

Effect of ZnO Nanoparticles on the Kinetics and Photo-degradation of Certain Textile Effluent Dyes

ABSTRACT

Untreated effluents especially in discharges from textiles and fabric industries, usually contain dyes. Synthetic dyes have adverse effects on all forms of life when discharged directly into the environment. This paper investigates the photo-degradation of a mixture of direct orange 39, chlorantine fast red 5B, Viscose Black B and direct sky blue K, all present in a real textile effluent based on the influence of ZnO photocatalyst dose and irradiation time at a specific UV power source. The photo-degradation experiments were conducted in a batch stirred photoreactor equipped with UV lamp of rated at 30 W, a magnetic stirring system and a thermometer. The photocatalyst used was zinc oxide nanopowder (ZnO). The results showed that changes in these parameters influenced the efficiency of the photo-degradation. The kinetic studies showed that the dyes degradation followed the Langmuir-Hinshelwood model that has been modified to accommodate reactions occurring at the solid-liquid interphase. At the catalyst dose of 0.5 g/l, the apparent first order rate constant, K' was 0.00411 min^{-1} ; but at 2.5 g/l, this reduced to 0.00384 min^{-1} . The best degradation was at the catalyst dose of 2.0 g/l with rate constant of 0.00811 min^{-1} .

Keywords: Photo-degradation, Dye effluent, ZnO nanoparticles, Kinetics

1. INTRODUCTION

Dyes are the important additives that are used in the textile industry. They are also used in the pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries, to mention but a few [1]. However, it is the textile industry that accounts for more than a half of the world's dye consumption. Among the various processes in this industry, dyeing is very prominent. It is known that the textile industry uses about 10 000 different dyes, with a worldwide annual production of over 7×10^5 tonnes [2]. Among several classes of textile dyes, the reactive dyes contribute about 50 % [3] of the total market share and the most common group used as chromophore is the azo (approximately 70 %), followed by anthraquinone [4].

It has been documented that the loss of dye pigment as textile effluents could vary up to 50 % during manufacturing or processing operations in the textile plants [5]. This leads to serious environmental impact that needs to be managed adequately. The chemical composition of these dyes that are deleterious in nature include heavy metals such as cadmium, nickel, cobalt and even lead [6]. Equally the presence of such anions such as nitrates, sulphates as well as metallic soaps in these dyes can result in increased turbidity and eutrophication [7]. These textile effluents are also known for having high values of several physicochemical and biological parameters such as coloring, temperature, salinity, pH, biological oxygen demand, chemical oxygen demand, total dissolved solids, total nitrogen, and total phosphorus to mention but a few, that influence the incidence of eutrophication. [8, 9, 10].

Research and technological efforts have been directed at safely and economically removing these dyes from textile effluents before the discharge. Such efforts have seen the development of various oxides and mixed oxide system [11, 12, 13]. Synthesis of novel adsorbents such as graphene [14, 15] and carbon nanotubes etc [16]. Other methods through which the dye discharged in effluents are mitigated include techniques such as membrane filtration, coagulation/flocculation, and biological methods, to mention but a few [17, 18].

Beyond the above, novel oxidation processes have also been developed. This involves essentially the generation of reactive species such as hydroxyl radicals which can oxidize a broad range of organic dyes benign and non-selective manner [19]. The novel oxidation processes are mostly facilitated by photocatalysts, which can effectively achieve nonselective degradation of organic dyes found in textile effluents in the presence of ultra-violet light. In this case, TiO_2 has been the prominent as a semiconductor photocatalyst due to its superb photocatalytic oxidation ability, non-photo-corrosive and non-toxic characteristics [20, 21, 22].

However, ZnO appears to be a suitable alternative to TiO_2 since its photo-degradation mechanism has been proven to be similar to that of TiO_2 [23]. Therefore, the objective of this paper is to investigate the kinetics and the influence of the time of UV light irradiation, amount of the photo-catalyst loading and the light intensity on the photocatalytic degradation of dyes in an actual textile effluent, in the presence of ZnO nanoparticles.

2. MATERIAL AND METHODS

The pure form of zinc oxide nanoparticles (ZnO, 99.95 %) used in this work was purchased from US Nanomaterials Incorporated, and used for all the experiments without any modification. The textile effluent was obtained from SAVCO Garments and Printers, 160 Ndoki Road, Aba, Abia State in Nigeria and was also used directly without any pre-treatment. A picture of the sample is as presented in Fig. 1.

The photocatalytic degradation of the textile effluent dyes was carried out in a rectangular batch stirred reactor with a capacity of 150 cm^3 and fitted with a thermometer, magnetic stirrer and UV lamps placed at 5 cm from the sample. The ultra-violet (UV) lamp, made by Sandiz Energy Limited, had a power rating of 30 W and was used in the photo-degradation experiments. To evaluate the ZnO nanoparticles, the Hitachi-4800 scanning electron microscope (SEM) as well as the Scintag 2000 X-ray diffraction (XRD) equipment was used. The ultra-violet spectrophotometric analysis involved the use of the UV-Vis spectrophotometer, Labomed 1286 series. The components of the dye effluent and their concentration was determined using a High Performance Liquid Chromatography (HPLC) Enhanced Integrator. Hydrogen was employed as the carrier gas, with a constant flow rate of 1.48 mL/min, an initial nominal pressure of 1.49 psi, and an average velocity of 44.22 cm/sec. 1 μL of each of the effluent sample was injected for the elution process.

2.1 Procedure for photolysis test

In the photolysis experiments, the behavior of the textile effluent was evaluated in the presence of the UV light (30 w) but without the ZnO nanoparticles. In this case, a specific amount of the textile effluent (50 ml) was introduced into the photocatalytic reactor and then stirred continuously with a magnetic stirrer for the various durations of 30, 60, 90, 120 and

180 minutes. UV spectrophotometric analyses of the dyes was carried out periodically to verify the degradation of the dye via concentration reduction.

2.2 Adsorption of the dye on the ZnO Photocatalyst in dark reaction

In this instance, 50 ml each of the textile effluent was agitated with 0.1 g of ZnO nanoparticles in the reactor that is the dark, using a magnetic stirrer for 180 minutes. Aliquots of the mixture (5 ml) were taken periodically at 0, 30, 60, 120 minutes and analyzed using the UV-Vis spectrophotometric technique for any changes in concentration. The differences in concentration (before and after adsorption test) was attributed to the adsorption of the dyes on the ZnO photocatalyst.

2.3 ZnO nanoparticles photocatalytic degradation of dyes in textile effluent

For the photo-degradation experiments, a specific volume of the textile effluent (50 ml) was mixed with 0.1 g of ZnO nanoparticles in the photocatalytic reactor and the suspension duly agitated with the magnetic stirrer while being irradiated by UV lamp rated at 30 W. This was done at room temperature. Aliquots of this mixture (5 ml) were analyzed periodically at 0, 30, 60, 90, 120, 150, and 180 minutes. The degradation process for each of the dye solutions was evaluated with a UV-Vis spectrophotometer at maximum absorbance wavelength of 510 nm. The percentage degradation (x %) of the dyes with respect to its initial concentration at any time can be obtained from equation 1

$$x \% = \frac{C_0 - C}{C_0} \times \frac{100}{1} \quad [1]$$

where C_0 and C are the initial and final concentration at a specified time.



Fig. 1: Textile effluent

3. RESULTS AND DISCUSSION

The results of the experiments performed are presented as follows:

3.1. SEM and XRD Characterization of ZnO Nanoparticles

The SEM image as well as the X-ray diffraction patterns of the nanoparticles, are shown in Fig. 2 (a and b)

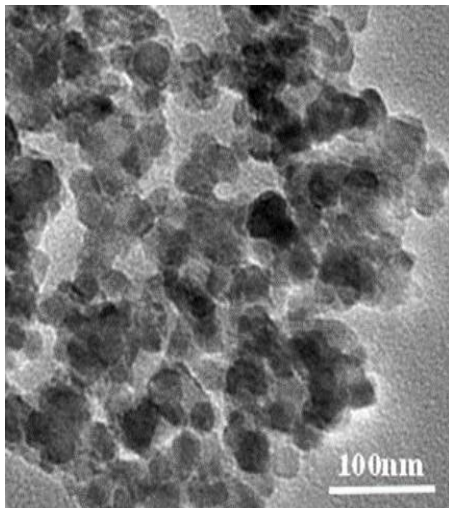


Fig. 2 (a): SEM image of ZnO nanopowder

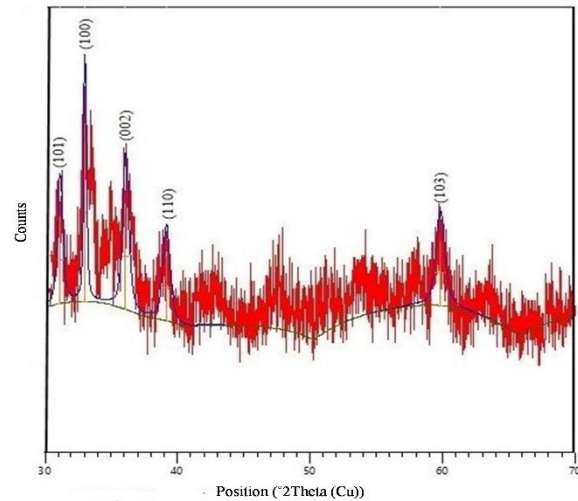


Fig. 2 (b): XRD of ZnO nanopowder

The SEM evaluation of the nanoparticles of ZnO showed that they were nearly spherical in morphology. From the evaluation of the particle sizes using the XRD diffraction, the average size of 17.46 ± 1.85 nm, with a maximum size of 18.98 nm and a minimum size of 15.31 nm was noted for the nanoparticles. The XRD image is as presented in Fig. 2 b. From the indexing, the notable peaks were for the (100), (101), (002), (110) and (103) planes based on the PDF x-ray diffraction card No 36-1451.

3.2 The Chemical Composition of the Textile Effluent

Chromatography, both HPLC and GC-MS are very effective analytical tools to determine the chemical composition of organic compounds, hence our choice of this method [24, 25]. The chromatogram obtained from our HPLC analysis of the textile effluent is as presented in Fig.3 below.

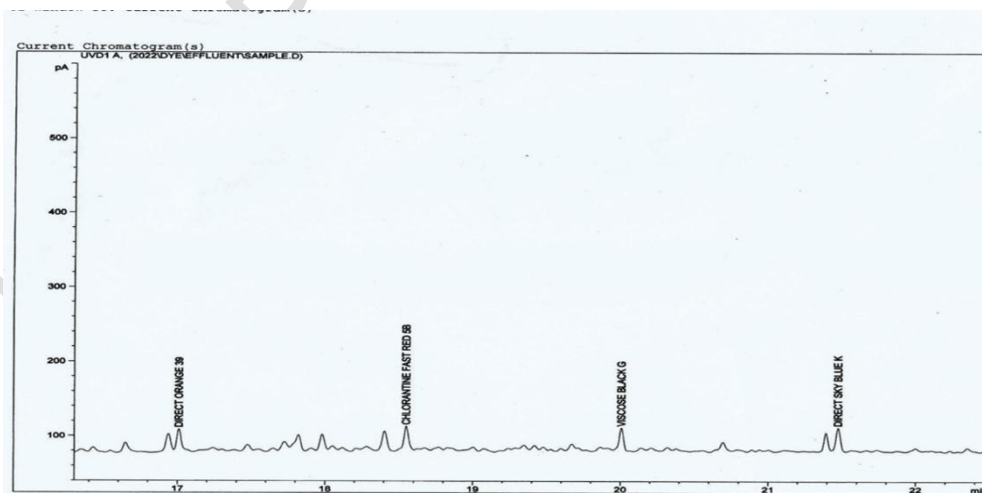


Fig. 3: Chromatogram of the Textile Effluent obtained through HPLC

It was confirmed that the textile effluent consisted of Direct Orange 39, Chlorantine Fast Red 5B, Viscose Black G and Direct Sky-Blue K dyes respectively. As can be seen from the

chromatogram, the most abundant dye in the effluent is chlorantine Fast Red 5B. The retention times, in minutes, of these various dyes that were noted in the HPLC chromatogram were 17.01, 18.56, 20.01 and 24.48, with the corresponding concentrations in mg/l of 3.20, 6.06, 0.31, 1.64 and 1.16 for the Direct Orange 39, Chlorantine Fast Red 5B, Viscose Black G and Direct Sky Blue K respectively. Based on the above, the total concentration of the dyes in the textile effluents was 11.21 mg/l.

3.3 Calibration curve for the determination the dyes concentrations after photolysis, dark reaction and photo-degradation

The calibration curve is based on the principle of the Beer-Lambert's law which relates the intensity of a monochromatic radiation with the thickness and the concentration of the absorbing medium. The textile effluent (11.21 mg/l) stock was diluted to the following concentrations, in mg/l: 1.0, 1.5, 5.0 l, 5.8, 7.2 and 10 respectively and the corresponding absorbance of these standard solutions determined using the UV-Vis spectrophotometer set at a wavelength of 510 nm. The calibration curve in Fig. 4, obtained from the plot of the values of absorbance against the concentrations (as stated in Table 1), was used to determine the changes of the concentration of dyes in the effluent after the photolysis, dark reaction and photo-degradation. The linearity of the calibration curve is expressed in this case by the coefficient of determination, R^2 . The very high value of the coefficient of determination (0.9988) shows that the variation of the absorbance with the concentration of the dyes in the effluent is sufficiently linear for it to be used for analysis.

Table 1: Data of absorbance and textile effluent concentration for the calibration curve

Concentration of dyes In Textile Effluent	Absorbance
1.0	0.075
1.5	0.105
3.0	0.215
5.0	0.340
5.8	0.418
7.2	0.500
10.0	0.720
11.2	0.810

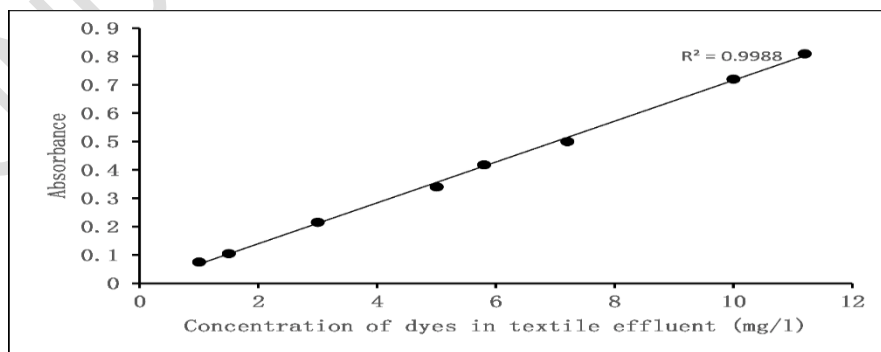


Fig. 4: Calibration curve of the dyes concentration (mg/l) at $\lambda_{\max} = 510 \text{ nm}$

3.4 The effect of photolysis and adsorption on ZnO dark reaction on dyes in the textile effluent

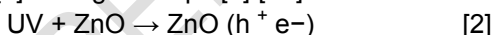
The results showed that 11.00 mg/L and 10.80 mg/l of the dyes was left in the effluent after 180 minutes of photolysis and adsorption dark reaction tests. The margins of decrease in the dyes' concentrations showed that photolysis and adsorption of the dyes on the ZnO nanoparticles in dark had little effects on the degradation of the dyes. The percent photo-degradation efficiencies obtained at the various times used for these experiments are stated in Table 2.

Table 2: Change in concentration with time during adsorption test and photolysis

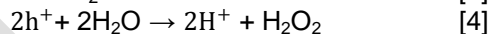
Irradiation Time (minutes)	Final concentration (without ZnO)	Final concentration (without UV light)	% degradation (without ZnO)	% degradation (without UV light)
0	11.21	11.21	0.00	0.0
30	11.10	11.10	0.98	0.98
60	11.10	11.10	0.98	0.98
90	11.00	10.90	1.87	2.76
120	11.00	10.80	1.87	3.65
180	11.00	10.80	1.87	3.65

3.5 The effect of exposure time to UV light

Table 3 presents the % degradation of the dyes after the exposure to the UV light over different time periods at optimum catalyst loading and dye concentration. Under the experimental conditions, 64 % of the dye degraded within 180 minutes of exposure. The degradation of the dyes followed these reaction steps on the surface of the ZnO nanoparticles, given by Eqn. [2] through to Eqn. [5] [26].



The h^+ and e^- are the positive holes and electrons generated within the semiconducting ZnO. The holes (h^+) converts the water molecules present in the textile effluent solution into $^{\circ}\text{OH}$ free radicals as follows:



It is these oxidative processes that generates a lot of hydroxyl free radicals that extends the photo-degradation in further reductive reactions with oxygen molecules trapped within the textile effluent and also with the dye molecules adsorbed on the surface of ZnO. The hydroxyl radicals therefore initiated the chemical deconstruction of the dyes, by reacting with their high electron-density functional groups [27, 28].

Table 3: Variation of % degradation with irradiation time

Irradiation Period (min)	Concentration (mg/l)	% degradation Efficiency
0	11.2	0.0
30	8.3	25.9
60	6.0	46.4
90	5.1	54.5
120	4.0	64.3
180	4.0	64.3

When the intensity of light as well as the concentrations of the dyes were constant, the number of °OH and °O₂ radicals increased with increased with the time of exposure to the UV light source. As seen in Table 3, further increase in time from 120 min to 180 min did not cause any further degradation of the dyes.

3.5 Effect of ZnO photocatalyst concentration

Table 4 below shows the relationship between degradation efficiency and catalyst loading. The photo-degradation efficiency increased with increase in amount of photo-catalyst until 2.0 g/l and then decreased. Increase in the number of ZnO nanoparticles increased the active sites of the catalyst. That caused enhancement in the hydroxyl and oxygen radical generation which also led to increase in degradation power because greater number of the dye molecules could be adsorbed on catalyst surface [29]. On the other hand, adding extra catalyst particles led to an opacity enhancement which in turn provided reductions in the light intensity penetration throughout the solution [30].

Table 4: Summary of degradation efficiency change with catalyst concentration

Concentration of ZnO (g/l)	Concentration of dye effluent (mg/l)	% degradation efficiency
0.0	11.2	0.0
0.5	6.7	40.2
1.0	5.4	51.8
1.5	5.0	56.3
2.0	4.0	64.0
2.5	6.9	38.4

3.7 Evaluation of the kinetics of the degradation of the dyes in textile effluent

We evaluated the photo-degradation kinetics of these dyes using the approached already reported elsewhere [31]. The apparent rate constant k_{ap} of the photo-catalytic degradation of the dyes in the textile effluent, consistent with the equation of Langmuir-Hinshelwood model is as stated in equation 6.

$$\ln \left(\frac{c_0}{c} \right) = k_{ap} t \quad [6]$$

In the above equation, c_0 and c are the initial and final concentrations of the dyes in the textile effluent. A plot of $\ln(c_0/c)$ versus time (t), yields a straight line. The slope determined from linear regression represents the value of k_{ap} [32, 33]. Also half-life of dye degradation can be calculated using equation [7].

$$t_{1/2} = \frac{0.693}{k_{ap}} \quad [7]$$

Our plot of $\ln(c_0/c)$ versus time (t), over the range of 0.5 g/L to 2.5 g/l catalyst concentration within the period of 120 minutes, were used to determine the values of the k_{ap} and the half-life of the process.

These values are as presented in Table 5. The increase in the ZnO loading from 0.5 g/l to 2.0 g/l increased the apparent rate constant from 0.00411 to 0.00811. Beyond the optimal dose, K_{ap} values decreases and $t_{1/2}$ values increases.

This can be rationalized in terms of availability of active sites on the ZnO surface and the penetration of photo-activating light into the suspension. The availability of active sites increased with catalyst loading, but the light penetration and hence the photoactivated volume of the suspension shrank [34].

Table 5: The calculated values of K_{ap} , half-life ($t_{\frac{1}{2}}$), regression coefficient (R^2), and the rate of degradation (r_o)

Concentration of ZnO	K_{ap} (min^{-1})	half-life ($t_{\frac{1}{2}}$, (min))	R^2	r_o (mg/min)
0.5	0.00411	168.6	0.9919	0.0460
1.0	0.00610	113.6	0.9969	0.0683
1.5	0.00654	105.9	0.9924	0.0732
2.0	0.00811	85.5	0.9861	0.0908
2.5	0.00384	178.4	0.9925	0.0430

The decreased K_{ap} values at higher ZnO catalyst loading could be due to the deactivation of activated molecules by collision with ground state molecules [35].

CONCLUSION

The ZnO nanoparticles showed good effectiveness in degrading the SAVCO Garments and Printers effluent. It showed a maximum % degradation efficiency of 64.3 %. In conclusion, the degradation efficiency of the ZnO photocatalyst with respect to the textile effluent was 64.3%. This maximum value of the % degradation efficiency was noted at a ZnO nanoparticles concentration of 2.0 g/l. The time of exposure influenced the photodegradation ability of the nanoparticles directly, as increase in exposure time of the effluents to UV light in the presence of the ZnO increased the rate of the photo-degradation. The mineralization process of the effluent followed a Pseudo-first-order reaction-kinetics as confirmed by their high correlation, R^2 values.

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