

Research Article

Rapid Decolorization of Cobalamin

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The photocatalytic decolorization of cobalamin was carried out in aqueous solution of different types of catalysts including ZnO, TiO₂ (Degussa P25), TiO₂ (Hombikat UV100), TiO₂ (Millennium PC105), and TiO₂ (Koronose 2073) by using UVA source of irradiation. The effect of various parameters such as photocatalyst amount, cobalamin concentration, type of catalyst, pH of aqueous solution, light intensity, addition of H₂O₂, flow rate of O₂, type of current gas, and temperature on photocatalytic oxidation was investigated. The results indicated that the photocatalytic decolorization of cobalamin was well described by pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. The effect of temperature on the efficiency of photodecolorization of cobalamin was also studied in the range 278–298 K. The activation energy was calculated according to Arrhenius plot and was found equal to $28 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ for ZnO and $22 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ for TiO₂ (Degussa P25). The results of the total organic carbon (TOC) analysis indicate that the rate of decolorization of dye was faster than the total mineralization. Decolorization and mineralization of cobalamin in the absence of light and/or catalyst were performed to demonstrate that the presence of light and catalyst is essential for the decolorization of this cobalamin. The results show that the activity of different types of catalysts used in this study was of the sequence: ZnO > TiO₂ (Degussa P25) > TiO₂ (Hombikat UV100) > TiO₂ (Millennium PC105) > TiO₂ (Koronose 2073).

1. Introduction

Frank and Bard in 1977 stated that it was possible to use TiO₂ to degrade the organic compound in water [1]. Photodegradation of organic and inorganic pollutants on different types of semiconductors has been studied by several researchers. Dyes have become one of the important industry pollutants that lead to environmental contamination. To find a general process for treatment of the color of dye used in dyeing processes is very difficult due to the complexity and variety of these types of industrial wastewater [2]. In recent years, the interest has been focused on the use of semiconductor in photocatalytic decolorization of different types of wastewater where the band gap for zinc oxide is ($\sim 3.2 \text{ e.V}$). In addition, their photocatalytic activities are shown only under UV irradiations. However, the presence of colored compounds on the surface of the semiconductor can absorb a radiation in the visible range and then is excited by a process called photosensitization process. The hydroxyl group radical ($\cdot\text{OH}$), which is formed by the photocatalytic process, from

the photosensitization processes, will oxidize all the organic compounds to CO₂ and H₂O (mineralization) [3]. Several processes were used for the treatment of pollutants such as biodegradation, catalytic oxidation, chemical treatment (chlorine, ozone, hydrogen peroxide), and degradation by high-energy ultraviolet light [4, 5]. One of the active methods to treat the colored wastewater is advance oxidation process (AOP) including photocatalysis degradation systems which use a semiconductor (TiO₂ or ZnO) and UV light [6]. Titanium dioxide is one of the best materials which have good ability to destroy the organic materials and active species to un-harmful material by using light/semiconductor system [7].

The photocatalytic activity of semiconductors can be enhanced by using different techniques [8–15]. Zhou et al. showed that doping of titanium dioxide with gold (Au-TiO₂) nanocomposites gives higher activity in visible-light for degradation of Rhodamine-B (RhB) in water [8].

Wang et al. observed that the calcination temperature of TiO₂ (P25) at 500°C caused to double the activity of TiO₂

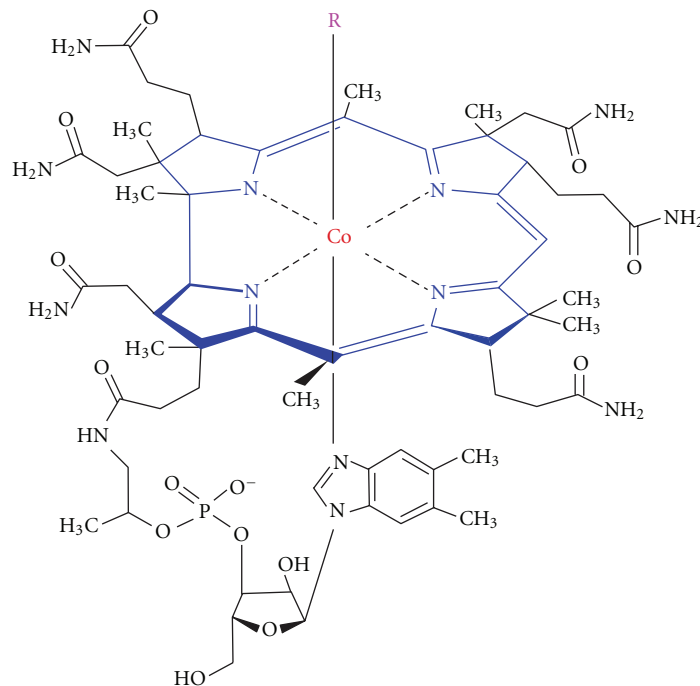


FIGURE 1: Structure of cobalamin.

(P25) for photocatalytic degradation of methyl orange (MO) [9]. Wu et al. studied a comparison between the photocatalytic activity (PC) and photoelectrocatalytic activity (PEC) of methylene blue (MB) [11]. They have noticed that the photoelectrocatalytic activity is more efficient than photocatalytic activity. There are different studies using doped metal on TiO_2 surface to enhance the activity of catalyst or to reduce the band gap of semiconductor [10–15].

Heterogeneous photocatalysis is a method used for the degradation of various types of organic pollutants in water and wastewater [16]. Different types of semiconductors such as TiO_2 , ZnO, CdS, and ZnS and irradiation source of UV or visible lights can be used in photocatalysis systems. In the process of irradiation of the semiconductor with energy equal or greater than the band gap, the electrons in valence band are promoted to the conduction band leaving a hole behind. The holes at the valence band have an oxidation potential of +2.6 V with normal hydrogen electrode (NHE) at pH = 7. This energy is enough to oxidize water molecule or hydroxide and produce hydroxyl radicals or oxidize wastewater containing various types of dyes [17, 18]. The photosensitization process is defined in summary term as photocatalytic decolorization of dyes, and this process also follows the mechanism of free radical, where the adsorbed dye molecules on the semiconductor surface have ability to absorb a radiation in with short wavelength or in the visible region [19–21]. Therefore the excited colored dye either in singlet or triplet states shall inject an electron to the conduction band for the chosen semiconductor [22].

Porphyrins are aromatic compounds that have a highly conjugated system and composed of four smaller 5-membered heterocycles. They are called pyrroles that contain one

nitrogen and four carbon atoms. In porphyrins, one carbon is typically referred to as the mesocarbon, serving the connection of each of the four pyrrole rings [23]. Porphyrins are intensely colored cyclic molecules which occur in nature as in green leaves and red blood cells. Porphyrins are characterized by the presence of four modified pyrrole subunits interconnected at their α carbon atoms with methane bridges ($=\text{CH}-$) [24].

Cobalamin, also known as vitamin B_{12} , is a complex organometallic compound which is formed by the situated cobalt atom in a corrin ring [25]. The structure of cobalamin is shown in Figure 1.

The central metal ion in the cobalamin is cobalt. While four of the six coordination sites are provided by the corrin ring, the fifth is provided by a dimethylbenzimidazole group. The sixth coordination site, the center of reactivity, is variable as it can be a cyano group ($-\text{CN}$), a hydroxyl group ($-\text{OH}$), a methyl group ($-\text{CH}_3$), or a 5'-deoxyadenosyl group (here the $\text{C}5'$ atom of the deoxyribose forms the covalent bond with Co), respectively, to yield the four cobalamin forms mentioned above [26].

Cobalamin is soluble in water and has the molecular formula $\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{O}_{14}\text{P}$, mole mass 1355.37 g/mol. The systematic (IUPAC) name is α -(5,6-dimethylbenzimidazolyl) cobamidcyanide. It can be produced industrially only through bacterial fermentation-synthesis. Cobalamin consists of a class of chemically-related compounds (vitamers) such as cyanocobalamin, methylcobalamin, adenosylcobalamin, and hydroxocobalamin. The various forms of isomers of B_{12} are all deeply red colored, due to the color of the cobalt-corrin complex [27]. Photolysis of cobalamin in aqueous solution produced hydroxocobalamin. The kinetics

of photolysis was found to follow zero-order kinetics at different pH and the rate was catalysed by both hydrogen and hydroxyl ions [28].

The idea of this work was derived from the announcement of NineSigma company in October 2010 about decolorization of porphyrin species proposal number 66645 (rapid decolorization of porphyrin species). The company aimed to decolorize porphyrin species to prevent staining or noticeable transfer to cloth and other absorbant surfaces. The aim of this study was to investigate the photocatalyst decolorization of cobalamin using different types of catalyst, namely, ZnO, TiO₂ (Degussa P25), TiO₂ (Hombikat UV100), TiO₂ (Millennium PC105), and TiO₂ (Koronose 2073). The effect of different parameters was studied to estimate the best condition for decolorization of cobalamin.

2. Experimental

Photocatalytic reactions were carried out in a batch photoreactor with the radiation source type Philips (CLEO), Poland, mercury lamps containing 6 lamps with 15 W for each. Aqueous suspensions of zinc oxide (ZnO) or titanium dioxide (TiO₂) containing cobalamin in beaker, under magnetic stirring, were irradiated in light of wavelength 365 nm with an irradiation intensity of (0.5–3 mW·cm⁻²). In all experiments, the required amount of the catalyst was suspended in 100 cm³ of aqueous solution of cobalamin. After illumination, 2 mL was taken from the reaction suspension, centrifuged at 4,000 rpm for 15 minutes in an 800 B centrifuge, and filtered to remove the particles. The second centrifuge was found necessary to remove fine particle of the zinc oxide or titanium dioxide (TiO₂). After the second centrifuge, the absorbance of the cobalamin was measured at 361 nm and 550 nm, respectively, using Cary 100Bio UV-visible spectrophotometer shimadzu. The measurements at the two wavelength produced equivalent results, when compared with the prepared calibration curves.

The photocatalytic decolorization rate of cobalamin is described by pseudo-first-order kinetics according to the Langmuir-Hinshelwood model, so the rate of photocatalytic decolorization of cobalamin could be expressed by the following:

$$C_t = C_o e^{-kt}, \quad (1)$$

where C_t represents cobalamin concentration at time t of irradiation, C_o is the initial concentration, k is the apparent reaction rate constant of the pseudo-first-order kinetics, and t is irradiation exposure time [3]:

$$\begin{aligned} \frac{C_t}{C_o} &= e^{-kt}, \\ \ln \frac{C_t}{C_o} &= -kt, \\ \text{or } \ln \frac{C_o}{C_t} &= kt. \end{aligned} \quad (2)$$

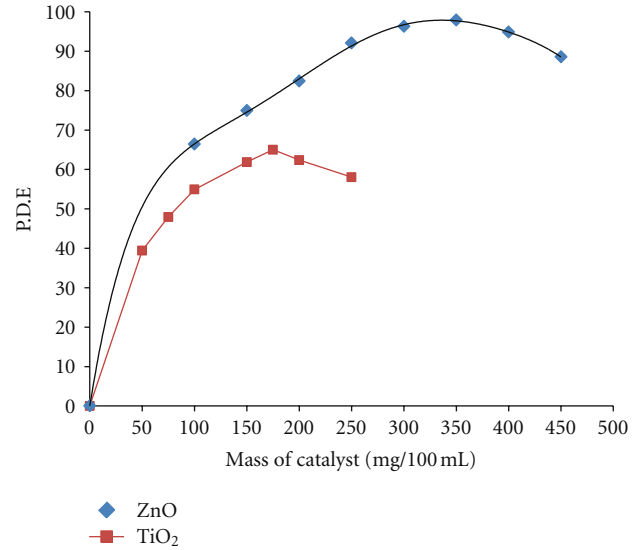


FIGURE 2: Effect of the masses of catalyst on photodecolorization efficiency of cobalamin.

The photodecolorization efficiency (P.D.E) of cobalamin was calculated from a mathematical equation adapted from measurements of decolorization used before [29]:

$$\text{P.D.E} = \frac{C_o - C_t}{C_o} \times 100, \quad (3)$$

where C_o is the initial concentration of cobalamin, C_t represents cobalamin concentration at time t of irradiation.

3. Results and Discussion

3.1. Effect of Mass Catalyst of ZnO or TiO₂. The photodegradation efficiency of cobalamin increased with the increase of the amount of catalyst up to an optimum value and then decreased slightly with the increase of the amount of catalyst as shown in Figure 2. One possible explanation for such behavior is that it is believed that an increase in the number of catalyst will increase the number of photons absorbed and the number of cobalamin molecules adsorbed. Therefore, the photodegradation rate can be expected to be enhanced on increasing the amount of catalyst due to the increase in total surface area available for contaminant adsorption. However, a further increase of the catalyst concentration may cause light-screening effects [30]. These screening effects reduce the specific activity of the catalyst [31].

3.2. Effect of Initial Dye Concentration of ZnO or TiO₂. The effect of the initial concentration of cobalamin on the photocatalytic decolorization was studied by varying the initial concentration over a wide range. At a fixed pH and amount of catalyst, photocatalytic experiments were carried out at different initial concentrations of cobalamin. The results in Figure 3 show that the rate constant of photodecolorization decreased with increasing the initial cobalamin concentration [32]. This behavior can have the explanation that

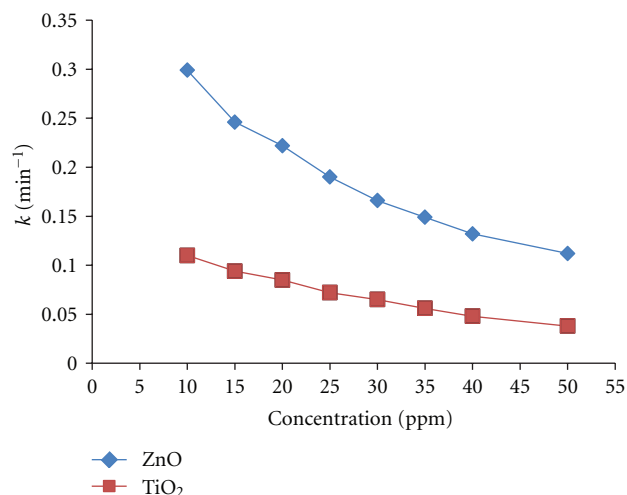


FIGURE 3: Effect of initial dye concentration on rate constant.

the initial concentration of the cobalamin increases because the path length of the photons log in the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [33].

3.3. Effect of pH. The results in Figure 4 show that the photodecolorization efficiency increased with the increase of the pH value of solution to pH 9.01 for ZnO and pH 6.59 for TiO₂ (Degussa P25) and then decreases. The production of hydroxyl radicals is also a function of pH. Therefore, pH is an important parameter in photocatalytic reactions. The photodecolorization of cobalamin was studied at different pH. In all the experiments, pH was adjusted by using appropriate amounts of base (NaOH) or acid (HCl) solutions [34–37]. The zero point charge (ZPC) is equal to 9.01 for ZnO and 6.59 for TiO₂ (Degussa P25) and the semiconductor surface will remain positively charged in acidic medium and negatively charged in alkaline medium, because the ionization state of the surface of semiconductor is according to the following reactions:



This behavior can be explained when the pH value of the solution is increased up to a maximum value and then decreased, this is because in alkaline medium the surface area of photocatalyst possesses much negative charge [38–41].

3.4. Effect of Temperature. The effect of temperature on photocatalytic decolorization of cobalamin in water solution was investigated in the range of 278.15–298.15 K. The results in Figure 5 show that the degradation efficiency of cobalamin

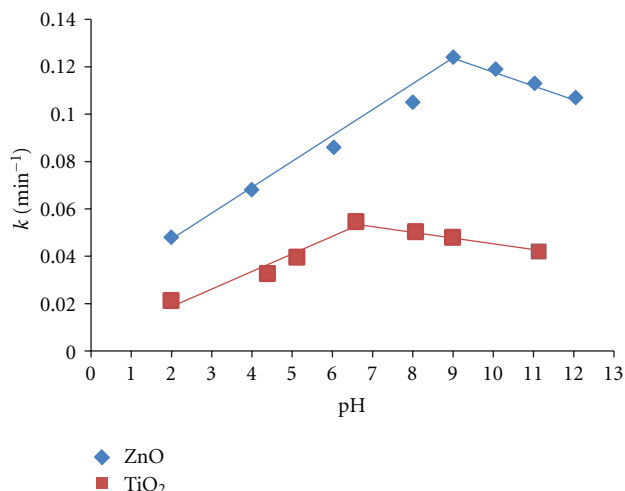


FIGURE 4: Effect of initial pH of solution on rate constant.

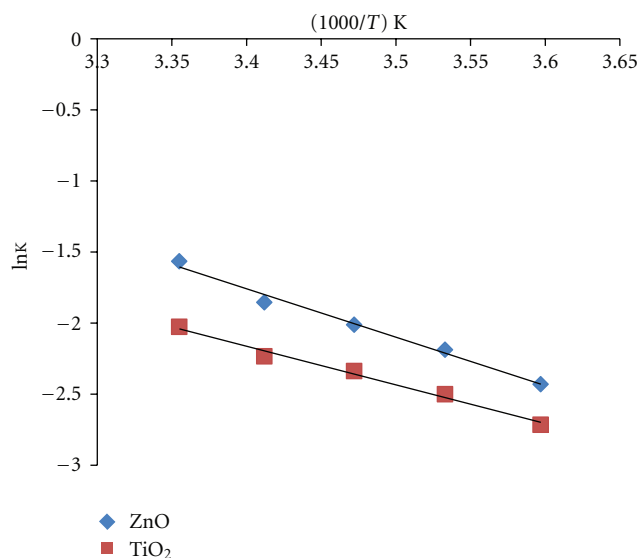


FIGURE 5: Arrhenius plot.

gradually increased with increase in the temperature. The increase in temperature would lead to generating the free radicals [42]. Therefore, the rise in temperature helped the reaction to compete more efficiently than electron-hole recombination [43]. The increasing of temperature may increase the oxidation rate of cobalamin and also reduce the adsorption capacities associated with cobalamin and dissolved oxygen [44]. Generally the rise in temperature can affect the amount of adsorption [45]. Arrhenius plot shows that the activation energy for photocatalytic decolorization of cobalamin is equal to $28 \pm 1 \text{ kJ mol}^{-1}$ for ZnO and $22 \pm 1 \text{ kJ mol}^{-1}$ for TiO₂ [46].

3.5. Effect of Light Intensity. The effect of light intensity on the decolorization efficiency for cobalamin was examined at constant initial cobalamin concentration (40 ppm). It is

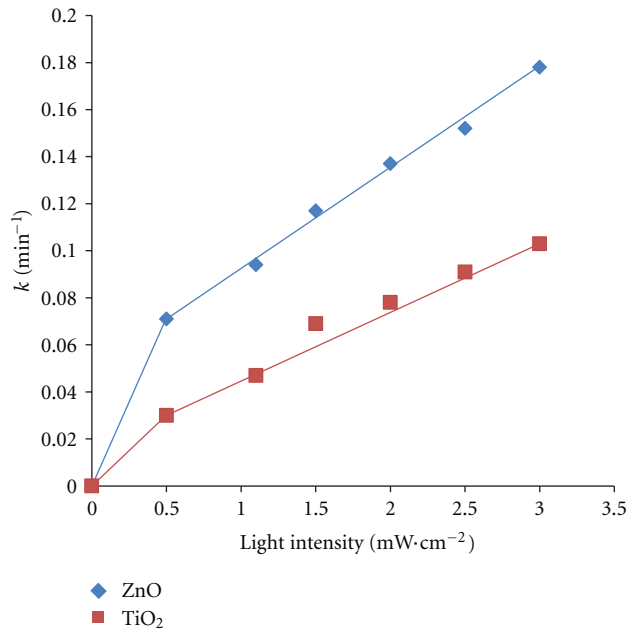


FIGURE 6: Effect of initial light intensity on the rate constant.

found that the percentage of decolorization and photodecolorization for cobalamin increases with increasing the light intensity as shown in Figure 6. The light intensity was studied in the range $(0.5\text{--}3)\text{ mW}\cdot\text{cm}^{-2}$ by changing the high and lowering the lamps. From these results it is found that the decolorization rate for cobalamin increased with increase in the light intensity [47]. This behavior can be explained that the UV irradiation production the photons required for the electron transfer from the valence band to the conduction band in the catalyst. photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of decolorization for cobalamin increases when more radiations fall on the catalyst surface and hence more $\cdot\text{OH}$ radicals are generated on catalyst surface [48, 49].

3.6. Effect of Current Gas. The results in Figures 7 and 8 show that the photodecolorization efficiency for cobalamin increased with the presence of the oxygen gas (O_2) but decreased or was extremely slow in the presence of the nitrogen gas (N_2). This behavior can be explained that in the presence of nitrogen gas (N_2) and TiO_2 (Degussa P25) will production grey-blue in color may be attributed to the sharing of lattice oxygen from the surface. The results indicated that the presence of oxygen is necessary [50, 51]. The presence of oxygen in the solution plays an important role in the photocatalytic decolorization of cobalamin. This behavior can be explained that the oxygen molecule acts as an electron acceptor and minimizes the chance of electron-hole pair recombination [52].

3.7. Effect of Addition of H_2O_2 . Hydrogen peroxide (H_2O_2) plays an important role in the production of hydroxyl radicals. The effect of addition of hydrogen peroxide H_2O_2

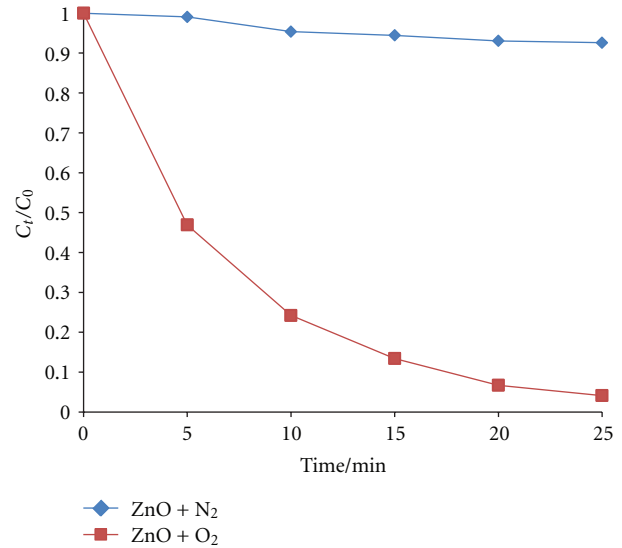
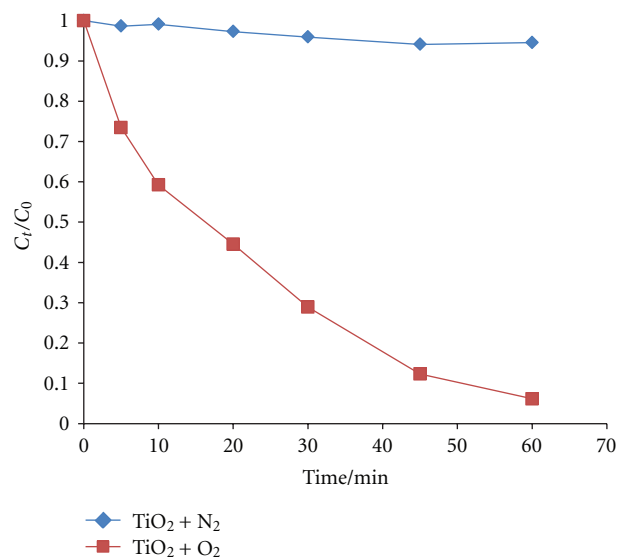
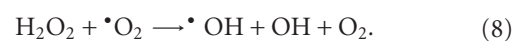
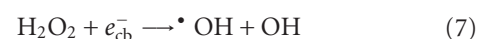


FIGURE 7: Effect of type of gas on photodecolorization of cobalamin by ZnO.

FIGURE 8: Effect of type of gas on photodecolorization of cobalamin by TiO_2 .

on the decolorization rate was studied for photocatalytic decolorization of the cobalamin. The results in Figure 9 show that the decolorization rate increase in with increases concentration of hydrogen peroxide H_2O_2 from 0.1 to 1.5 mmol/L, becomes maximum at 1.5 mmol/L and then $\cdot\text{OH}$ starts decreasing from 1.5 to 4.0 mmol/L with increase in the concentration of hydrogen peroxide H_2O_2 [53].

This behavior is due to increasing the concentration of hydroxyl radical since it inhibits the hole-electron recombination according to the following equations:



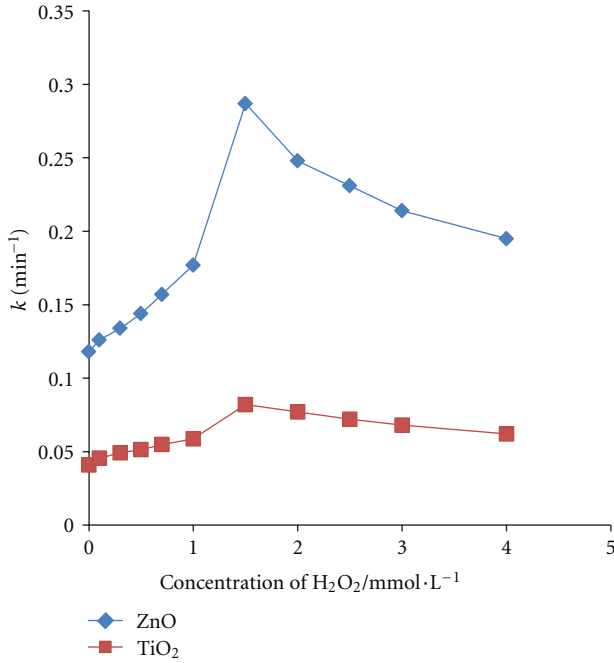
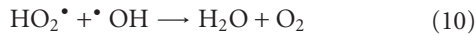
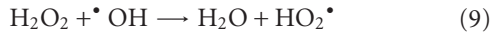


FIGURE 9: Effect of addition of H₂O₂ on rate constant.

At high concentration of hydrogen peroxide H₂O₂ the photocatalytic processes decrease because of its hydroxyl radical scavenging effect, according to the following equations [54]:



3.8. Type of Catalyst. The results in Figure 10 show the relationship between the photodecolorization of cobalamin with irradiation time in the existence of oxygen gas by using different types of TiO₂, under the experimental conditions, initial cobalamin concentration of 40 ppm, solution pH equal to 7.8, light intensity equal to 1.3 mW·cm⁻², TiO₂ concentration 175 (mg/100 mL), and the temperature equal to 298.15 K. The results show that the activity of different types of catalyst used in this study was of the sequence:

TiO₂(Degussa P25) > TiO₂(Hombikat UV100) >

TiO₂ (Millennium PC105) > TiO₂ (Koronose 2073).

(11)

3.9. Mineralization of Cobalamin. The results in Figures 11, 12, and 13 show the relationship between the TOC degradation % with irradiation time and it is found that the TOC degradation % increased with the increase of the irradiation time. These results indicate that the color photodegradation for cobalamin is faster than the decrease of total organic carbon (TOC). From these results it is found that the ZnO

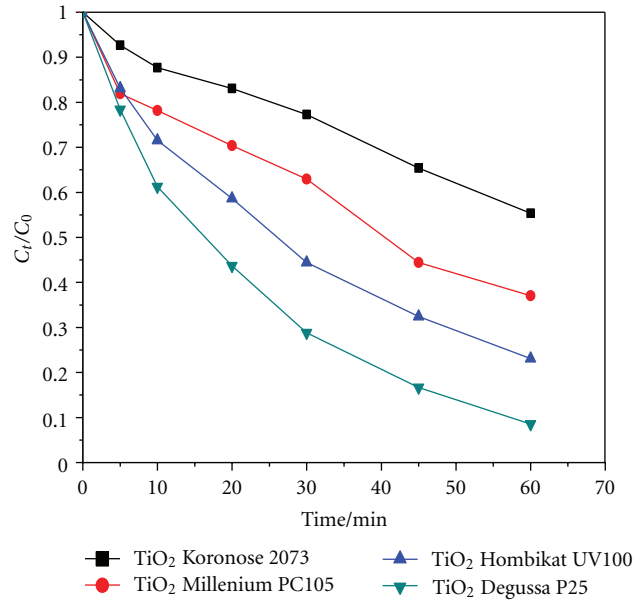


FIGURE 10: Photodecolorization of cobalamin by different types of TiO₂.

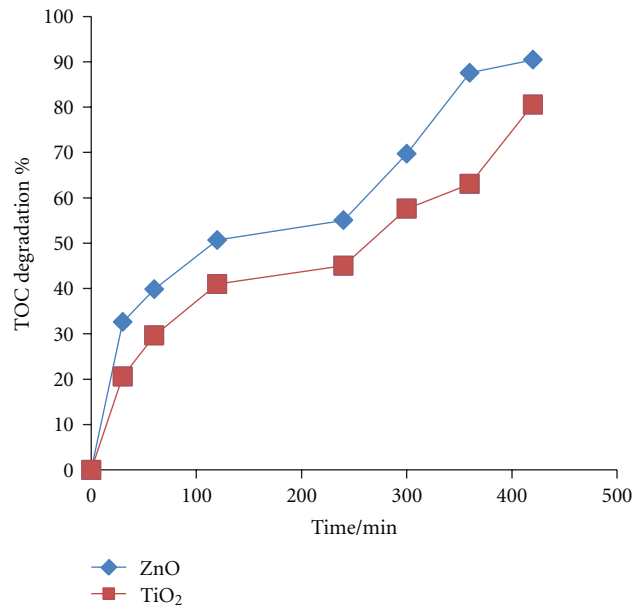


FIGURE 11: Mineralization of cobalamin.

is more active than the TiO₂ (Degussa P25). The efficiency of these catalyst arrangements is as follows:

ZnO > TiO₂(Degussa P25). (12)

4. Conclusions

Complete decolorization of cobalamin was achieved in less than thirty minutes. PH was changed at the end of reaction

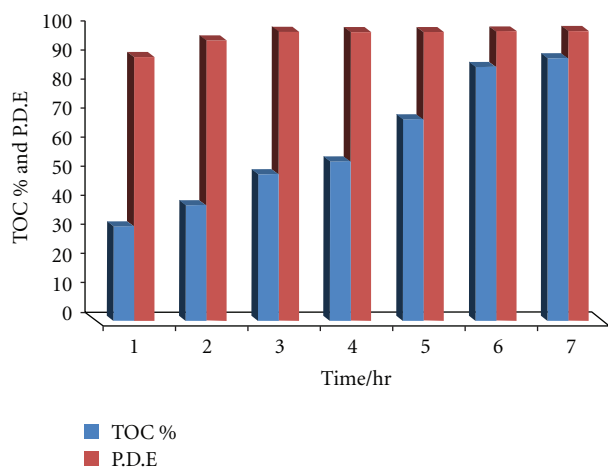
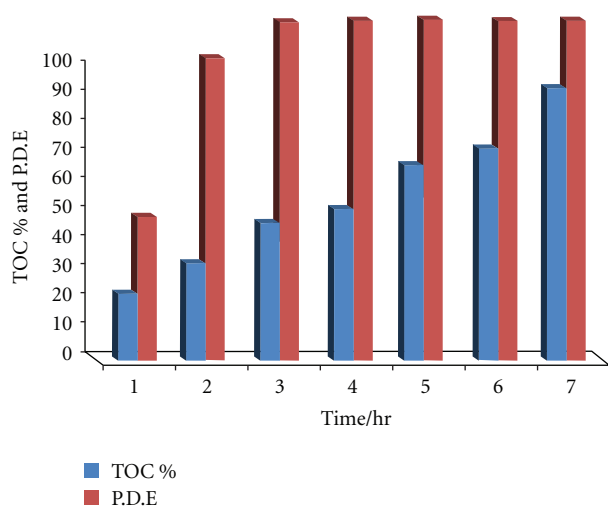


FIGURE 12: TOC degradation % and P.D.E for cobalamin by ZnO.

FIGURE 13: TOC degradation % and P.D.E for cobalamin by TiO₂ (Degussa P25).

towards 7 (neutral). The photocatalytic process can be expressed by both the pseudo-first-order reaction kinetics and the Langmuir-Hinshelwood kinetic model.

The controlled experiment indicates that the presence of UV light, oxygen, and catalyst was essential for the effective destruction of cobalamin. It is important to choose optimum degradation parameters to obtain a high photocatalytic decolorization rate.

The enhancement of decolorization efficiency of cobalamin increasing masses of catalysts is attributed to the increase of the availability of photocatalytic sites. Nevertheless, the decrease of catalytic activity often the plateau region is related to a shielding effect of excess partials and resulted in a reduced performance.

The photocatalytic decolorization of cobalamin using different types of catalysts like photocatalyst strongly depends on the amount of catalyst, cobalamin concentration, pH of solution, light intensity, type of current gas, and addition of H₂O₂.

The phenomenon of increasing the photodecolorization efficiency of cobalamin with decreasing the concentration of solution is due to the decrease of the concentration of OH⁻ adsorbed on catalyst surface. The increasing of cobalamin concentration increases the competitions between OH⁻ and cobalamin to adsorb on active site of catalyst.

The photocatalytic decolorization efficiency of cobalamin increases with the increase of the pH of solution up to a maximum value and then decreases. This behavior could be explained on the basis of zero point charge (ZPC).

The decolorization of cobalamin increases with the increase of light intensity. Nevertheless, the increase of light intensity leads to the increase of the number of electron-hole pair and, hence, increases the decolorization efficiency of cobalamin.

The temperature is the factor that has the smallest effect on the photocatalytic decolorization of cobalamin. Photocatalytic decolorization of cobalamin is faster than the decrease of total organic carbon (TOC).

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