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Kinetic studies on the photo decolourisation of textile dyes (reactive) using ZnO catalyst

T Sivakumar* & K Shanthi **

Department of Chemical Engineering, Anna University, Chennai 600 025, India

**Department of Chemistry, Anna University, Chennai -600 025, India

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Zinc oxide

Photo decolourisation of various reactive textile dyes such as Procion Brilliant Yellow M-4G (PBY), Procion Brilliant Magenta M-B(PBM) and Procion Brilliant Orange M-2R(PBO) have been studied using ZnO as photocatalyst. Complete decolourisation (100%) of dyes by sunlight was obtained when ZnO was used as a catalyst. Decolourisation of dyes by sunlight was found to be more effective as compared to UV light. This paper also discusses the effect of pH, H₂O₂ concentration, dye concentration and catalyst weight on the decolourisation of dyes. The decolourisation was not affected by changes in pH. The degradation kinetics involving Langmuir-Hinshelwood model for PBY has been studied in detail.

25 mg

Dyeing and finishing processes are two important steps in the textile manufacturing processes. Synthetic dyes are used extensively for textile dyeing and approximately 10,000 different dyes and pigments are used in industries and over 7×10^5 tonnes of these dyes are produced annually worldwide. These industries produce large quantities of wastewater varying from 50 -100 litres per kg of cloth processed¹. Other industries such as pulp and paper, leather, wool, silk, etc., also use dyes in large quantities, which result in increased discharge of wastewater. Discharge of these coloured wastes into natural water bodies is undesirable from aesthetic point of view. This also in turn, stops the reoxygenation capacity of receiving waters and cut-off sunlight thereby upsetting biological activity in water. As these dyes are toxic and carcinogenic, environmental contamination due to these, is a serious global concern. In contrast, bleached dye solutions are non-toxic and harmless for these may be used for washing, cooling, irrigation and cleaning purposes. The characteristics of textile wastewater have been discussed in detail by Lin *et al.*². These reactive dyes have been identified as problematic compounds in textile effluents as they are water-soluble and not removed by traditional methods, which consist of various combinations of biological, physical and chemical methods³. Degradation of organic compounds into simpler fragments in the presence of light and catalyst is

known as photocatalysis⁴. Semiconductor photocatalysis is intended to be both supplementary and complementary to some of the more conventional approaches (to the destruction or transformation of hazardous chemical wastes) such as high temperature incineration, activated sludge digestion, anaerobic digestion and conventional physico-chemical treatment. Over the last 10 years, the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially⁵⁻⁷. This heterogeneous photocatalysis is a newly emerging field. The photocatalytic degradation is usually used to refer to complete mineralisation that is conversion of organic compounds into CO₂, H₂O, NO₃⁻, phosphate and halide ions. Extensive work has shown that many organic waste products can be completely mineralised on irradiated semiconductors⁸. This technique has been shown to be useful for colour removal and TOC/COD reduction originating from dyestuffs belonging to triaryl methyl, azo, heterocyclic, anthraquinonoid and phthalein classes⁹⁻¹¹.

Several books and reviews have been recently devoted to this problem¹²⁻¹⁴. A recent review has reported more than 1200 references on the subject¹⁵. The authors have also reported the photodecolourisation of remazol supra red and Congo red and photodegradation of anthraquinone elsewhere¹⁶⁻¹⁸.

In this paper, the results of ZnO catalysed degradation of three different textile dyes, viz., Procion Brilliant Yellow M-4G (PBY), Procion Brilliant Magenta M-B(PBM) and Procion Brilliant

*For correspondence

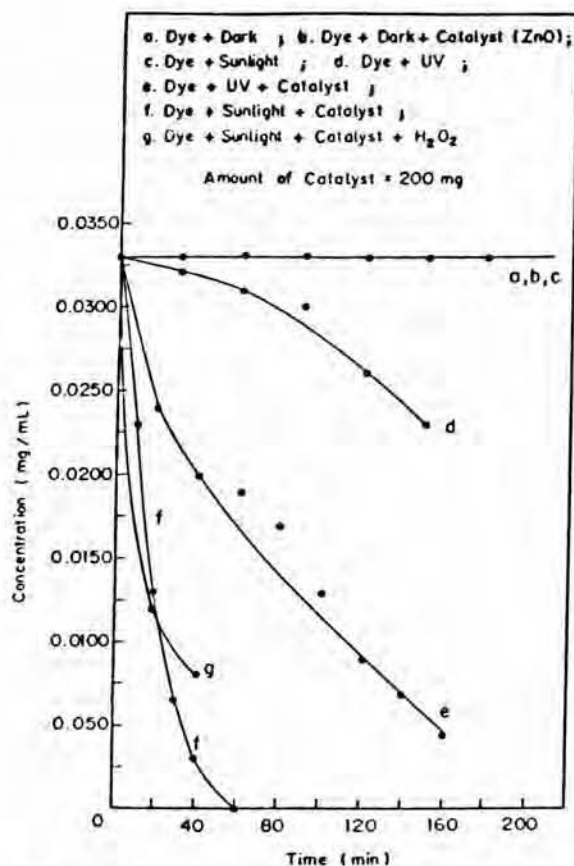


Fig. 1 — Photo decolourisation of Procion Brilliant Yellow M-4G (PBY) under different conditions

Orange M-2R (PBO) have been presented. These procion dyes are the derivatives of trichloro triazine (Cyanuric chloride) and were synthesized by the reaction between existing dyes and trichlorotriazine.

Experimental Procedure

The textile dyes viz., PBY, PBM and PBO were obtained from ATIC Industries, Gujarat, India and ZnO from CHENCOL Industries, Chennai, India. BET surface area of ZnO was determined by using Micromeritics Pulse Chemisorb-2700 System and the particle size was measured by Shimadzu Particle Size Analyser (SALD). Experiments were carried out with 80 mL of different concentrations of dye solutions (0.1 mg/mL for both PBY and PBM and 0.04 mg/mL for PBO) using different amounts of catalysts, viz., 150, 170 and 200 mg for PBY, PBM and PBO respectively, under exposure to UV-irradiation in a specially designed double-walled reactor vessel made up of pyrex glass (7 cm height, 4 cm diameter) fitted with low pressure mercury ultra-violet lamp (8 watts Spectroline Penray Lamp, UV Products, Inc., California) emitting light through a quartz envelope

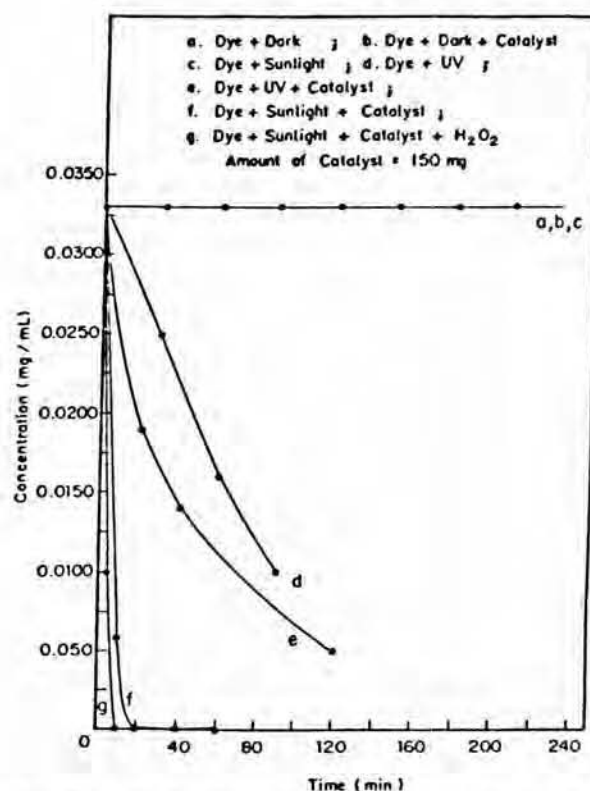


Fig. 2 — Photo decolourisation of Procion Brilliant Magenta M-B (PBM) under different conditions

with the wavelength maximum at 253.9 nm with power supplier (230 V, 50 Hz, Spectronic Corporation, New York, U.S.A.).

A set of experiments was also carried out under sunlight with different amounts of catalysts (150, 170 and 200 mg for PBY, PBM and PBO respectively) by using an open pyrex glass vessel (9.5 cm height, 6.5 cm diameter). The intensity of sunlight and UV rays were measured by using a Digital Lux-meter LX-101. 80 mL of dye containing the initial concentration of 0.1 mg/mL in the case of PBY and PBM and 0.04 mg/mL in the case of PBO were used for the experiments with UV and sunlight irradiations. At regular intervals of time, 2 mL of the reaction mixture were withdrawn, diluted to 6 mL with water and centrifuged. The supernatant was analysed by using UV-visible spectrophotometer (Hitachi U-2000). The calibration graphs were constructed for each dye at their respective λ_{\max} values (405 nm, 529 nm, 489 nm for PBY, PBM, PBO respectively) and the decolourisation was followed. Experiments were also carried out by adding 1 mL of 30% (v/v) H_2O_2 to the above dye solution for the degradation by sunlight. Blank experiments were carried out (without

light/catalyst) to ascertain that the decolourisation was purely photocatalytic.

Results and Discussion

BET surface area of ZnO was found to be $7.49 \text{ m}^2/\text{g}$ and the particle size was 0.45 microns. The intensity of UV and sunlight were found to be 74 and $8-12 \times 10^4 \text{ Lux}$, respectively.

Figs 1 - 3 show the photodecolourisation of PBV, PBM and PBO respectively under different conditions. It is clear from the figure that no significant decolourisation was observed in the absence of catalyst/sunlight, which suggested that decolourisation of all the three dyes was purely photocatalytic. UV irradiation alone decolourised these dyes to a smaller extent. However, in the presence of ZnO catalyst, increased photodecolourisation was observed. ZnO catalyst was found to be more efficient when the dyes were exposed to sunlight. Almost 100% decolourisation

was achieved under the experimental conditions. Increased photodecolourisation of dyes with ZnO in presence of sunlight may be attributed to the fact that the band gap of ZnO is favourable for sunlight. Among the dyes studied, PBM underwent decolourisation quickly followed by PBO and then PBV. Since the structures of these dyes are not known, it is difficult to identify the intermediates. In all the cases, addition of hydrogen peroxide enhanced the rate of decolourisation. This may be due to the generation of hydroxyl radicals for the decolourisation of dyes⁵.

Effect of pH on $t_{1/2}$ values—To optimize pH, the experiments were also carried out at different pH values. The $t_{1/2}$ values (time taken to degrade 50% of initial concentration) were found out for a particular concentration of each dye after adjusting their pH values ranging from 2 to 12. These $t_{1/2}$ values were plotted against their pH for the three different dyes (Fig. 4). It is seen from the figure that PBM

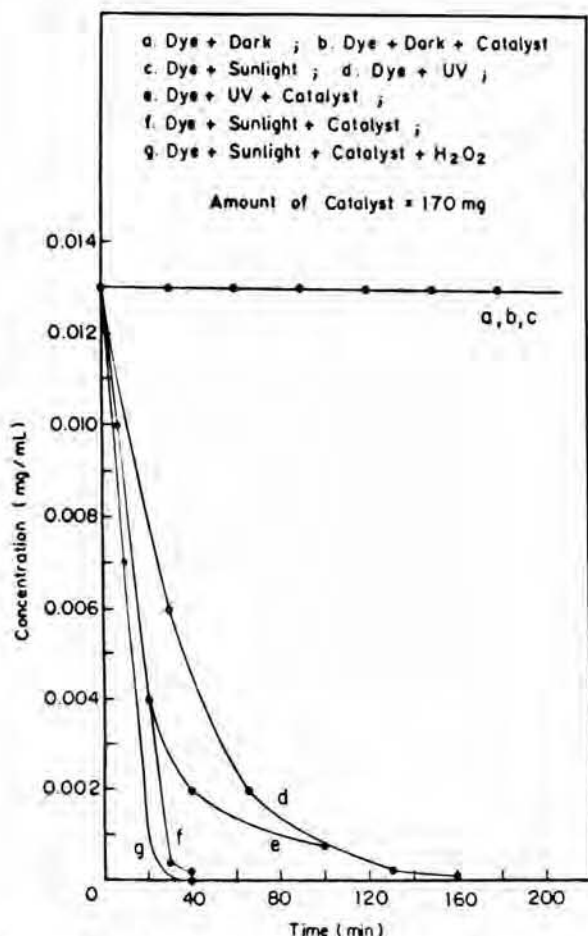


Fig. 3—Photo decolourisation of Procion Brilliant Orange M-2R (PBO) under different conditions

Concentration (mg/mL)	$k' \text{ min}^{-1}$	$t_{1/2} \text{ min (calculated)}$
0.025	0.160	6
0.050	0.080	9
0.100	0.055	13
0.150	0.040	17
0.175	0.024	29
0.200	0.020	35

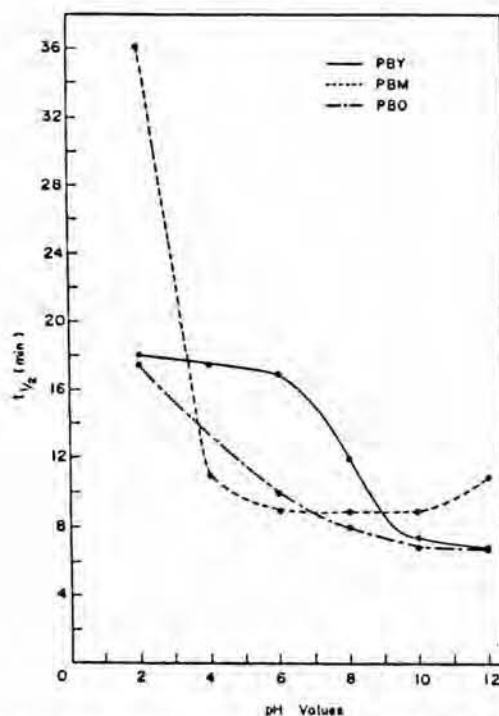


Fig. 4—Plot of pH versus $t_{1/2}$ (min) for PBV, PBM & PBO

underwent decolourisation to similar extent in the pH range 6 to 12, but at pH 2, decolourisation prolonged. Increase in pH from 2 to 12 decreased the $t_{1/2}$ values in the case of PBO. But, fairly constant higher $t_{1/2}$ values were obtained between pH 2 to 6 in the case of PBV and further increase in pH value resulted in decrease of $t_{1/2}$ values. The higher $t_{1/2}$ values obtained below pH 6 can be attributed to the dissolution of semiconductor ZnO in highly acidic condition and hence low pH range is unfavourable. There is no beneficial effect observed for all the dyes when pH was altered. Hence further experiments were carried on their own pH values.

Optimisation of catalyst weight—The weight of the catalyst was varied from 50 to 500 mg for studies using UV radiation and for experiments using sunlight, keeping the volume and concentration of dyes constant. The concentrations of each dye obtained at different intervals of time were found out. The $t_{1/2}$ values were determined as described earlier and plotted against the weight of catalyst (Figs 5 and 6) under illumination of UV and sunlight respectively. It can be seen from the figures that increase in the amount of ZnO decreases $t_{1/2}$ values. This is due to an increase in the exposed surface area of

semiconductor. However, after a certain limit (400 mg for PBV and 300 mg for both PBM and PBO), further increase in the amount of the catalyst did not reduce $t_{1/2}$ values. This saturation point is reached because there may be no increase in the surface area of the catalyst. These plots demonstrated that 400 mg of catalyst was needed to decolourise PBV, 300 mg for both PBM and PBO under UV-irradiation. Beyond these amounts of catalyst, no significant reduction in $t_{1/2}$ values were observed (Fig. 5), whereas when the studies were carried out under exposure to sunlight, significant reduction in both $t_{1/2}$ values and weight of catalyst were obtained. It was observed from the Fig. 6 that 150, 170 and 200 mg of catalyst were required for 80 mL of solution containing 0.1 mg/mL of PBV and PBM and 0.04 mg/mL of PBO respectively. Since PBO shows strong absorbance at the concentration of 0.1 mg per mL, a lower concentration viz., 0.04 mg per mL was taken. With sunlight and UV radiation, the degradation profiles were found to be the same but with different rates. This indicates that the degradation follows the same path.

Kinetics of decolourisation of PBV—Solutions containing different initial concentrations of PBV ranging from 25 to 200 ppm were decolourised (without H_2O_2) under sunlight irradiation by using optimised catalyst weight (200 mg) in order to study the kinetics of decolourisation of PBV. The degradation profiles were plotted as a function of time

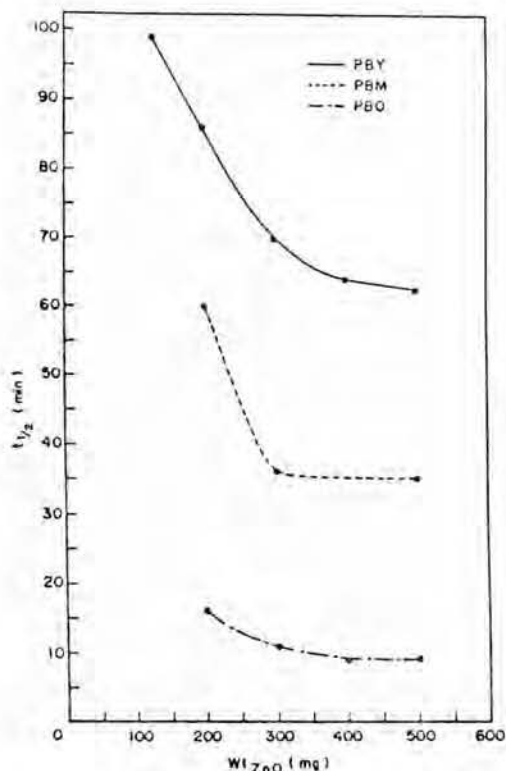


Fig. 5—Variation of $t_{1/2}$ values with weight of ZnO (UV irradiation) for PBV, PBM & PBO

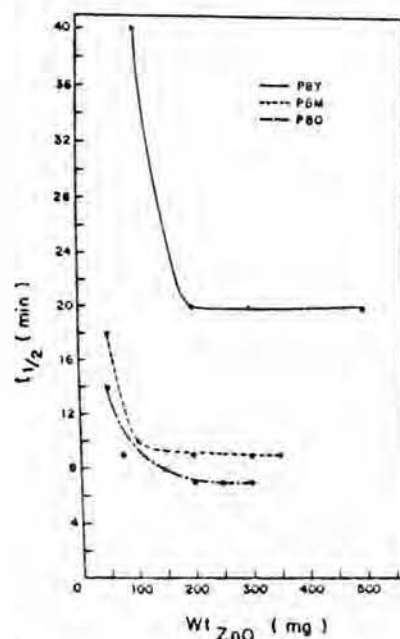


Fig. 6—Variation of $t_{1/2}$ values with weight of ZnO (sun light irradiation) for PBV, PBM & PBO

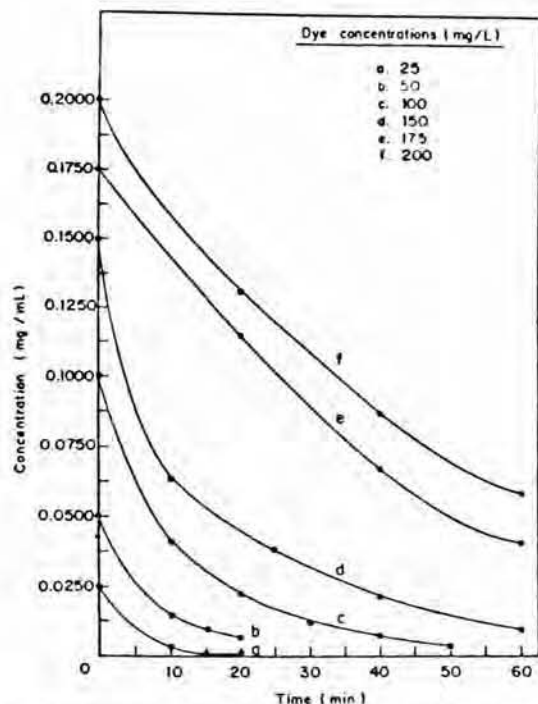


Fig. 7—Photo degradation of PBY versus time for various initial concentrations of PBY

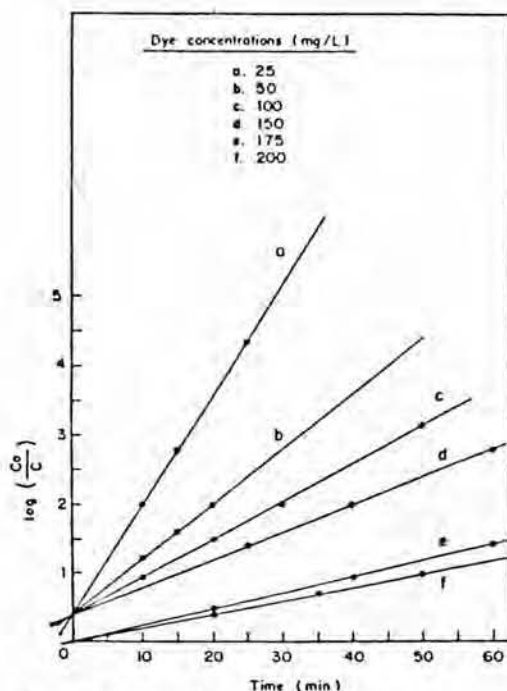


Fig. 8—Plot of $\ln(C_0/C)$ versus irradiation time for different concentrations of PBY in presence of ZnO

(Fig. 7). Generally, the influence of initial concentration on the photocatalytic degradation rate is described by pseudo-first order kinetics involving Langmuir-Hinshelwood Model¹⁹⁻²⁰

$$R = -dC/dt = k_r K C / (1 + K C) \quad \dots (1)$$

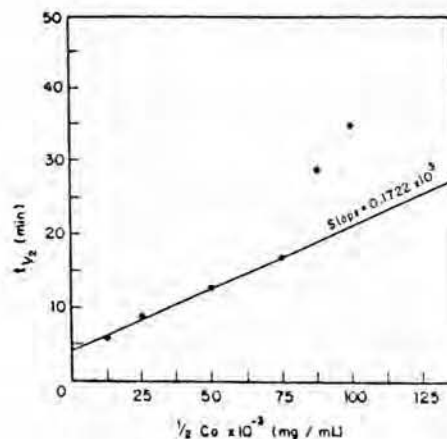


Fig. 9—Plot of $t_{1/2}$ versus $1/2 C_0$ for PBY at different initial concentrations

where R represents the initial rate of disappearance of the dye, C is the initial concentration, K is the equilibrium constant for the adsorption of dye on ZnO and k_r reflects the limiting rate of reaction at maximum coverage at the experimental conditions. On integrating Eq. (1),

$$t = (1/k_r K) \ln(C_0/C) + (C_0 - C)/k_r \quad \dots (2)$$

where t is the time in minutes required for the initial concentration of dye (C_0) to decrease to C ²¹⁻²². At low initial concentration of dye, the second term in Eq. (2) becomes insignificant and hence it may be neglected.

$$\ln(C_0/C) = k_r K t = k' t \quad \dots (3)$$

where k' is the apparent rate constant (min^{-1}) of the photo-decolourisation. The plots of natural logarithm of the ratio of C_0 to C versus initial concentrations of PBY (25, 50, 100, 150, 175 and 200 ppm) were presented in Fig. 8. This figure showed that all the lines represented good approximations over a wide range of dye concentrations. k' values were determined from the slopes of the plots in Fig. 8 by the method of least squares and $t_{1/2}$ values were obtained from the Eq. (3) for $C/C_0 = 0.5$. The values of k' and $t_{1/2}$ were listed in Table I. The decrease in k' with increasing concentration might have been attributed to the competition between intermediates and the substrates for the semiconductor active sites²³⁻²⁴ or may be due to diminished penetration depth of sunlight at higher concentration which prevents the direct excitation of semiconductor ZnO²⁵. When $t = t_{1/2}$ and $C/C_0 = 0.5$, the Eq. (2) can be modified as,

$$t_{1/2} = (0.5 C_0)/k_r + 0.693/(k_r K) \quad \dots (4)$$

The plot of $0.5 C_0$ versus $t_{1/2}$ gave a straight line (Fig. 9) with the slope equal to $1/k_r$ and the intercept

equal to $0.693/k_r K^{23-24}$. The k_r and K values were calculated and found to be $5.81 \text{ ppm min}^{-1}$ and 0.028 ppm^{-1} respectively. The product of equilibrium constant K and the limiting rate of reaction k_r at maximum coverage for the experimental conditions was equal to $0.1629 \text{ minute}^{-1}$ which represented the apparent rate constant k' for very small initial concentrations of the dye and this value was found to be in very good agreement with the value obtained for the initial concentration of 25 ppm of dye ($k' = 0.16 \text{ minute}^{-1}$).

Conclusion

In this study, a detailed investigation on the photo-decolourisation of three different reactive dyes has been made using ZnO as photocatalyst. Almost 100% decolourisation was achieved by photo catalytic method. Sunlight illumination seems to be more advantageous requiring a smaller amount of catalyst for complete decolourisation in contrast to UV irradiation. Addition of hydrogen peroxide enhanced the decolourisation. The decolourisation followed pseudo-first order kinetics with respect to dye concentration. Calculated and observed k' values were consistent with each other.

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