 2.

The results indicated that the smallest size of 10 nm ZnO nanoparticles prepared by chemical deposition method indicated the lower efficiency contrast to 200 nm ZnO powders prepared by thermal evaporation method. The results indicated that preparation method is the decisive factor rather than size and morphology. Moreover, the experimental results show that 50 nm ZnO nanoparticles act as better photo catalyst than any others due to its particle nature and size.

Effect of changes in the dose of photocatalyst: A series of experiments are carried out by varying the catalyst from 0.5

to 3.5 g/L in the solution with 500 mg/L dye concentration, reaction temperature = 30°C, time = 60 min to investigate the effect of catalyst loading on the final decolorization efficiency. The profile behaviour of photocatalytic degradation is illustrated in fig. 3.

Fig. 3 shows the relationship between the catalyst loading and the degradation rate and the photocatalytic degradation efficiency of the dye, respectively. From fig. 2, it is clearly observed that when the amount of the catalyst increases, the degradation rate goes up first and then keeps unchangeable in certain scale, but when the amount exceeds 2.5 g.L^{-1}, there is no change in the degradation rate. It is probably due to the aggregation of the free catalyst particles and the "screening" effect[12].

The result is consistent with many other researches that there is an optimal amount of catalyst loading[13]. When the concentration of the catalyst is below the optimal value, the effective surface of the catalyst and the absorption of the light are the main factors, which determine the photocatalytic degradation rate[13,14].

The initial increase in rate of dye degradation with increase in amount of catalyst is due to increase in number of active sites on the surface of photocatalyst. Due to this, there is an increase in number of photo generated electron–hole pair which results in an increase in number of hydroxyl radicals responsible for dye degradation[14,16,17].
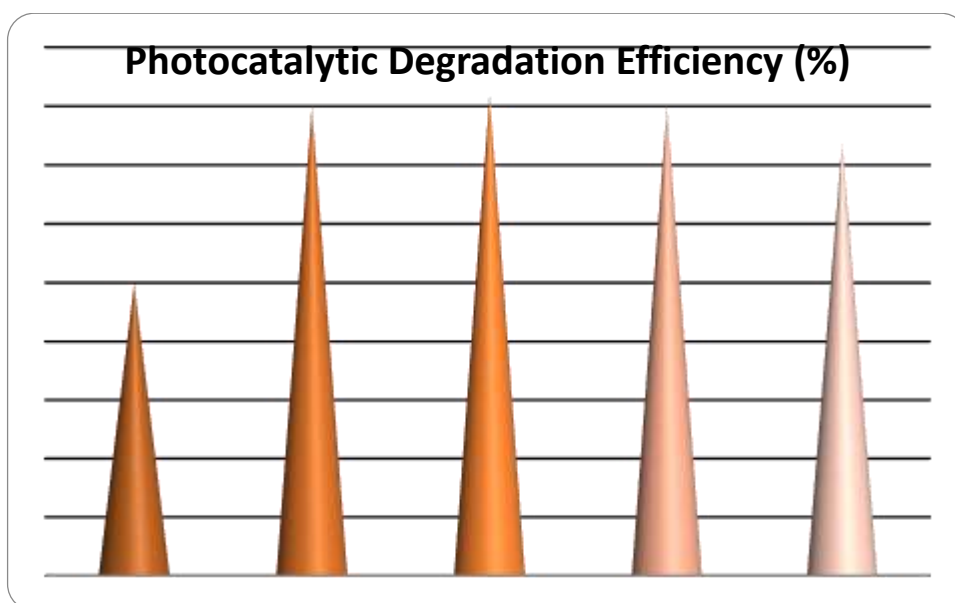
Fig. 2: Photocatalytic degradation of RhB dye at different photocatalyst size in the experimental conditions of Ci=500 mg L^{-1}, Temperature=30°C and Light Intensity= 2.42 mW.cm^{-2}
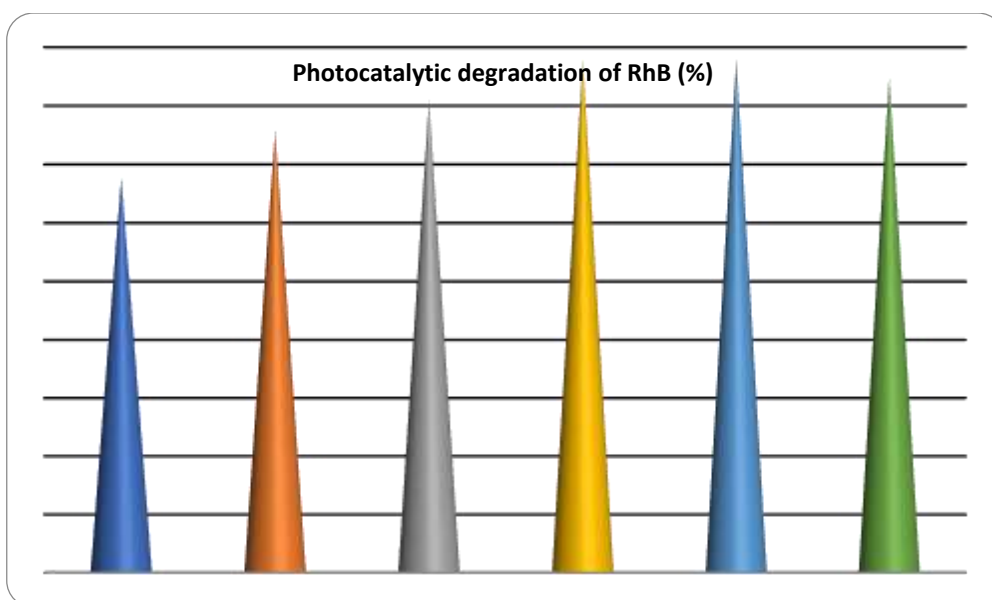
Fig. 3: Photocatalytic degradation of RhB dye at different dosage mass in the experimental conditions of Ci=500 mg L^{-1}, Temperature=30°C and Light Intensity=2.42 mW.cm^{-2}

Effect of concentration of dye: The initial concentration of dye solution plays a crucial role in deciding the rate of dye degradation[15,17-19]. In the present studies, the initial concentration of dye is varied from 100 to 500 mg.L^{-1} at a constant catalyst loading of 2.5 g.L^{-1}. Fig. 4 shows the time dependence of photocatalytic degradation of RhB dye under different concentrations.

Fig. 3 shows the effect of initial dye concentration on the photocatalytic degradation efficiency by varying the initial concentration from 100 to 500 mg.L^{-1} with the constant ZnO catalyst loading (2.5 g.L^{-1}) and pH values. The results reveal that the initial dye concentration influences the degradation efficiency severely.

With the increase of initial dye concentration, the degradation efficiency decreases remarkably, especially when the initial dye concentration varies from 100 to 500 mg.L^{-1}. The negative effects of the initial dye concentration are ascribed to the competence between the dye and OH⁻ ion adsorption on the surface of catalyst.

The adsorption of dye depresses the OH⁻ ion adsorption which results in the reduction on the formation of hydroxyl radicals. At the same time, as the initial dye concentration increases, the path length of photons entering the solution decreases. Hence, in the solution with constant catalyst concentration, the formation of hydroxyl radicals that can attack the pollutants, decreases, thus leading to the lower decolorization efficiency[18].

Light intensity and wavelength: Light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation of photocatalysis, electron–hole formation in the photochemical reaction is strongly dependent on the light intensity[19].

Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency[20]. Consequently, the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations of various organic pollutant while in some cases the reaction rate exhibited a square root dependency on the light intensity, others observed a linear relationship between the two variables. Experiments are conducted by varying light intensity from 1.92 to 6.64 mW.cm⁻². The time dependence of the photocatalytic degradation on light intensity is shown in fig. 4.

The rate of photocatalytic degradation and the photocatalytic degradation efficiency are illustrated in fig. 4. It is clear from results in fig. 5 that the rate of photocatalytic degradation and photodegradation efficiency increased with increasing UV light intensity as more radiation is available to excite the catalyst and hence more charge carriers are generated resulting in a higher rate of photocatalytic removal.

However, the relation between the light intensity and the photocatalytic removal is found to be nonlinear due to the fact that at high photon flux, the recombination rate of the charge carriers also increases as compared with a lower photon flux[21].

Conclusion
The obtained results show that Rhodamine B (RhB) can be easily degraded by ZnO (acts as photocatalyst) assisted process in aqueous dispersions under UV irradiation. The photodegradation of the dye follows first order kinetics and parameters like ZnO concentration, light intensity and initial dye concentration affect the photodegradation effect.
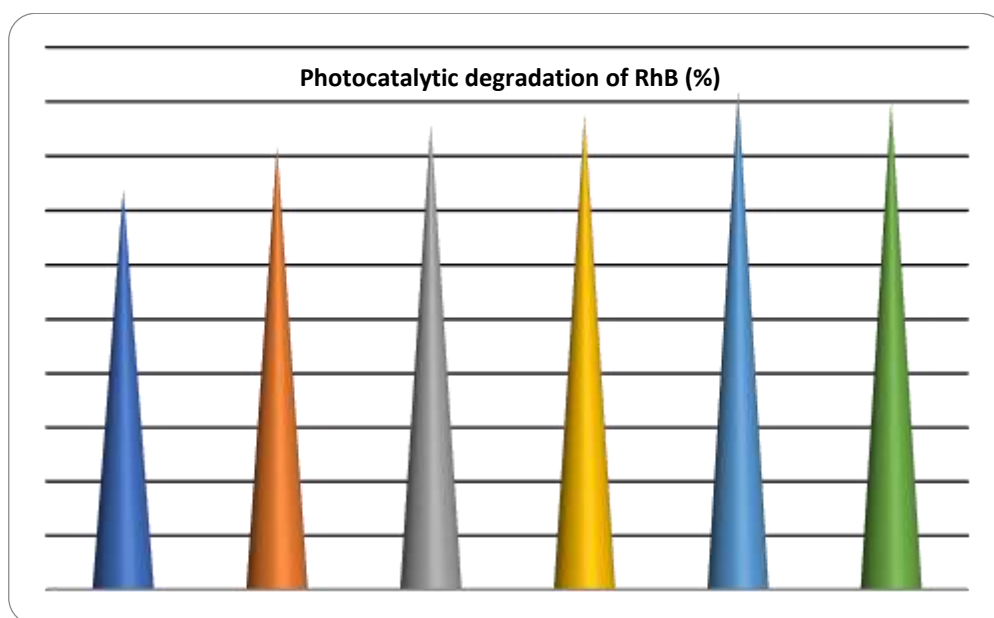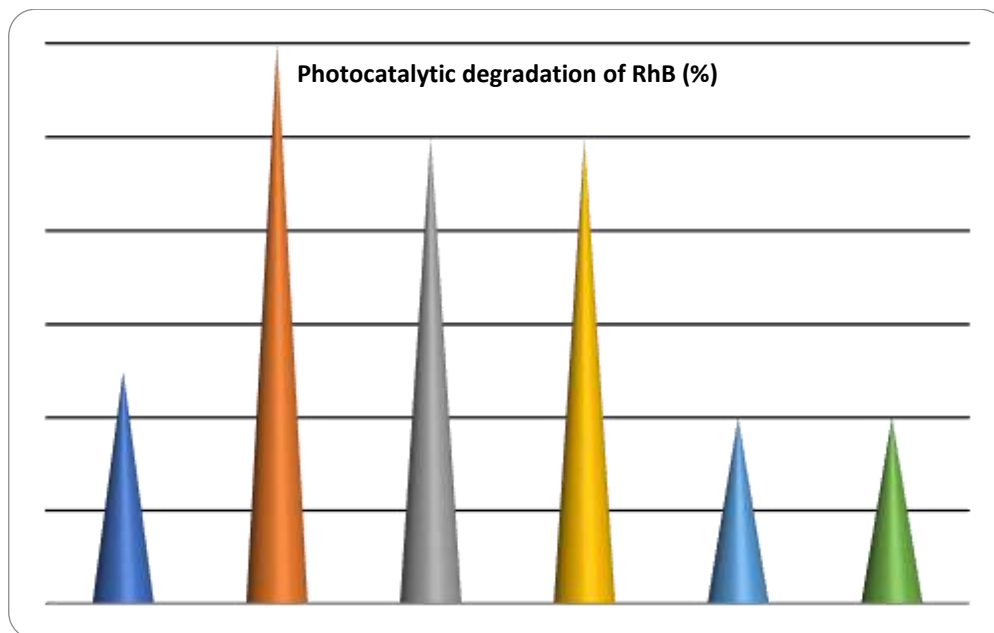

Fig. 4: Photocatalytic degradation of RhB dye at different initial concentration. Experimental conditions: Catalyst amount=2.5 g.L⁻¹, Temp= 30ºC and Light Intensity= 2.42 mW.cm⁻²

Fig. 5: Photocatalytic degradation of RhB dye at different light intensities under the experimental conditions of Initial conc. 500 mg.L^{-1}, Temp. 30°C and catalyst mass 2.5 g.L^{-1}

The results indicated that the catalyst loading, light intensity and the initial dye concentration affected the degradation efficiency of ZnO powder obviously. However, the smallest size of 10 nm ZnO nanoparticles prepared by chemical deposition method indicated the lower efficiency contrast to 200 nm ZnO powders prepared by thermal evaporation method. The results that indicated preparation method is the decisive factor rather than size and morphology.

Moreover, the effects of catalyst loading, pH value and the initial dye concentration on the final degradation efficiency were discussed through the photocatalytic experiments using 50 nm ZnO nanoparticles as better photocatalyst. From this study, we learned that the photodegradation efficiency is enhanced with the increase of catalyst loading and the reverse effect is obtained with the increase of initial dye concentration in our experiments. The photocatalytic decomposition of RhB dye was most efficient in the solution at lower initial concentration and higher light intensity.

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