Original Research Article

Photocatalytic Degradation and Kinetics of Dyes in Textile Effluent Using UV – ZnO-Al System

ABSTRACT

This study investigates the photodegradation of a mixture of 4 azo dyes (direct orange 39, chlorantine fast red 5B, viscose black B and direct sky blue K) present in textile effluents and the influence of catalyst dose, irradiation time, UV power intensity on the overall photodegradation process. The photocatalytic experiments were conducted in a batch stirred photoreactor equipped with a 30W UV lamp, magnetic stirrer and thermometer. The photocatalysts used was zinc oxide nanoparticle doped with aluminium (AZO, 15nm, 99.99 to %). The results obtained showed that variation in the physical parameters influenced the efficiency of photodegradation. Kinetic study obtained indicated that the colourant photodegradation followed the Langmuir-Hinshelwood model modified to accommodate reactions occurring at a solid-liquid interphase. At the catalyst dose of 0.5g/l, the apparent first order rate constant K^1, was 0.00615 min^{-1} but at 2.5g/l it reduced to 0.00567 min^{-1}. The best degradation was at the catalyst dose of 2.0g/L with the rate constant of 0.0134 min^{-1}.

Keywords: Photodegradation, synthetic dye, kinetics, Zinc Oxide- Aluminium Catalyst, Dyes.

1.0 INTRODUCTION

Dyes and pigments are the chemicals used to add colour or to change the colour of materials. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries (Sharmar and Kaur, 2018). The textile industries account for about fifty percent of the world's dye consumption. The textile industry uses about ten thousand different dyes and the worldwide annual production of dyes and pigments is over 7 x 10^5 tonnes (Guivarch, et al, 2003). Among the several classes of textile dyes, it is the reactive dyes that contribute about fifty percent of the total market share while the most common chromophore groups used as chromophore are the azo and anthraquinone groups (Sleiman et al, 2007; Lee and Pavlosta, 2004).

It has been documented that dye loss in waste water could vary up to fifty percent during manufacturing or processing operations (Sleiman et al, 2007). And it is known that synthetic

dyes have adverse effects on life forms when discharged directly into the environment (Sharmar and Kaur, 2018). Kant, 2012, stated that the presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes, chromium compounds and heavy metals make the textile effluent highly toxic. The colloidal matter present along with colours and oily scum increase the turbidity, give the water a bad appearance and foul smell and prevent the penetration of sunlight necessary for the process of photosynthesis (Vijayaraghavan, 2008). This interferes with the oxygen transfer mechanism thus impeding marine life and the self-purification process of water. Thus, it is important to remove these dyes from the waste waters before their final disposal.

Consequently, technological systems for the removal of organic pollutants such as adsorption on activated carbon, reverse osmosis, ion exchange on synthetic resins, ozonation and biological methods have been developed to deal with this problem. However, most of these methods face the drawbacks of having high operational cost and lower efficiency in removing the dyes from effluents (Galindo et al, 2001).

To this end, advanced oxidation processes have been developed to circumvent these stated drawbacks and these processes are based on the generation of very reactive species that can oxidize these dyes in waste water effleunts. The generated reactive species can oxidize a broad range of organic pollutants quickly and non-selectively (Saien and Khezrainjoo, 2008). Heterogeneous photocatalysts appear as an emerging option for the generation of reactive chemical species needed in the oxidization of environmental pollutants. This process consists of the nonselective destruction of organic compounds in the presence of UV light and photocatalysts such as TiO_2, CdS, WO_3 and ZnO.

For years, TiO_2 has been the dominant semiconductor photocatalyst; the domination of this catalyst can be attributed to its superior photocatalytic oxidation ability and non-photo-corrosive and non-toxic characteristics (Saien and Khezrianjoo, 2008). However, the

widespread use of TiO_2 and platinum catalyst is uneconomical for large scale water treatment operations. ZnO appears to be a suitable alternative of TiO_2 since its photodegradation mechanism has been proven to be similar to that of TiO_2 (Dinder and Icli, 2001). Many researchers are of the opinion that the photocatalytic properties of ZnO can be improved considerably when doped with suitable element or compound.

Consequently, the objective of this work is to study or investigate the kinetics influence of various physical parameters (irradiation time, catalyst loading, light intensity) on the photocatalytic degradation of dyes in actual textile effluent, in the presence of ZnO doped with aluminium, irradiated by the UV light in a batch stirred reactor.

2.0 Experimental

2.1 Materials

The materials that were used for these experiments include Zinc Oxide doped with Aluminium (ZnO-Al) nanoparticles. The ZnO-Al nanoparticles was obtained from US Nano Incorporated, with the average size of 15 nm as well as 99.99 % purity. This ZnO-Al nanoparticles was used as the photocatalyst without further treatment. The textile effluent, consisting of dyes, was obtained from SAVCO Garments and Printers, Aba in Abia State, Nigeria, it was used directly without further treatment.

The Photocatalytic degradation of the effluent dyes was carried out in a rectangular batch stirred reactor with a capacity of 150 cm^3 fitted with thermometer, magnetic stirrer and UV lamps, placed 5cm from the sample. The Ultra-violet (UV) lamps used were 10 W, 30 W and 60 W power ranting. For the Ultra-violet Spectrophotometric analysis, the UV-Vis spectrophotometer, LABOMED 1286 series was used. High Performance Liquid Chromatography (HPLC) Enhanced Integrator was used to determine the components of the dye effluent and their concentrations.

2.2 Method

2.2.1 Evaluation of the Chemical Composition of the textile effluent

We used the High-Performance Liquid Chromatographic technique to evaluate the chemical constituents of the textile effluents that was obtained from SAVCO Garments and Printers.

2.2.2 Photodegradation Test

50 ml of the textile effluent was introduced into a photocatalytic reactor and was stirred continuously with a magnetic stirrer for various durations of 30, 60, 90, 120 and 180 minutes respectively under UV light irradiation. After these specified time frames of exposure of the textile effluent to UV-irradiation, some of the effluent sample was characterized via the UV spectrophotometric analysis of the dyes was carried out periodically for evidence of reduction in dye concentration.

2.2.3 Procedure for dark reaction in presence of the photocatalyst

50 ml of the effluent was mixed with 0.1 g of ZnO-Al nanoparticles in the photocatalytic reactor and the suspension was further mixed in dark using a magnetic stirrer for 30, 60, 90,120 and 180 minutes respectively. The resultant suspension was filtered and filtrate was analyzed using the UV spectrophotometric technique.

2.2.4 Procedure for photocatalytic degradation of the textile effluent

50ml each of the effluent was mixed with 0.1g of ZnO-Al in the photocatalytic reactor, as done previously in 2.2.3. The suspension was continuously stirred with a magnetic stirrer while being irradiated into ultra-violet light from ultra-violet lamps rated at 10 W, 30 W and 60 W respectively. This irradiation was done at room temperature. Aliquots of the mixture (5ml) were centrifuged and analyzed periodically at 0, 30, 60, 90, 120, 150, and 180 minutes respectively. The degradation process for each of the effluent via the UV spectrophotometric technique, at maximum absorbance wavelength of 510 nm. The percentage degradation of the dyes present in the effluent with respect to its initial concentration at any time can be obtained by

$$X = \frac{C_o - C}{C_o}$$

where C_o and C are the initial and final concentrations at a given time.

The resultant suspension was filtered and the filtrate was analyzed for any change in concentration. The difference in concentration (before and after adsorption test) was attributed to the photodegradation of the dyes by the photocatalyst.

3.0 Results and Discussion

The results obtained from the experimental processes stated under experimental stated and discussed as follows

3.1 Chemical composition of textile effluent

The results of the HPLC performed on the textile effluent are stated in Table 1

Table 1: Table showing the chemical composition of textile effluent from SAVCO Garment and Printers, Nigeria The result show that the dominant dye in the textile effluent is Chlorantine Fast Red 5B. It is because of the dominance of this particular dye that gave the effluent its reddish colour.

Chemical Composition	Amount (mg/l)
Direct orange 39	3.21
Chlorantine fast red 5B	6.06
Viscose black G	0.31
Direct sky blue K	1.64
Total	11.21

The total concentration of the dyes found in the textile effluent is 11.21 mg/l. This is a little lower than the standard textile effluent concentration (30-50 mg/l). It may be due to the particular fabric that was involved when the effluent was generated.

3.2 Working curve

In order to determine the changes in the concentration of the dyes in the effluent, a working curve was generated using known concentrations of the effluent.

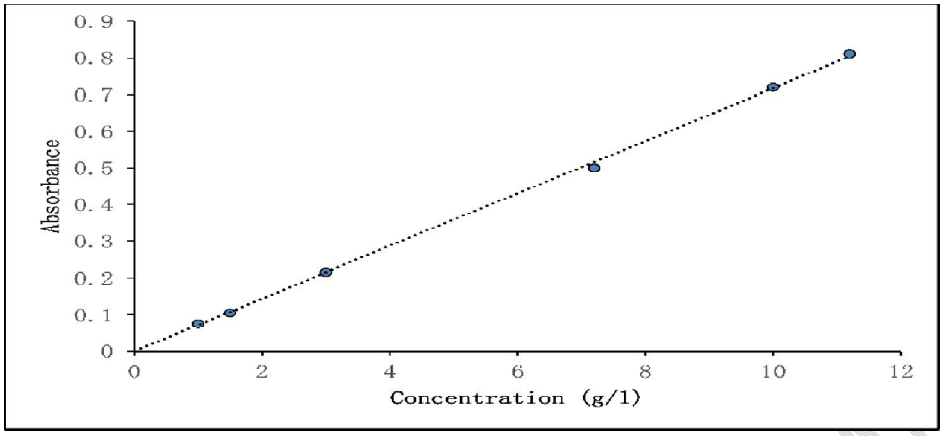

Fig 1: Calibration curve of the dyes Concentration (mg/l) (Wavelength of absorbance at 510nm)

3.3 Behaviour of textile effluent in the presence of UV irradiation only

There results for the change in the concentration of the dye constituents of the textile effluents are as presented in the Table 2 below. The results showed that in the absence of the photocatalyst there was just a marginal decrease in the concentration. In this case, the concentration of the dyes in the textile effluent decreased from an initial concentration of 11.21 mg/l to a final concentration value of 11.0 mg/l indicating a mere 1.80 % removal of the dyes when the ZnO-Al nanoparticles acting as photocatalyst is absent

3.4 Effect of ZnO-Al photocatalyst on photodegradation of the dyes in the textile effluent in the absence of UV-light irradiation

With a photocatalyst dose of 2.0 g/l, there was still insignificant level of degradation in the absence of UV irradiation as can be seen in Table 2. From an initial concentration of 11.21 mg/l in the textile effluent, the photocatalyst only degraded the dyes to a total concentration value of 10.80 mg/l when the process was done in the dark, in the absence of UV irradiation. This implied that only 4% of the dyes were removed after 120 minutes of exposing the effluents to the ZnO-Al photocatalyst.

Table 2: Table showing the values of the concentration and % degradation efficiency for experiments done in without exposure to ZnO-Al photocatalyst and UV-irradiation source

Time (minutes)	Final Concentration (without ZnO-Al)	Final Concentration (without UV light)	% degradation (without ZnO-Al)	% degradation (without UV light)
0	11.20	11.20	0.00	0.00
30	11.10	11.10	0.90	0.90
60	11.10	11.10	0.90	0.90
90	11.00	10.90	1.8	2.70
120	11.00	10.80	1.8	3.60
180	11.00	10.80	1.8	3.60

Therefore, the processes presented in 3.3 and 3.4 played limited, inconsequential roles in the photodegradation of the dyes and their influence on the mineralization of the dyes insignificant.

3.5 Effect of Irradiation Time

Under the experimental conditions, 77 % degradation of the dye mineralized within 120 minutes of irradiation. The effect of the time of UV irradiation of the effluent is presented in Table 3 where the % degradation of the dye at different irradiation periods of 30, 60, 90, 120 and 180 minutes are expressed. These values were obtained for the optimum photocatalyst loading of 2.0 g/l. The photocatalytic degradation of the dye occurs on the surface of ZnO-Al photocatlyst where $^{\circ}OH$ and $^{\circ}O_2^-$ radicals are trapped in its holes (Shankar et al, 2001). The $^{\circ}OH$ radicals are strong enough to break the bonds of the dye molecules adsorbed on the surface of ZnO-Al photocatalyst (Shankar et al, 2001).

Table 3: Table showing the values of the dye concentration and % degradation for various UV irradiation times at catalyst concentration of 2.0g/l and 30 W UV light source

Irradiation Period (minutes)	**Concentration (mg/L)**	**% Degradation**
0	11.2	0
30	8.0	28.6
60	4.5	59.8
90	2.8	75.0
120	2.5	77.7
180	2.5	77.7

When the intensity of light and concentration of dye are constant, it is known that the number of $^{\circ}OH^{-}$ and $^{\circ}O_2^{-}$ radicals increase with increase irradiation period. As the irradiation time increases, several intermediate products are formed due to fragmentation of the dye molecules. These intermediates undergo degradation on further irradiation (Lee and Pavlostathia, 2003).

As seen in Figure 2, further increase in time from 120min to 180min did not cause any further degradation of the dyes in the textile effluent.

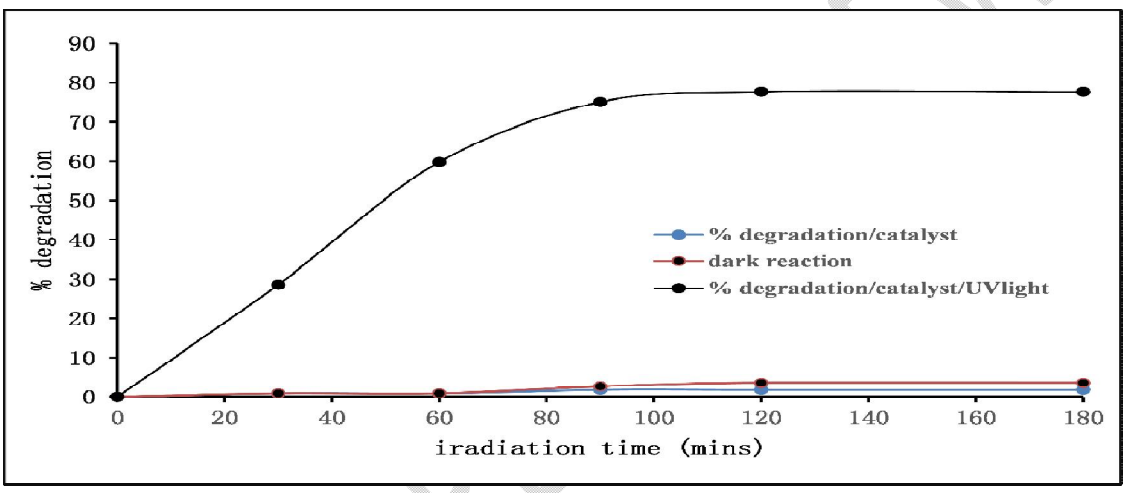

Fig. 2: Effect of irradiation time on degradation of the dyes. UV=30W, Catalyst concentration = 2.0mg/L, pH = 10.7, Initial dye concentration = 11.2 mg/L.

This may be due to opacity problem caused by too many fragmented molecules, preventing further penetration of UV light into the suspension (Ekwere et al, 2018).

3.6 Effect of ZnO-Al photocatalyst concentration

The variation of the concentration and the % degradation of the dyes in the textile effluent with the amount of ZnO-Al photocatalyst showed that as the amount of the ZnO-Al increased the concentration of the dyes in the effluent reduced, with attendant increase in the % degradation efficiency. Using 0.5, 1.0, 1.5, 2.0 and 2.5 g/l as the concentration of the photocatalyst, concentration of the dyes in the effluent varied from its initial concentration of 11.2 mg/l to 5.2, 4.6, 3.6, 2.5 and 5.6 mg/l respectively. This corresponded to the %

degradation efficiency of 53.6 %, 58.9 %, 67.8 %, 75.6 % and 50.8 %. The variation of the % degradation with the concentration of the ZnO-Al photocatalyst is depicted in Figure 3.

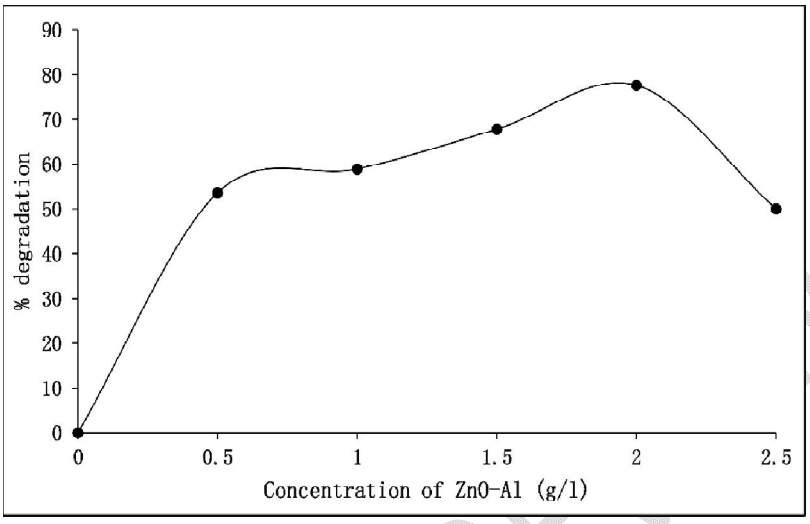

Fig. 3: Effect of the amount of ZnO-Al on the degradation of dyes in textile effluent at irradiation time of 180 minute, dyes concentration in effluent = 11.21 mg/l, UV = 30 W

The percent photodegradation efficiency increased with the increase in the amount of photocatalyst until 2.0g/l and then decreases sharply. As stated earlier, this increase is due to the availability of more active sites for photocatalysis due to the higher concentration of ZnO-Al nanoparticles. This causes enhancement in the hydroxyl and oxygen radical generation and which also lead to the increase in the degradation power because the greater number of the dye molecules could be absorbed on catalyst surface. Equally, photocatalyst concentration above 2.0g/l results in enhancement of opacity which causes a reduction in the light penetration throughout the solution and a drop in the percent degradation efficiency (Saien and Khezrainjoo, 2008).

3.7 Effect of UV power intensity

Because the dye decomposition is a heterogeneous reaction occurring on the ZnO-Al particle surface with the active site concentration increasing with the UV energy received, a higher UV power intensity is expected to give a higher decomposition rate (Ekwere et al, 2018). A

series of experiments were conducted under the same operating conditions but varying UV power intensities and the results are shown in Table 4.

Table 4: Table showing the concentration of the dyes in the textile effluent of different times of irradiation under 10 W, 30 W and 60 W UV light source

Time (m)	10 W UV source	30 W UV source	60 W UV source
	Concentration (mg/L)	Concentration (mg/l)	Concentration (mg/L)
0	11.2	11.2	11.2
30	10.4	8.0	7.3
60	8.6	4.5	3.4
90	7.1	2.8	2.1
120	6.0	2.5	1.7
180	6.0	2.5	1.8

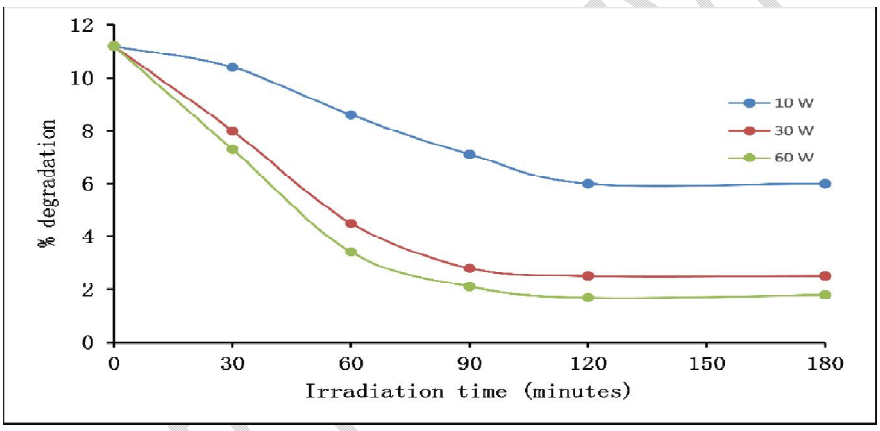

Fig. 4: Effect of UV irradiation of different intensities on the degradation of the dyes in the textile effluent. Initial dye concentration in textile effluent = 11.21 mg/l, optimum ZnO-Al concentration = 2.0 g/l.

As shown clearly in Figure 4, the dyes cannot be decomposed without UV irradiation. As expected, the initial dye decomposition rate increases with the UV power intensity.

3.8 Kinetics of degradation of dyes in textile effluent

The kinetics of the photocatalytic degradation of many organic compounds in suspensions of photocatalysts under illumination has been modeled using the equation of Langmuir-Hinshelwood (Valente et al, 2006). This model considers that the reaction rate is proportioned to the photocatalyst surface fraction covered by the substrate (θ) as shown in (i).

$$r = \frac{-dc}{dt} = k\theta \qquad (i)$$

with

$$\theta = \frac{K_1 C}{1 + K_1 C} \qquad (ii)$$

where k is the kinetic constant and K_1 is the constant of the reactant adsorption on the surface of the photocatalyst. C is the concentration of the dye solution in mol/litre.

Substituting Eq. (i) in Eq. (ii) yields:

$$r = \frac{-dc}{dt} = \frac{kk_1 c}{1 + K_1 C} \qquad (iii)$$

Integrating (iii):

$$In\left(\frac{C_0}{C}\right) + K_1 (C_0 - C) = kk_1 t \qquad (iv)$$

where t is the irradiation time and C_o is the initial concentration.

Equation (iii) is zero order when the concentration C (mol/L) is high ($C > 5 \times 10^{-3}$). When the solution is diluted ($C < 10^{-3}$) the reaction is an apparent first-order reaction as $k_1 C << 1$. (ref)

$$r = \frac{-dc}{dt} = kk_1 c \qquad (v)$$

where k_{ap} is the apparent kinetic constant of a pseudo first order reaction.

Integrating (v), we have:

$$-\int_{C_o}^{c} \frac{dc}{c} = \int_{o}^{+} k_{ap} dt \qquad (vi)$$

$$In\left(\frac{C_0}{C}\right) = k_{ap} t \qquad (vii)$$

Plotting $In(C_0/c)$ versus t, it is possible to determine the apparent kinetic constant (k_{ap}). A plot of $In\left(\frac{C_0}{C}\right)$ vs time gives a straight line, and its slope from linear regression represents the value of k_{ap}. This approach is considered the main path for evaluating dye degradation

kinetics, followed by many researchers (Konstantinou and Albanis, 2003). In this path, k and k_1 are lumped together as one parameter.

The plot of natural logarithm of the normalized concentration of the dye effluent versus the irradiation time, shown in Figure 5, give a good approximation over the range of 0.5g/L to 2.5g/L catalyst concentration within the period of 120min.

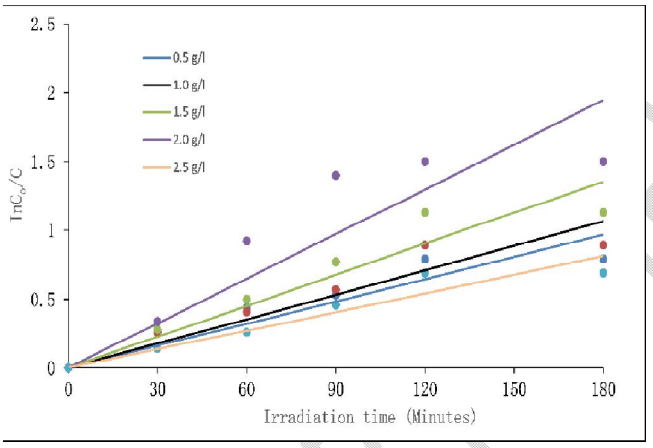

Fig. 5: Plot In[C_o/C] versus irradiation time for various ZnO-Al concentration at constant effluent concentration in 11.2 mg/l, UV = 30 W

Considering that our kinetic model represents a pseudo first-order reaction. We can evaluate the half-life $t_{1/2}$ for the relationship given in (viii)

$$t_1/_2 = \frac{0.693}{K'} \qquad viii$$

Table 5: Table showing the calculated values of K_{ap}, half-life ($t_{1/2}$), regression coefficient (R^2), and the rate of degradation (mg/min)

Concentration of ZnO-Al (g/L)	K′ (min^{-1})	$t_1/_2$ (min)	R^2	r_o (mg/min)
5	0.00615	112.7	0.968	0.0688
10	0.00698	99.3	0.988	0.0781
15	0.01071	64.7	0.992	0.1199
20	0.01340	51.7	0.948	0.1500
25	0.00567	122.2	0.982	0.06350

The increase in the ZnO-Al loading from 0.5 g/L to 2.0 g/L has increased the apparent rate constant from 0.00615 to 0.0134. Beyond the optimal dose, K_{ap} value decreases and $t_{\frac{1}{2}}$ value increases. This can be rationalized in terms of availability of active sites on the ZnO-A1 surface and the penetration of photoactivating light into the suspension. The availability of active sites increases with catalyst loading, but the light penetration and hence the photoactivated volume of the suspension shrinks (Vijayaraghavan et l, 2007). The trade-off between these two effects is that at low solution concentration, when there are excess active sites, the balance between the opposing effect is evenly poised and change in photocatalyst loading makes little difference on the rate of degradation. At high catalyst concentration, availability of excess active sites outweighs the diminishing photoactivated volume and significantly greater rate of degradation is achieved at increased ZnO-Al loading (Matthew, 1990). The decreased K' value at higher catalyst loading may be due to the deactivation of activated molecules by collision with ground state molecules (Chen and Chou, 1993).

CONCLUSION

In conclusion, the degradation efficiency of the ZnO-Al photocatalyst with respect to the textile effluent was 77% under optimum experimental conditions. It was found that the catalyst loading, irradiation time and UV power intensity influenced the photodegradation process. Generally, it was observed that the mineralization process of the effluent followed the Pseudo-first-order-kinetics as confirmed by their high correlation, R^2 values. The apparent first order rate constant, K' increases as the catalyst loading increases. Catalyst loading beyond 2.0g/L witnessed a reduction in the K' value.

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