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Industrial Wastewater Treatment by using Nanocrystalline Photo-catalysts

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Abstract - Photocatalytic process plays an important role in wastewater treatment and is affected by contaminants, catalyst, and photoreactor and so on. Semiconductor materials are efficient photo-catalysts and widely applied for prevention and control of pollution. The catalytic efficiency is greatly influenced by the crystal structure, particle size, and effective surface area. Nano-TiO_2 and Nano-ZnO present good catalytic activity because of the quantum size effect when the particle size becomes extremely small
This work involves preparation and characterization of titanium dioxide and zinc oxide in nano-size.
The prepared nanostructured titanium dioxide and Zinc oxide were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and X-ray Diffraction (XRD).
The photocatalytic performance of TiO_2 and Zinc oxide nanoparticles were investigated by the decomposition of black 5 dye in an aqueous solution under UV light ($_2$54 nm) by different systems (UV/TiO_2, UV/ZnO, using a slurry photochemical reactor.
The photocatalytic degradation of Black 5 was found to increase with increasing TiO_2 loading from 0.$_2$ to 1.6 g/L. It was found that the photocatalytic degradation of Black 5 in the presence of irradiated TiO_2 was enhanced in the presence of low concentrations of inorganic oxidants. This may be due to the trapping of the photogenerated conduction band electrons from TiO_2 more efficiently than O_2.

***Keywords*:** Photo-catalytic degradation; Wastewater treatment, Titanium dioxide; Zinc oxide.

1. Introduction

Photocatalytic process (PCP) plays an important role in wastewater treatment and is seriously affected by contaminants, catalyst, and photoreactor and so on. Semiconductor material, TiO_2, is an efficient photocatalyst and widely applied for prevention and control of pollution. The TiO_2 catalytic efficiency is greatly influenced by the crystal structure, particle size, and effective surface area. Nano-TiO_2 presents excellent catalytic activity because of the quantum size effect when the particle size becomes extremely small. (1)

Semiconductor photocatalysis by TiO_2 has been widely studied for 50 years. Potential uses include destruction of bacteria, the oxidation of pollutants, e.g., dye residues, and removal of organic films from glass and polymer substrates. (2)

The release of colored wastewaters is considered to be a dramatic source of non-aesthetic pollution, eutrophication, and perturbations in aquatic life. Therefore, new efficient methods of their removal need to be evaluated. Among advanced oxidation processes (AOPs), heterogeneous photocatalysis seems to be the most efficient. Therefore, it is commonly used in the removal of undesired substances.(3) It has already been applied among other dyes in the removal of malachite green(4), reactive blue 181(5), and titan yellow.(6)

Dyes are also used as model compounds in studies concerning synthesis and/or preparation of new photocatalysts. (7,8) Photocatalysis was also used for the degradation of other compounds. They include insecticides imidacloprid (9), pharmaceuticals olanzapine (10), and bezafibrate. (11) Photodegradation also has been applied in decontamination of complex mixtures like petroleum refinery waste- water. (1_2)

The AOPs are reactions that bring about a nearly complete mineralization of the pollutants to yield CO_2 and H_2O. This includes the use of oxidants such as ozone or hydrogen peroxide with ultraviolet (UV) light or UV with photocatalyst (TiO_2). (13)

II. Materials and Methods

II.1. Materials

Titanium isopropoxide (97%), acetic acid (≥99.7%), isopropanol (99.5%), triethanolamine (≥99%), zinc nitrate (98%) and black 5 dye (figure 3) were purchased from Sigma-Aldrich. Hydrogen peroxide (35%), sodium persulfate (98%), sodium periodate (99.8%) were purchased from Acros organics.

II.2. Preparation of TiO_2 nanoparticles

Anatase TiO_2 colloids were made from a sol–gel hydrolysis, autoclaving, and condensation of titanium isopropoxide in acetic acid solution. A typical synthesis of the TiO_2 nanoparticles can be described as follows:

160 ml of H_2O and 51 ml of acetic acid (Aldrich, 99.7%) were poured into a flask in an ice bath and stirred. 6 ml of isopropanol were added to a dropping funnel followed by 24 ml of titanium isopropoxide. The titanium isopropoxide/isopropanol solution was dripped into the acetic acid solution at a rate of approximately 1–2 drops per second. After refluxing for 4 h, the colloidal solution was loaded into an autoclave equipped with a Teflon beaker at 200 ^oC for 1_2 h. The autoclaved colloidal solution was sonicated to break up the agglomerated particles, and then condensed to a final TiO_2 powder using a rotary evaporator. (14)

II.3. Preparation of ZnO nanoparticles

500 ml of 0.1 M triethanolamine were mixed with 500 ml of 0.1 M $Zn(NO3)_2$, then the resulting solution was aged at 100 ^oC for 24 h. The obtained powder was washed with distilled water to remove any residual salts, centrifuged and finally dried. (15)

II.4. Methods

Bench scale batch photoreactor was used to study the photocatalytic degradation of black 5 dye.

II.5. Measurement of Photocatalytic Activity

The photocatalytic performance of TiO_2 and ZnO nanoparticles were investigated by the decomposition of black 5 dye in an aqueous solution under UV light (254 nm).

Absorbance is readily described by the Beer-Lambert law: (16)

$$A = \varepsilon l Co \qquad (1)$$

Where A is absorbance, ε is the extinction coefficient, l is the light path length (1.00 cm) and Co is concentration. ε can be determined from the slope of the plot of A versus concentration. The absorbance given at each irradiation time was related to a specific dye concentration using a calibration curve for black 5 solutions with different concentrations. The degree of degradation of the dye could be calculated according to equation (2)

$$\text{Degradation rate} = (Co - C / Co) \times 100 \qquad (2)$$

Where Co = initial concentration of dye solution, C = concentration of dye solution after photoirradiation at time t.

III. RESULTS AND DISCUSSION

III.1. Characterization of the prepared TiO_2 catalyst

III.1.1. Scanning Electron Microscopy (SEM)

Figure (2) shows SEM of the prepared TiO_2. The detailed examination of the micrograph of the TiO_2 reveals that the particles have spherical shape, and homogeneously distributed.

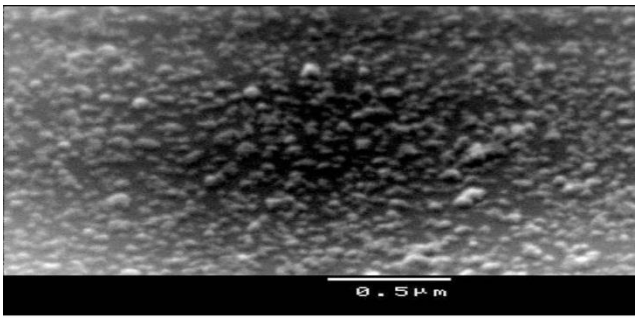

Figure (2): SEM for TiO_2 (50000 X)

III.1.2. Transmission Electron Microscopy (TEM)

Figure (3) shows TEM of the prepared TiO_2. The detailed examination of the TiO_2 reveals that the particles diameters were approximately 8 nm.

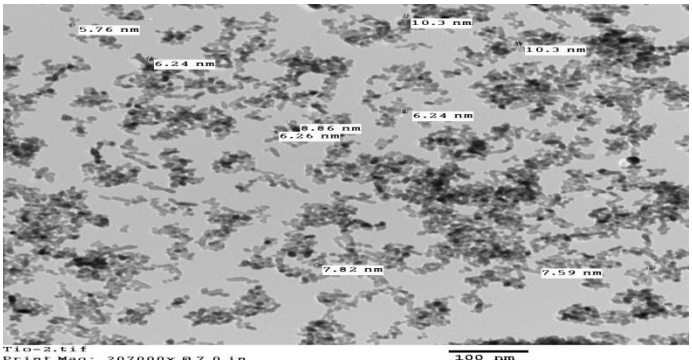

Figure (3): TEM for TiO_2 (15000 X)

III.1.3. X-ray Diffraction (XRD)

Figure (4) shows the XRD patterns of the prepared TiO_2 sample which exhibits diffraction peaks at 2θ = 25.3, 37.8, 48.0, 54.0, 55.0, 62.7, 68.7, 70.3 and 75.0 corresponding to the anatase phase (101), (004), ($_2$00), (105), ($_2$01), ($_2$04), (116), ($_{22}$0), and ($_2$15) of TiO_2 with tetragonal geometry. These main peaks corresponding to standard TiO_2 are confirmed using (ICSD card No 202242) indicating that the bulk TiO_2 composition is anatase.

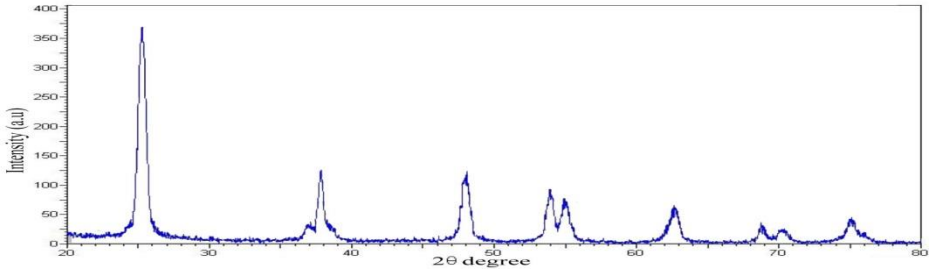

Figure (4): XRD for TiO_2 catalyst

III.2. Characterization of the prepared ZnO catalyst

III.2.1. Scanning Electron Microscopy (SEM)

Figure (5) shows SEM of the prepared ZnO. The detailed examination of the micrograph of ZnO reveals that the particles have spherical shape, with homogeneous distribution.

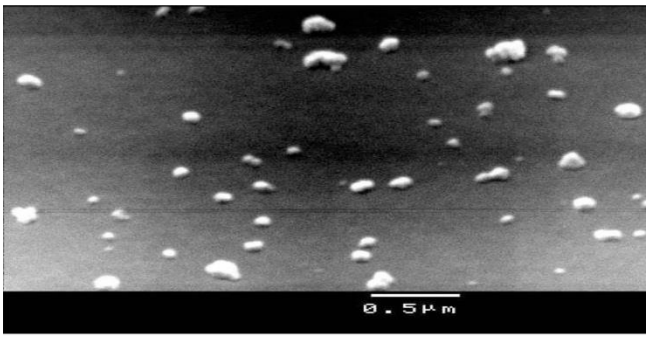

Figure (5): SEM for ZnO (35000 X)

III.2.2. Transmission Electron Microscopy (TEM)

Figure (6) shows TEM of the prepared ZnO. The detailed examination of ZnO reveals that the particles diameters were approximately 36 nm.

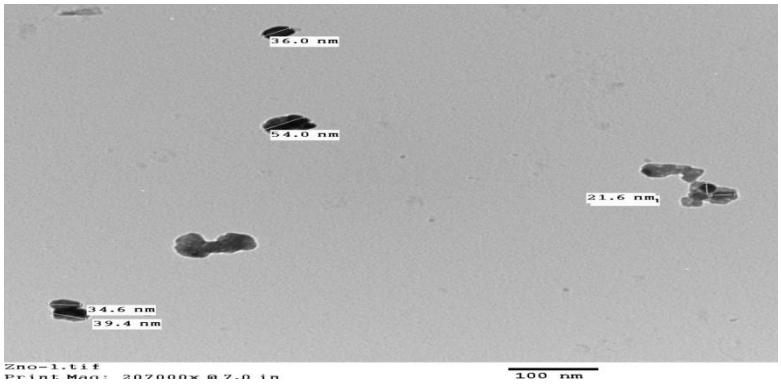

Figure (6): TEM for ZnO (15000 X)

III.2.3. X-ray Diffraction (XRD)

Figure (7) shows the XRD patterns of ZnO sample which exhibits diffraction peaks at 2θ = 31.7, 34.4, 36.2, 47.5, 56.5, 62.8, 66.3, 67.9, 69.0, 72.5 and 76.9 corresponding to ZnO (ICSD card No 034477).

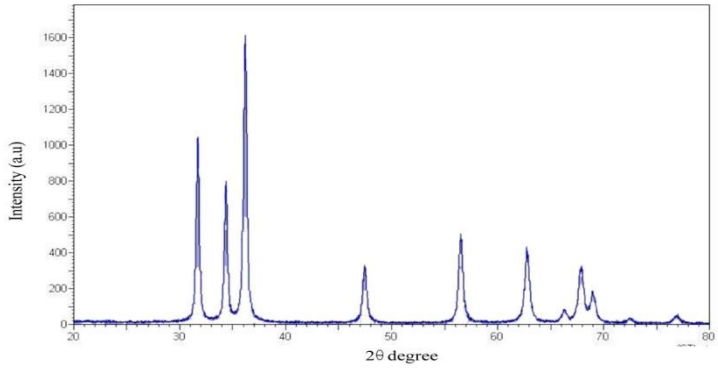

Figure (7): XRD for ZnO catalyst

III.3. Photocatalytic degradation of black 5 dye

The photocatalytic degradation of aqueous black 5 dye was studied with different advanced oxidation processes using UV/TiO_2, UV/ZnO. The photoreactor used in all experiments was the batch photoreactor.

III.3.1. Effect of TiO_2 and ZnO as photocatalysts

Concerning dyes degradation, the photocatalysis efficiency depends basically on the semiconductor used and on the chemical structure and functional groups in the molecules. Not all semiconductors can be used in the photocatalytic process but some such as TiO_2, ZnO and SnO_2 are known to be efficient photocatalysts. Although ZnO and TiO_2 have the same band gap (3.2 eV), the efficiency of ZnO in the degradation of some organic compounds still insignificant when compared with that of the traditional TiO_2. (17)

Figure (8) shows the photocatalytic degradation of black 5 dye using 1.$_2$ g/L of the prepared TiO_2 or ZnO with UV light (λ=254 nm). It was found that TiO_2 exhibited a higher photocatalyic degradation of the dye compared with ZnO. This may be due to the lower particles size of TiO_2 (8 nm) compared to ZnO (36 nm), as well as the fast recombination rate of e-/h+ pair and a low quantum yield of ZnO in aqueous solutions.(17)

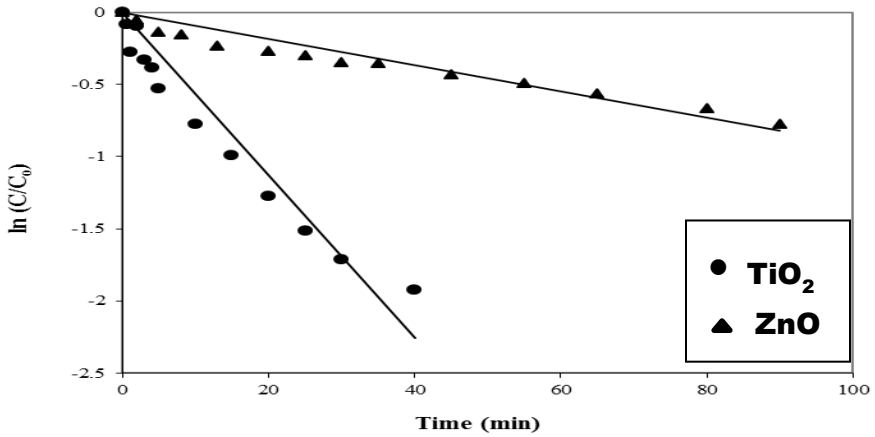

Figure (8): Photocatalytic degradation of black 5 day using 1.$_2$ g/L ZnO and TiO_2.

III.3.2. Effect of TiO_2 as a photocatalyst

The photocatalytic degradation of black 5 dye was studied using TiO_2 as it is more effective than ZnO.

III.3.2.1. Effect of TiO_2 Concentration

When the irradiation of black 5 dye solution was performed in the presence of UV alone, there was no observable decrease of the residual dye concentration over the longest time employed in the experiment. This indicated that the direct photolysis of black 5 dye by UV irradiation alone was slow. Irradiation of TiO_2 (0.2 g L−1) with UV light of wavelength 254 nm resulted in photodegradation of black 5 dye compared to UV only. This can be explained by eq. (2-4) as mentioned in the introduction chapter. (18-20)

The effect of increasing TiO_2 loading from 0.2 to 1.6 g L^{-1} on the photodegradation of the studied black 5 dye was investigated (figure 13). Plotting the experimental data in this form was diagnostic by the first-order kinetics. The lines shown in the figure were obtained using least squares linear regression techniques. Increasing the loading of TiO_2 from 0.2 to 1.6 g L^{-1} resulted in an increase in the rate of dye degradation. The results of analysis of the effects of TiO_2 concentration according to a power law model:

$$kapp = K [TiO_2] n \qquad (3)$$

Where kapp is the apparent rate constant, K the true rate constant and n is an exponent are shown in figure 9. The reaction order with respect to TiO_2 concentration was 1.4 (table 1).

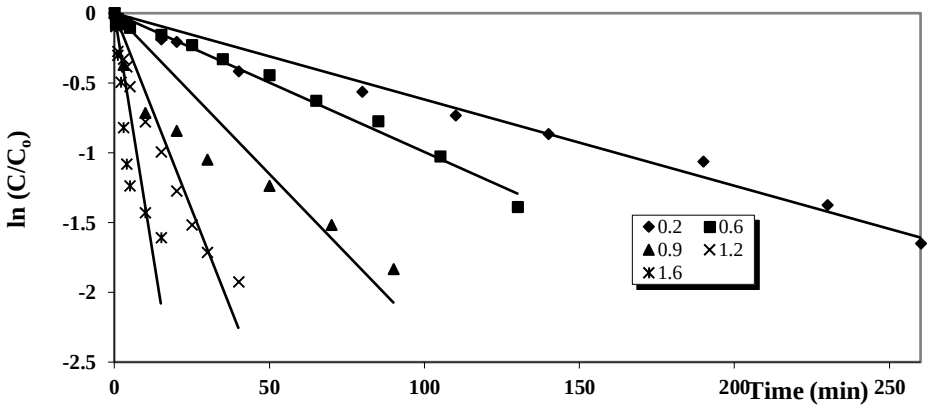

Figure (9): Effect of TiO_2 concentration (g/L) on the photodegradation of black 5 dye.

Table (1): Apparent rate constants, half-life times, and reaction orders for degradation of black 5 dye using UV/TiO_2.

Catalytic system	Concentration (g/l)	kapp (min-1)	t1/$_2$ (min)	Apparent reaction order (n)
UV/TiO_2	0.$_2$ 0.6 0.9 1.$_2$ 1.6	6$_2$ x10-4 99 x10-4 $_2$3x10-3 56 x10-3 139 x10-3	11$_2$ 70 30 11 5	1.4

Increasing the concentration of TiO_2 from 0.2 to 1.6 g L^{-1} leads to an increase in the number of photons absorbed by TiO_2 from the UV source. Therefore, excitation of more electrons from the valence to the conduction band was observed and the concentration of holes was increased. Thus by increasing the number of hydroxyl radicals generated, the photodegradation rate will be enhanced. (22-24)

CONCLUSIONS

TiO_2 and ZnO were prepared in Nanocrystalline scale were TiO_2 crystals has size 8 nm and ZnO crystals has size 36 nm

Heterogeneous photocatalytic degradation using UV/TiO_2 was found to be more effective than UV/ZnO.

The photocatalytic degradation of investigated Black 5 dye was found to increase with increasing TiO_2 loading up to 1.6 g/L.

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