A Comparative study between TiO\textsubscript{2} and ZnO photocatalysis: 
Photocatalytic degradation of textile dye

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Abstract. The present study involves the photocatalytic degradation of three dyes: Reactive Bézactiv yellow (RBY); Direct Triamine yellow 86 (DY 86); and Methyl Orange (OM) with different structure and containing different substitute groups. The photocatalytic degradation has been investigated using two types of synthesis semiconductors namely titanium dioxide (TiO\textsubscript{2}) and zinc oxide (ZnO), as photocatalyst, in aqueous solution under solar irradiation. The synthesized nanoparticles were characterized by: Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), UV visible diffuse reflectance spectroscopy and scanning electron microscopy (SEM). The progress of photocatalytic degradation of the commercial dyes, has been observed by monitoring the change in substrate concentration of the compound employing High-Performance Liquid Chromatography (HPLC). The photodegradation rate was determined for each experiment and the highest values were observed for ZnO. 

Keywords: Comparative; Photodegradation; Solar light; Textile dye; TiO\textsubscript{2}; ZnO.

1. Introduction:  
Many industries such as textile, plastics, paper, and pulp generate streams of waste effluents, which contain a considerable amount of organic dyes. When these compounds are discharged to the main water bodies without any prior treatment, they can cause havoc to the ecological balance in the environment, as these molecules have carcinogenic and mutagenic properties towards aquatic organisms and thus pose threat to human life at the end of the food chain [1].  

Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation [2], elimination by adsorption on activated carbon, etc. are applied for color removal from textile effluents. One difficulty with these methods is that they are not destructive
but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [2].

In particular, photocatalysis is a more promising tool. Moreover, photocatalysis can be used to cause redox transformations and decompose a dye molecule. The use of photosensitive semiconductors such as \( \text{TiO}_2 \), \( \text{ZnO} \), \( \text{Fe}_2\text{O}_3 \), \( \text{CdS} \), \( \text{ZnS} \) and \( \text{V}_2\text{O}_5 \) has been reported in the literature for their use in reducing the color of the dye solutions due to their environmental-friendly benefits in saving resources such as water, energy, chemicals, and other cleaning materials [3].

The main aim of this present work is to study the photocatalytic degradation of different textile dyes with different molecular structures like reactive dye, direct dye, and the methyl orange in the presence of synthesized \( \text{ZnO} \) and \( \text{TiO}_2 \) by Solar light(SL). X-ray diffraction (XRD), MEB, UV-vis and FT-IR were used to characterize these catalysts.

2. Material and Methods

2.1. Material

Zinc chloride, NaOH is a reactive agent to synthesize \( \text{ZnO} \) nanoparticles; the titanium n-butoxide \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) and ethanol is a reactive agent to synthesize \( \text{TiO}_2 \) were purchased from Sigma-Aldrich. Reactive Bezactiv Yellow (RBY), Direct Triamine yellow86 (DY86) are azo dyes used in the industry for the dyeing of cotton and cellulose fiber; and Methyl Orange (OM) is an indicator.

2.2. Synthesis

\( \text{TiO}_2 \) nanoparticles were synthesized by a sol-gel method using titanium n-butoxide \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) as precursors. \( \text{ZnO} \) nanoparticles were synthesized by direct precipitation method using zinc chloride and NaOH as precursors.

2.3. Characterization

The powder X-ray diffractograms (XRD) of the \( \text{ZnO} \) and \( \text{TiO}_2 \) samples, were recorded and analysed to determine their crystal structure and lattice parameters. The average particle size of each metal oxide was estimated using the Debye–Scherrer formula. The particle morphology was analyzed through scanning electron microscopy (SEM) imaging and the Fourier transform infrared (FTIR) was recorded on VETEX70, the spectrum of the precursor was between 400 and 4,000 cm\(^{-1}\) and diffuses reflectance. The optical properties of the catalyst were analysed by diffuse reflectance UV–Vis spectroscopy using a Shimadzu UV–Vis spectrophotometer with an integrating sphere and a spectral reflectance standard over a wavelength range of 200–800 nm.

2.4. Methods

The photocatalytic degradation of dyes by nanopowders was studied in \( \text{TiO}_2 \) and \( \text{ZnO} \) suspension under solar irradiation between 11.00 a.m. to 3 p.m. The average intensity of sunlight during this period is 78000 Lux unit measured with a lux metre Testo 545; every experiment is recorded in the same conditions (Contact time, pH; anions and intensity irradiations).

Initially, the nanopowder was added to the dye solution to form a suspension. Before irradiation, the suspension was magnetically stirred for 30 min in the dark to reach an adsorption-desorption equilibrium. After given time intervals, the suspensions were filtered to remove the photocatalysts and aliquot of the residual solutions were transferred to HPLC measurement. The extent of removal of the dye, in terms of the values of residual concentration \( C_r \) of dye, has been calculated using the following equation:
\[ Cr = \frac{C_t}{C_i} \]  \hspace{1cm} (1)

Where \( C_i \) is the initial concentration of dye (ppm) and \( C_t \) is the final concentration of dye (ppm) at a given time.

3. Results and discussion

3.1 Characterization

3.1.1 Scanning Electron Microscopy (SEM). The morphology of TiO\(_2\) and ZnO, presented in figure 1 and 2 respectively, shows mono-dispersed nanoparticles, uniformly distributed and spherical shape. The larger particles in these figures may be attributed to the aggregates of the smaller particles.

![Figure 1. SEM of TiO\(_2\)](image1)

![Figure 2. SEM of ZnO.](image2)

3.1.2 DRX: TiO\(_2\) support structure. The diffraction peaks of TiO\(_2\) (2\(\theta\)=25.25°, 2\(\theta\)=37.8°, 2\(\theta\)=47.9°, 2\(\theta\)=53.59° and 2\(\theta\)=62.36°) which are the typical characteristic peaks of anatase TiO\(_2\). The diffraction data were in good agreement with JCPDS files # 21-1272; with a nanoparticle size 12 nm.

The diffraction peaks of ZnO (31.75°, 34.44°, 36.25°, 47.54°, 56.55°, 62.87°, 66.38°, 67.91°, 69.05°, and 72.61°) can be indexed to those of hexagonal wurtzite ZnO and these values correspond to the file (JCPDS Card No.00-005-0664); with a nanoparticle size 43 nm. [4] [5].

3.1.3 FT-IR analysis. The FT-IR spectrum of TiO\(_2\) showed various characteristic peaks an absorption band at 3434.88 cm\(^{-1}\) is related to stretching vibration of hydroxyl (OH); the other peaks at 1634 cm\(^{-1}\) were indicated to stretching of titanium carboxylate, which formed from TTIP and ethanol as precursors only the strong absorption band between 501 and 444 cm\(^{-1}\) was remained, which attributed to formed of TiO\(_2\) nanoparticles[6][7].

The FT-IR spectra of the synthesized ZnO particles. The peaks at 599 cm\(^{-1}\) are related to the stretching vibrations of Zn-O bonds. The peak at 3436 cm\(^{-1}\) indicates the presence of –OH residue[8][9].

3.1.4 UV–Visible absorption spectrum. ZnO possess a higher absorption than TiO\(_2\) in UV region about 400 nm and TiO\(_2\) spectrum possess an intense absorbance band at 360 nm, indicating a higher efficiency for the generation of electron-hole pairs than TiO\(_2\). Excess absorbance in ZnO requires more exposure for the valence band electrons, which may be possible to create more vacant anionic sites on the catalyst surface.

The more photogenerated electron hole pairs together with their much higher mobility in the microscale ZnO than in TiO\(_2\) suggest that ZnO would show higher photocatalytic activity than TiO\(_2\).[8] [9].
3.2 Photocatalytic activity

The experimental data, of different photocatalytic degradation of three dyes are shown in figure 3.

The three dyes (RBY, DY86, and OM), has a different efficiency, of degradation in the presence of two ZnO and TiO$_2$. The degradation rate of the dyes, follow the order RBY > OM > DTY. It can be seen also that ZnO showed a better degradation efficiency than that TiO$_2$ suggesting that ZnO absorbs a larger fraction of the solar spectrum and absorption of more light quanta than TiO$_2$ [10].

The degradation of all dye occurs at a faster rate with the solar light in the first 30 min (first step) and became slow after 30 min of irradiation (second step) and more slow or constant after 60 min (third step).

The results of the first step, can be attributed to the availability of a larger number of active sites on the surface of the photocatalyst, leading to an increase in the number of hydroxyl and superoxide radicals; but during the second step, the degradation became slow; this result is probably due to the formation of intermediates and its competitiveness, with parent dye molecules in the photocatalytic degradation process, and/or to the difficulty in converting the N-atoms, of dye into oxidized nitrogen compounds, another reason for this slow kinetics is the slow reaction of short-chain aliphatics with OH radicals [11].

3.3 Chromatogram analysis

To improve the formation of intermediate products; we analyse the HPLC chromatogram of dyes, at 0 min and 240 min.

In figure 4, we observed that the surface area of the major peak at (t=0 min) was reduced for all the three dyes and new peaks were appeared with a new retention times in the case of RBY and DY86; confirming the degradation of dye and/or the transformation of parent dye on an intermediates products.
4. Conclusion
This study demonstrates that certain commercial dyes with different structure and different substitute groups can be decolorized and degraded by solar photocatalysis. The results of degradation are not the same is depends on the nature of the dye and the nature of the catalyst.

The formation of intermediates and its competitiveness, with parent dye molecules slow down the photocatalytic degradation process.

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