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ZnO MEDIATED PHOTODEGRADATION OF AQUEOUS SOLUTIONS OF CRYSTAL VIOLET AND PONCEAU S BY VISIBLE LIGHT

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ABSTRACT

An anionic dye, ponceau s (PS), undergoes adsorption on ZnO from aqueous solution at a pH of 5.75 whereas a cationic dye, crystal violet (CV), undergoes only a little adsorption. The isotherm for adsorption of PS is of Langmuir type and the nature of adsorption is predominantly electrostatic. The adsorption coefficient is 6.2×10^{-2} *L* mol^{-1} *at 30 °C. Both the dyes undergo photodegradation by the visible light of intensity* 1.80×10^{-4} Wcm^{-2} *in the presence of ZnO suspension. Both the dyes follow Langmuir-Hinshelwood kinetic model indicating that the photodegradation occurs at the surface of the ZnO particles. More than 60% colour of* 5.3×10^{-5} *M PS in 80 mL suspension containing 0.35 g ZnO disappears within an hour of illumination. On the other hand, almost 80%colour of the CV solution disappears under the same conditions. Both the dyes are suggested to be completely mineralized by visible light in the presence of ZnO.*

Keywords:*Adsorption isotherms, Langmuir isotherms, photodegradation, Langmuir-Hinshelwood equation.*

1. INTRODUCTION

The photocatalytictreatment of wastewater by irradiated semiconducting oxides has been of growing interest because of its ability to mineralize the organic substrates completely (Saquib and Muneer, 2002; Mahmood *et al.*, 2003; Zhigang *et al.,* 2001; Hossain *et al.*, 2011). Dyes from the textile dying industries are known to be one of the major sources of environmental contamination. In most cases, TiO_2 (degussa P25, anatase, rutile) with a band gap energy in the range of 3.0-3.2 eV corresponding to wavelength 413-388 nm is used as a photocatalyst under UV irradiation to decompose these dyes from aqueous environment. Unavailability of solar UV radiation on the earth surface (< 5%, Kuo 2001) forced the scientists to use expensive artificial light source to carry out the degradation, which is not viable economically. However in some previous reports (Zhang *et al.*, 1998; Annaporani and Renganathan, 1997; Shivakumar and Shanti, 2000) dyes were shown to be degradated even by sunlight in the presence of TiO_2. ZnO is another semiconducting oxide with almost equal band gap energy. It is much cheaper and easier to prepare as well as modify. Considering these properties of ZnO, one may assume it as an alternative to TiO_2. Some authors as well as we have already reported the high catalytic activity of ZnO by both UV (Chen *et al.,* 2011) and visible light (Saktivel *et al.*, 2000; Mahmood *et al.*, 2003; Hossain *et al.,* 2011). The present understanding of degradation by visible light in the presence of TiO_2 or ZnO indicates that adsorption of the substrates on these oxides is likely a precondition for the photodegradation. Since, ZnO remains positively charged below pH 6.8 (pH_{zpc}), anionic dyes as substrate are the best choice for the efficient photodegradation. Accordingly, we already reported the degradation of two anionic dyes, brilliant orange (Mahmood e*t al.*, 2003; Hossain *et al.*, 2011) and bractive T blue (Mahmood *et al.*, 2003), in the presence of ZnO by visible light.

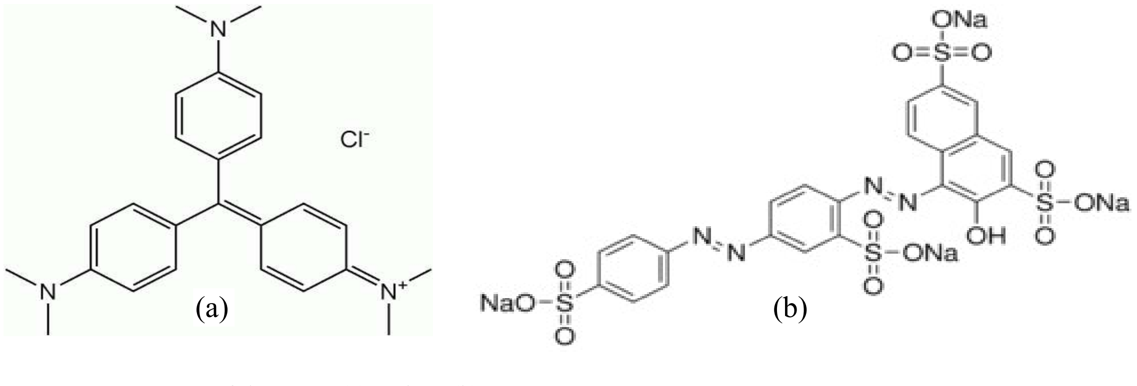

Figure 1: Structures of dyes, CV (a) and PS (b)

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The aim of the present work is to observe the photodegradation of CV (a cationic dye) by visible light in the presence of ZnO. To compare these results, the study of degradation of another anionic azo dye, ponceau S (PS), is presented. The structures of these two dyes are shown in Figure 1.

2. EXPERIMENTAL

2.1 Materials

ZnO (Fluka, Switzerland), CV and PS (commercial grade, BDH, England), were used without further purification. Deionized water was used throughout the present study. All the experiments were performed at the pH5.75 of aqueous solution.

2.2 Photochemical reactor and light source

The reactor for photochemical degradation consisted of an open beaker (volume 100 mL) was placed in an aluminium-foil covered wooden box. The light source comprised of five 40 W fluorescent lamps were arranged inside the box. The resultant intensity emitted by the light sources (1.80×10^{-4} Wcm^{-2}) was measured by chemical actinometry. A fixed volume of solution containing suspension of ZnO was taken into the reactor, which was maintained at a fixed position so that the intensity of the incident light remains the same for all the experiments. Temperature inside the box was constant at 35.0 ± 1 ^{o}C and no significant weight loss of the contents was recorded up to one-hour of photolysis.

2.3 Experimental Procedure

Adsorption: Adsorption experiment was carried out in batch method.30.0 mL solutions of a definite concentration of the dyes were taken in different stoppered bottles, each of which contained 0.35 g ZnO (previously socked overnight in 10.0 mL water). The stoppered bottles were placed in a thermostated shaker maintained at 30 ^{0}C. The bottles were successively withdrawn with time and clear solutions after centrifugation were taken for spectrophotometric (UV-1800, SHIMADZU Spectrophotometer) determination of concentration. Adsorption experiments were also carried out to obtain the isotherm at room temperature.

Photodegradation: A typical photodegradation experiment was carried out in the following way: 0.35 g ZnO powder was taken in a beaker. 80.0 mL CV of 5.3×10^{-5} Msolutionwas added to it. The content of the beaker was stirred magnetically in the dark for 30 minutes. Then the beaker was placed into the box for photolysis. During photolysis the contents of the reactor were also stirred magnetically and the concentration of the solution was followed spectroscopically. Photodegradation of dyes was studied with different initial concentrations of both CV and PS, with different amount of ZnO at the usual pH 5.75 of the aqueous solutions.

2.4 Measurement of initial rate

Aqueous suspension containing 0.35 gZnO and 80.0 mL CV solutionof a definite concentration were taken in the reactor. The mixture was stirred for 30 minutes in the dark. The suspension containing ZnO is then illuminated and the samples were withdrawn at regular intervals for measuring the absorbance. The slope of the straight line drawn through the first few points of lnAvs time plot was determined. This slope is the apparent rate constant (k_a).The concentration of CV at zero time, $[CV]_o$, was determined by measuring the absorbance (A) of the solution with no ZnO. Thus, the initial rate of degradation, R_i, is

$$R_i = k_a [CV]_o \qquad (1)$$

A similar set of treatment was also done for the dye PS.

3. RESULTS AND DISCUSSION

3.1 Adsorption of CV and PS on ZnO

A considerable amount of PS is adsorbed on ZnO from aqueous solution whereas the amount of CV adsorption on it is less prominent (Figure 2). The time for adsorption to reach the equilibrium is about 30 minutes for both the cases. However, in the case of CV amount of adsorption becomes initially higher which then undergoes desorption to reach equilibrium.

The isotherm for PS on ZnO is of Langmuir type in the concentration range from 1.9×10^{-5}M to 6.1×10^{-5} M (Figure 3). Above this concentration range, isotherm shows the tendency to form multiplayer of PS on ZnO. The Langmuir plot is drawn by employing Equation (2).

$$\frac{C_e}{(x/m)} = \frac{1}{K_L k_L} + \frac{C_e}{k_L} \tag{2}$$

Where C_e is the equilibrium concentration, x/m is the amount of dye adsorbed per gram of ZnO, K_L is the Langmuir adsorption coefficient and k_L is the proportionality constant.

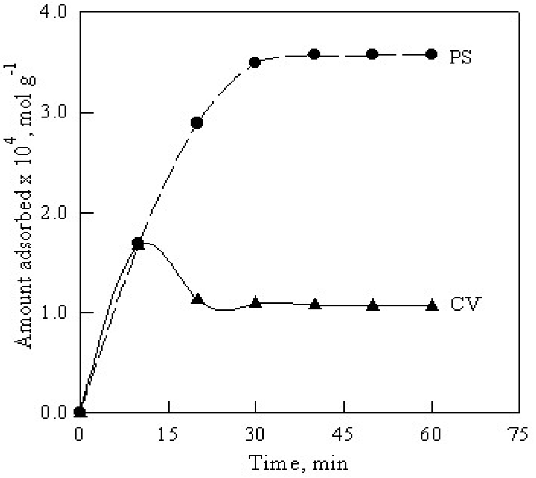

Figure 2: A plot of amount of CV and PS adsorbed on ZnO with time.

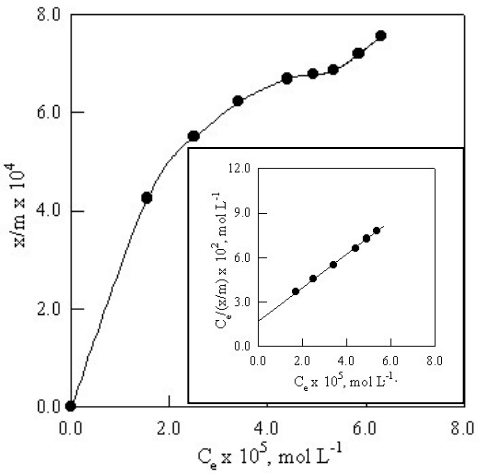

Figure 3: Adsorption isotherm of PS on ZnO at 30 °C. Langmuir plot for adsorption of PSon ZnO is shown in the inset.

The pH at zero charge, pH_{zpc} for ZnO is about 6.8 which is above the pH of the experimental solutions. This suggests that at the normal pH of dye solutions, the surface charge ofZnO is positive. Since the PS is anionic in nature, the initial adsorption process on the positively charged ZnO should be predominantly influenced by electrostatic attraction. However, ion exchange process, involving adsorbed OH^- and the dye anion, is likely to occur at the surfaceof the adsorbent (Mills *et al.,* 1993).The value of K_L, which is 6.2× 10^{-2} L mol^{-1} at 30 °C, is evaluated from the slope and the intercept of Langmuir plot. These results are consistent with some previous reports (Kim and Chung, 2001; Mahmood *et al.,* 2003). However, the less significant amount of adsorption of cationic CV on ZnO is also desirable if one assumes the electrostatic nature of adsorption. Still, some molecules are adsorbed. This indicates that the surface charge may not be the only factor to cause adsorption. The small amount of adsorption of CV on ZnO may be due to the weak interactions of the three $-N(CH_3)_2$ groups present in the molecule. The weak nature of the interaction becomes further evident from observed desorption of CV which initially undergoes adsorption (Figure 2). It is also possible that the functional groups of the dye and their positions in the aromatic rings play a kinetically important role in the adsorption process (Zhao *et al.*, 1998).

3.2 Photodegradation of PS and CV

In the absence of ZnO, the photodegradation of both the dyes by visible light are insignificant. Both the dye solutions can be completely decolourized if these are illuminated for sufficiently long time in the presence of ZnO. For instance, more than 60% colour of 5.3 × 10^{-5} M PS in 80 mL suspension containing 0.35 g ZnO disappears within an hour of illumination (Figure 4). On the other hand, almost 80% colour of the CV solution disappears under the same conditions. At the initial stage, the rate of degradation is lower for CV, which then exceeds that of PS after 15 minutes. Since, the adsorption in CV is less prominent than PS, rate of degradation is also lower in CV. This result suggests that, initially only the adsorbed molecules undergo photodegradation. However, at the latter stage, bulk photodegradation caused by different radicals produced in the system causes higher rate of photodegradation for CV.

A plot of initial rate, R_i with a fixed initial concentration of dyes, ($[PS]_o = 5.0 \times 10^{-5}$ M, $[CV]_o = 2.0 \times 10^{-5}$ M) against the concentration of ZnO is shown in Figure 5. With the increase in the concentration of ZnO, the initial rate of degradation for both the dyes increases. This is because the increased amount of ZnO accommodates more dye molecules on its surface because of higher surface area. These adsorbed dye molecules predominantly undergo fragmentation in the presence of light. However, at a sufficiently high concentration of ZnO, the initial rate shows almost a limiting value. This should be related with the opacity of suspension which prevents light entering into the bulk of the system.

Plots of R_i for different initial concentrations, $[Dye]_o$, with a fixed quantity of ZnO (0.35 g/80 mL solution) against these concentrations are shown in Figure6. With an increase in the concentration of dyes the initial rate of photodegradation increases. In both the cases, the initial rate shows almost a limiting value at the latter stage. This behavior is apparent for a reaction following first-order kinetics.

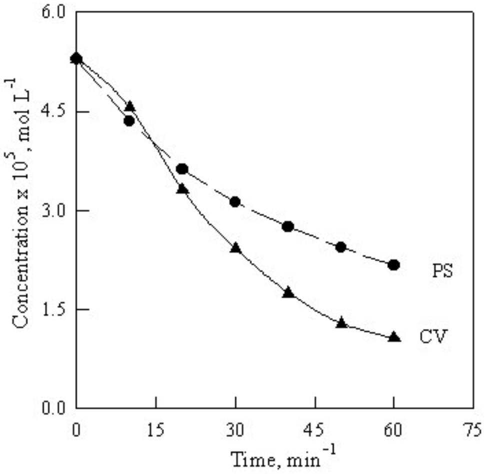

Figure 4: Decolourization of PS and CV in the presence of ZnO (0.35 g/ 80 mL).

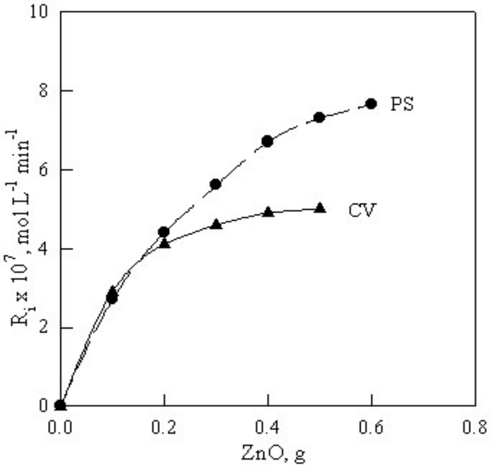

Figure 5: Variation of initial rate (Ri) with ZnO $[PS]_o$= 5.0 × 10^{-5} M; $[CV]_o$= 2.0 × 10^{-5} M

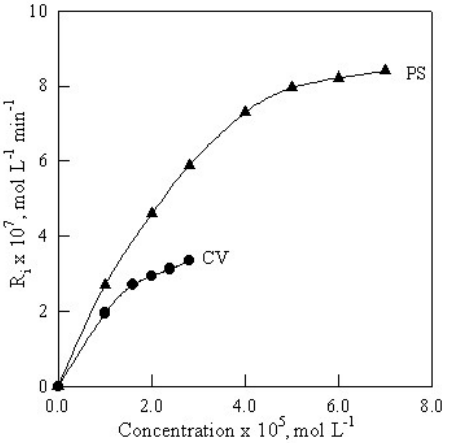

Figure 6: Variation of initial rate (Ri) with concentration of the dyes. ZnO = 0.35 g/80mL

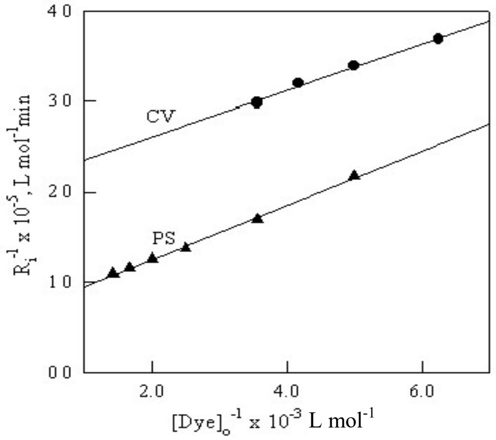

Figure 7: Langmuir-Hinshelwood plot for both the dyes

The Langmuir-Hinshelwood kinetic model (Mills 1997; Wu 1998; Liu 2000)is widely used to describe the kinetics of the heterogeneous photocatalytic reaction of dyes. This model can be best presented by the following equation:

$$1/R_i = 1/k_{LH} + 1/(k_{LH}K_{LH}[Dye]_o) \qquad (3)$$

Where R_i is the initial rate of color disappearance of the dye, $[Dye]_o$ is the initial concentration of the dye, K_{LH} is the Langmuir adsorption coefficient of each dye on the ZnO surface and k_{LH} is the proportionality constant and a measure of the intrinsic reactivity of the surface with photo activated dye molecule.

Figure 7 shows that the plots of $1/R_i$ against $1/[Dye]_o$ give straight line with positive slopes. The values of correlation coefficients are 0.998 and 0.999 for CV and PS respectively. Thus, the results of photodegradation of both the dyes on ZnO clearly fit the above model (Eq. 3) within the experimental error. This means that the degradation reaction proceeds on the surface of the ZnO particle. The values of K_{LH} at 35.0 °C are 5.3×10^2 $Lmol^{-1}$and 1.2×10^2 $Lmol^{-1}$ for PS and CV respectively. The higher value of K_{LH} compared to K_L of Langmuir isotherm indicates that light causes degradation of the dye molecules leaving some more active sites on ZnO to favour higher adsorption of PS on its surface. However $K_L$of Langmuir isotherm for CV was not determined because of less prominent adsorption of CV on ZnO.

3.3 Mechanism of Degradation

ZnO has a band gap energy of 3.2 eV corresponding to λ=385 nm (Mills and Hunte, 1997). This oxide cannot be excited by visible light, but can absorb the dye molecules. As a result the dye molecule, $\mathrm{Dye_{ads}}$ which is already adsorbed on ZnO surface becomes excited ($\mathrm{{}^*Dye_{ads}}$). $\mathrm{{}^*Dye_{ads}}$ can subsequently inject an electron to the conduction band of ZnO. Originally this idea and the different steps involved during photodegradation were put forwarded to TiO_2 (Mills and Hunte, 1997; Wu *et al.,* 1998; Liu *et al.,* 2000) photocatalyst with absorption threshold λ=385 nm. Since, ZnO is a semiconductor similar (by band gap energy and by nature) to TiO_2, we can borrow the idea and propose the following steps that are likely to be involved.

(i) $\mathrm{Dye_{ads}} + h\nu \rightarrow \mathrm{{}^*Dye_{ads}}$
(ii) $\mathrm{{}^*Dye_{ads}} + \mathrm{ZnO} \rightarrow \mathrm{ZnO(e^-)} + \mathrm{Dye_{ads}^+}$
(iii) $\mathrm{ZnO(e^-)} + \mathrm{O_2} \rightarrow \mathrm{ZnO} + \mathrm{O_2^-}$
(iv) $\mathrm{O_2^-} + \mathrm{H^+} \rightarrow \mathrm{HO_2^{\cdot}}$
(v) $\mathrm{HO_2^{\cdot}} + \mathrm{H^+} + \mathrm{ZnO(e^-)} \rightarrow \mathrm{H_2O_2}$
(vi) $\mathrm{H_2O_2} + \mathrm{ZnO(e^-)} \rightarrow \mathrm{OH^{\cdot}} + \mathrm{OH^-}$
(vii) $\mathrm{Dye_{ads}^+}$ + ($\mathrm{OH^{\cdot}}$, $\mathrm{O_2^-}$ and/or $\mathrm{O_2}$) $\rightarrow$ degraded products.

$\mathrm{Dye_{ads}}$ is the dye adsorbed on the surface of ZnO. $\mathrm{ZnO(e^-)}$ indicates an electron trapped at the ZnO matrix. The photolysis has been carried out in an open reactor. Consequently, there was generous involvement of aerial oxygen. The step-(vii) is the significant step that degrades the dye adsorbed on the surface of the mediator. However, there could be reactions in the bulk producing $\mathrm{Dye^+}$, which undergoes reactions with radicals, oxygen, etc. like that given by step-(vii). The latter reaction is expected to be more prominent in CV than PS.

4. CONCLUSION

Both ponceau S (PS) and crystal violet (CV) dyes can be degradated completely by visible light in the presence of aqueous suspension of ZnO after sufficient time of photolysis. The anionic dye, PS undergoes adsorption which has an effect on the initial rate of photodegradation. However, the overall photodegradation of CV becomes prominent at the latter stage when the bulk reactions by active species become important. The initial rate of degradation increases for both the dyes with increasing catalyst dosage and dye concentration. The degradation kinetics follows Langmuir-Hinshelwood equation.

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