



PHOTOCATALYTIC DEGRADATION OF ANILINE YELLOW IN AQUEOUS SOLUTION BY ZnO USING VISIBLE RADIATIONS

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ABSTRACT

The textile industry consumes considerable amount of water during dyeing and finishing operations. Hence, wastewater discharged in rivers or public sewage treatment plants are highly contaminated. Their treatment had been necessary for human welfare and sustainable environment. Present study deals with the detailed investigation of photocatalytic degradation of aniline yellow carried out in the presence of an aqueous suspension of ZnO irradiated with visible light in a batch reactor. It was observed that photocatalytic degradation of aniline yellow obey pseudo-first order kinetics according to Langmuir-Hinshelwood model. The influences of various factors viz irradiation time, initial dye concentration, Na₂CO₃, NaCl and K₂S₂O₈ on degradation efficiency were systematically studied. The decolorization and extent of degradation of dye was determined by UV-Vis spectrophotometer and COD reflux method, respectively.

Key words: Aniline yellow, Photocatalytic degradation, ZnO.

INTRODUCTION

In recent years arising ecological problems connected with the presence of potentially carcinogenic compound have been widely observed. In addition, these dangerous compounds are often non-biodegradable or toxic to microorganism and have very long degradation time in the environment.

Environment pollution by organic dyes also sets several ecological problems, which are increased by the fact that most of them are difficult to degrade using standard biological methods. For the removal of such recalcitrant pollutants, some traditional or physical techniques such as adsorption on activated charcoal, ultra-filtration, reverse osmosis, coagulation etc. are used efficiently. Nevertheless they are non-destructive.

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Recently there has been considerable interest on the utilization of advanced oxidation processes (AOPs) for the destruction of organic compounds contaminated water. The key advantage of this degradation method is that it can be carried out under ambient condition and lead to complete degradation of organic compounds. Among the advanced oxidation processes, heterogeneous photocatalysis appears as an emerging technology leading to the total mineralization of most of the organic pollutants.

If a fine suspension of a suitable semiconductor is irradiated with visible or UV light; electron excitation from valence band to conduction band results and a vacancy or hole is left in the valence band; such holes have the effect of a positive charge. Thus, in turn it generates the formation of “holes” on the surface of the semiconductor, which can react with oxygen, water and hydroxide ion to form hydroxyl radicals.

Further more, super oxide radicals are formed from the reaction of excited electrons with oxygen molecules. The highly reactive oxygen species so formed react with the organic pollutants resulting in their oxidation.

The kinetics of photocatalytic degradation of many organic compounds in ZnO suspensions under visible irradiation has often been matched to the simple Langmuir-Hinshelwood equation.

$$r = -dc/dt = K_r K_c / (1 + K_c) \quad \dots(1)$$

Where r is the rate of disappearance of the dyes and c is the initial concentration of the dye. K represents the equilibrium constant for absorption of the dye on ZnO particle and K_r represents the limiting rate of the reaction at maximum coverage under the experimental condition. The integrated form

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

Where t is the time in minutes required for the initial concentration of dye C_0 to become C . At low concentration of the dye, the second term in equation (2) is negligible compared to the first term. On neglecting the second term, the final form of the equation is -

$$\ln (C_0/C) = K_r K_c t = k' t \quad \dots(3)$$

Where k' is the apparent rate constant of photocatalytic degradation. The plot of (C_0/C) vs time yield a straight line and its slope is K_r

$$t_{1/2} = 0.693/k' \quad \dots(4)$$

ZnO as photocatalyst

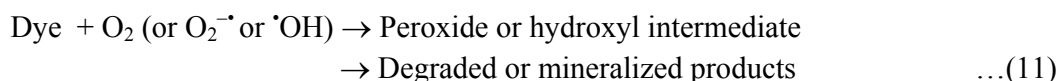
ZnO is a semiconductor, which is used as photocatalyst in various photocatalytic reactions. Generally, semiconductors having large band gaps (1.5 – 3.0 eV) are good photocatalysts. ZnO and TiO₂ with band gaps larger than 3 eV show strong activity. The conduction and valence band potentials of both ZnO and TiO₂ are larger than the corresponding redox potentials of H⁺/H₂ and H₂O/O₂ and the photogenerated electron and hole can be separated efficiently.

Photocatalyst	Band gap (eV)
ZnO	3.2
TiO ₂	3.1
CdS	2.3
α-Fe ₂ O ₃	2.3

Chemistry of photocatalytic reaction

Photocatalytic reaction involves electron-transfer process from semiconductor to substrate or vice versa. The visible light mechanism can be depicted as follows:

The dye molecule has the ability to absorb visible light and electron transfer from dye to photocatalyst has been found to be very effective. The degradation mechanism in the presence of visible light can be shown as



The equation (5) depicts the absorption of light by the dye molecule to give excited state of the dye (D^{*}). This excited dye (D^{*}) injects an electron to the conduction band of

ZnO, where it is scavenged by O₂ to form active oxygen anion radical as shown in equation (7) and (8). Further active oxygen anion radical formed in equation (8) subsequently reacts with H₂O to generate •OH radicals. These active radicals drive the photodegradation of the dye molecule.

EXPERIMENTAL

All chemicals used were of AR grade. Aniline yellow dye was used as a system with the photocatalyst ZnO.

Experimental procedure

The photo catalytic reaction was carried out in a batch reactor with dimension of 7.5 x 6 cm (height x diameter) provide with a water circulation arrangement in order to maintain the temperature in the range of 25-30°C. The irradiation was carried out using 500 W halogen lamp. In all cases during the photolysis experiments, the slurry composed of dye solution and the catalyst was placed in the reactor and stirred magnetically with simultaneous exposure to visible light. Sample was withdrawn at periodic intervals from the reactor to assess the extent of decolorization. The intensity of light was measured by Lux meter (Lutron LX-101). The pH was constantly monitored using pH meter. A systronic UV-Vis spectrophotometer (Systronic 106) was used for measuring absorbance at different time intervals at 465 nm.

RESULTS AND DISCUSSION

Effect of irradiation time

Fig. 1 depicts photocatalytic degradation of 3.0×10^{-5} M dye solution containing 200 mg ZnO. The change in concentration of the dye in the solution was plotted as function of irradiation time. It is seen that 9.5% of the initials concentration of the dye was removed after 1.00 hr irradiation and complete decolorization was observed with 1.15 hr. irradiation time.

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured at $\lambda_{\text{max}} = 465$ nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of aniline yellow decreases with increasing time of exposure. Plots of $1 + \log A$ (absorbance) versus time was linear and follows pseudo-first order kinetics. The rate constant was measured using following expression:

$$k = 2.303 \times \text{slope} \quad \dots(12)$$

The results of typical run for photocatalytic degradation of aniline yellow are shown in the Table 1 and graphically represented in Fig. 1.

Table 1: Typical run

Amount of ZnO = 200 mg		pH = 8.00
Light intensity = 17500 Lux		$\lambda_{\max} = 465 \text{ nm}$
[Aniline yellow] = $3.0 \times 10^{-5} \text{ M}$		
Time (min.)	Abs.	1 + log Abs.
0	0.382	0.5821
10	0.361	0.5575
20	0.320	0.5051
30	0.287	0.4579
40	0.240	0.3802
50	0.212	0.3263
60	0.208	0.3181
70	0.198	0.2967
80	0.182	0.2601
90	0.152	0.1818
$k = 2.22 \times 10^{-4} \text{ (min.}^{-1}\text{)}$		

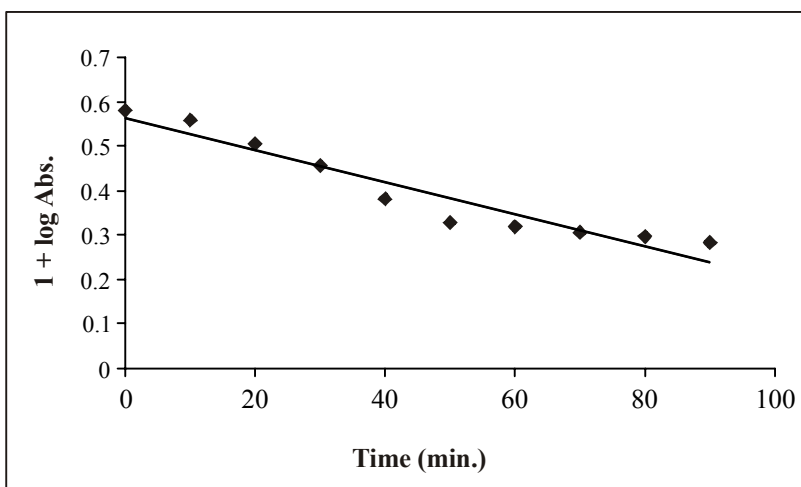


Fig 1: A typical run

Effect of aniline yellow concentration

The effect of concentration of aniline yellow on the rate of photocatalytic degradation was observed by taking different concentrations of aniline yellow. The results are reported in the Table 2. It is obvious to expect a decrease in reaction rate on increasing the concentrations. It is evident that as the concentration of aniline yellow was increased, the rate of photocatalytic degradation of aniline yellow was increased but after reaching a certain concentration (4.0×10^{-5} M) the rate of the reaction was decreased.

Table 2: Effect of aniline yellow concentration

Amount of ZnO = 200 mg	pH = 8.00
Light intensity = 17500 Lux	$\lambda_{\max} = 465$ nm
[Aniline yellow] x 10^5 M	k x 10^4 (min^{-1})
1.0	1.29
2.0	1.32
3.0	2.22
4.0	2.26
5.0	1.72
6.0	1.33

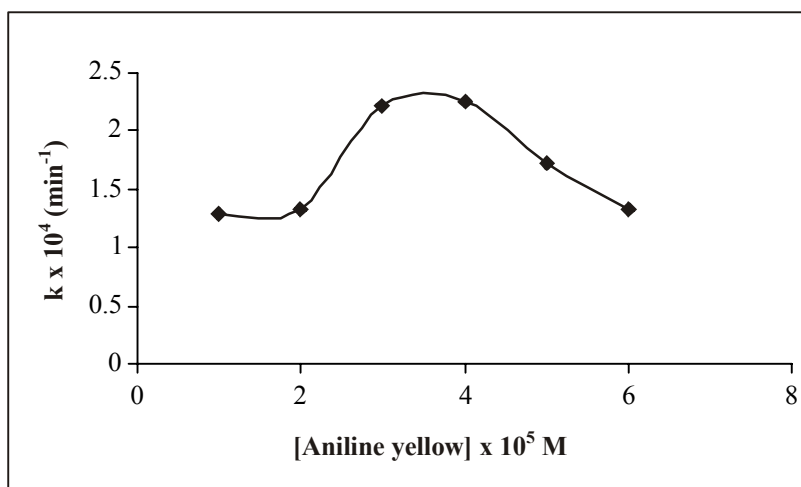


Fig 2: Effect of aniline yellow concentration

From the experimental result, we have observed that the decrease of k value with increase in initial concentration of the dye can be ascribed to the decrease in the path length of photons entering the solution due to impermeability of the dye solution. At low concentration, the reverse effect was observed; hereby increasing the number of photon absorption by the catalyst. This decreasing phenomenon can further be explained in terms of the increase in requirement of catalyst. Surface for the increased concentration of the dye. But here the irradiation time and amount of catalyst had been kept constant. Hence, the relative number of O_2^- and $\cdot OH$ radicals formed on the surface of ZnO are also constant. As a result the relative number of O_2^- and $OH\cdot$ attacking the dye molecule decreases with increasing initial concentration of the dye. The plot of C_0 vs k should yield a straight line.

The k_r and k values were calculated from slope of the straight line and intercept respectively.

Effect of amount of photocatalyst

The effect of change in the amount of photocatalyst was performed in the range of 50-400 mg in 50 mL of dye solution, for the dye concentration of 3.0×10^{-5} M. The change in the ZnO amount from 50-200 mg has increased the rate. Experimental studies have revealed that the catalyst loading of 200 mg/50 mL as the optimal dose for the complete mineralization of 3.0×10^{-5} M in 1 hr irradiation. Further increase in the amount of ZnO to 400 mg has decreased the k value. These observations can be rationalized in terms of availability of active sites of ZnO surface and the penetration of photoactivating light into the suspension. Owing to an increase in the number of ZnO particles, as the concentration of catalyst increased the availability of active sites increases but the light penetration and hence, the photoactivated volume of the suspension shrinks. At low solute concentration, when there are excess active sites, the balance between the opposing effects is evenly posed and change in the amount of ZnO makes little differences to the reaction rate. At high solute concentration, availability of excess active sites out weights the diminishing photoactivated volume and substantially high k values are obtained at increase in ZnO concentration. The increased amount of ZnO increases the quantity of photons absorbed as well further increases in catalyst concentration beyond 400 mg might result into deactivation of activating molecule due to collision with ground state molecule as described below.

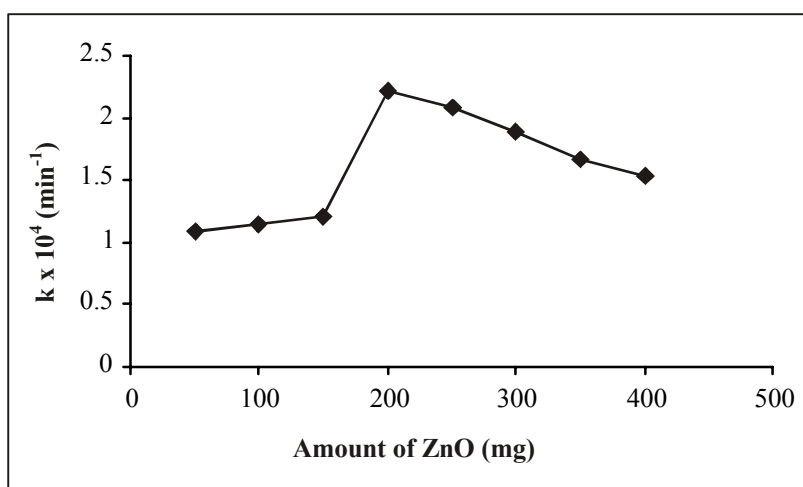


ZnO^* = ZnO with active species adsorbed on its surface.

$ZnO^\#$ = Deactivated form of ZnO^* , shielding by ZnO may also take place.

Table 3: Effect of amount of photocatalyst

Amount of photocatalyst (mg)	$k \times 10^4 (\text{min}^{-1})$
50	1.08
100	1.15
150	1.21
200	2.22
250	2.09
300	1.89
350	1.66
400	1.54

**Fig 3: Effect of amount of photocatalyst****Effect of pH**

The effect of pH on the rate of photocatalytic degradation of aniline yellow was investigated in pH range of 5.00 to 10.0. The results are tabulated in Table 4. The semiconductor dissolves in highly acidic medium and therefore, photocatalytic degradation could not be investigated in lower pH range. It has observed that when pH was increased, the rate of photocatalytic degradation of aniline yellow also increased. It may be attributed to

the greater probability of generation of radicals like $\cdot\text{OH}$, O_2^- etc. as pH was increased, but after a certain value of pH (pH=8), the value of k decreases on increasing pH further.

Table 4: Effect of pH

Amount of ZnO = 200 mg	pH = 8.00
Light intensity = 17500 Lux	$\lambda_{\text{max}} = 465 \text{ nm}$
[Aniline yellow] = $3.0 \times 10^{-5} \text{ M}$	
pH	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
5.0	1.77
6.0	1.82
7.0	1.89
8.0	2.36
9.0	2.16
10.0	1.28

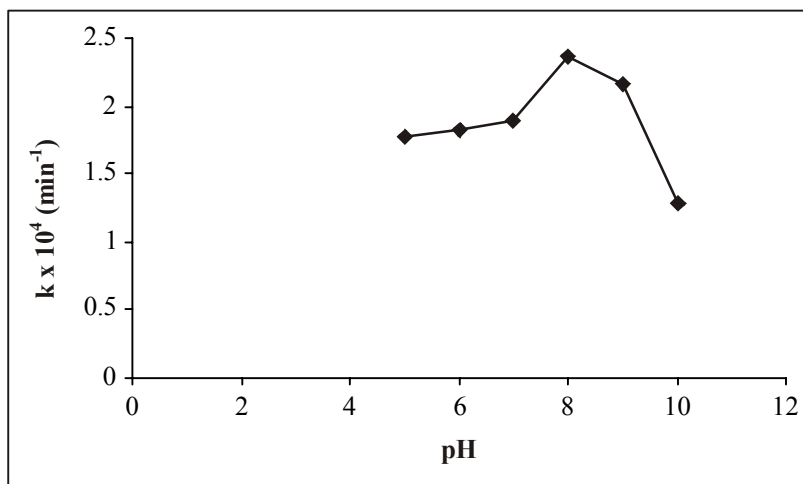


Fig 4: Effect of pH

Effect of other photocatalysts

Experiments were performed with other photocatalysts as well (Table 5). Generally, semiconductors having large band gaps (1.5 – 3.0 eV) are good photocatalysts. It has already been reported that semiconductors such as ZnO and TiO_2 having band gaps larger than 3 eV

show strong photocatalytic activity. The conduction and valence band potentials of both ZnO and TiO₂ are larger than the corresponding redox potentials of H⁺/H₂ and H₂O/O₂ and the photo-generated electron and hole can be separated efficiently. CdS with smaller band gaps show less activity since its conduction band is much lower than that of ZnO and TiO₂. Electron (CB) in these semiconductors rapidly falls into the hole; thus, showing reduced activity.

Table 5: Effect of other photocatalysts

Photocatalyst	$k \times 10^4$ (min ⁻¹)	Band gap (eV)
ZnO	0.042	3.2
TiO ₂	0.0210	3.1
CdS	0.0188	2.3

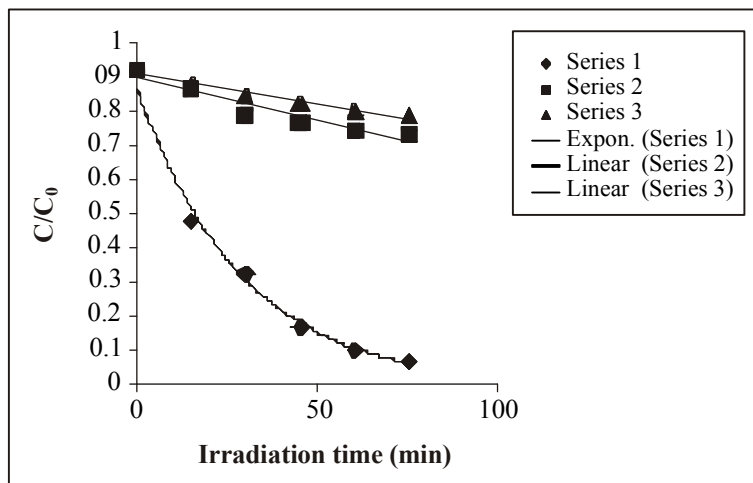


Fig 5: Effect of irradiation time in absence of ZnO (Δ), in absence of light (\blacksquare) and in presence of light and ZnO (\blacklozenge)

CONCLUSION

The present study describes pseudo-first order kinetics of heterogeneous catalytic reaction applied to wastewater treatment. It's a novel technique for the determination of the kinetics of photocatalytic degradation of pollutants in aqueous solution. It further substantiates the importance of AOPs in clean technologies. This technology is safe and simple.

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