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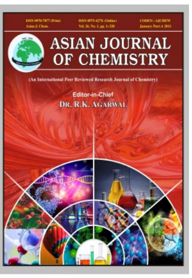

Photocatalytic Decolorization of Cobalamin in Aqueous Suspensions of TiO_2 and ZnO Under Solar Irradiation

AHMED F. HALBUS and FALAH H. HUSSEIN*

Chemistry Department, College of Science, Babylon University, Hilla, Iraq

*Corresponding author: E-mail: abohasan_hilla@yahoo.com

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Photolysis and photocatalysts treatments of aqueous solution of cobalamin were carried out over a suspension of titanium dioxide and zinc oxide. Heterogeneous photocatalytic processes applied under natural weathering conditions, in the presence of solar radiation show a promising degradation capability. Under solar radiation a complete removal of color was achieved in a relatively short time of about 10 minutes, when ZnO was used and in 45 min when TiO_2 was used. However, in the presence of artificial UV-light, complete decolorization of cobalamin was obtained in 20 min of irradiation when ZnO was used and in 60 min, when TiO_2 was used at the same temperature. The results indicate that the degree of photocatalytic decolorization of cobalamin was obviously affected by different parameters such as, catalyst mass, type of catalyst and addition of H_2O_2.

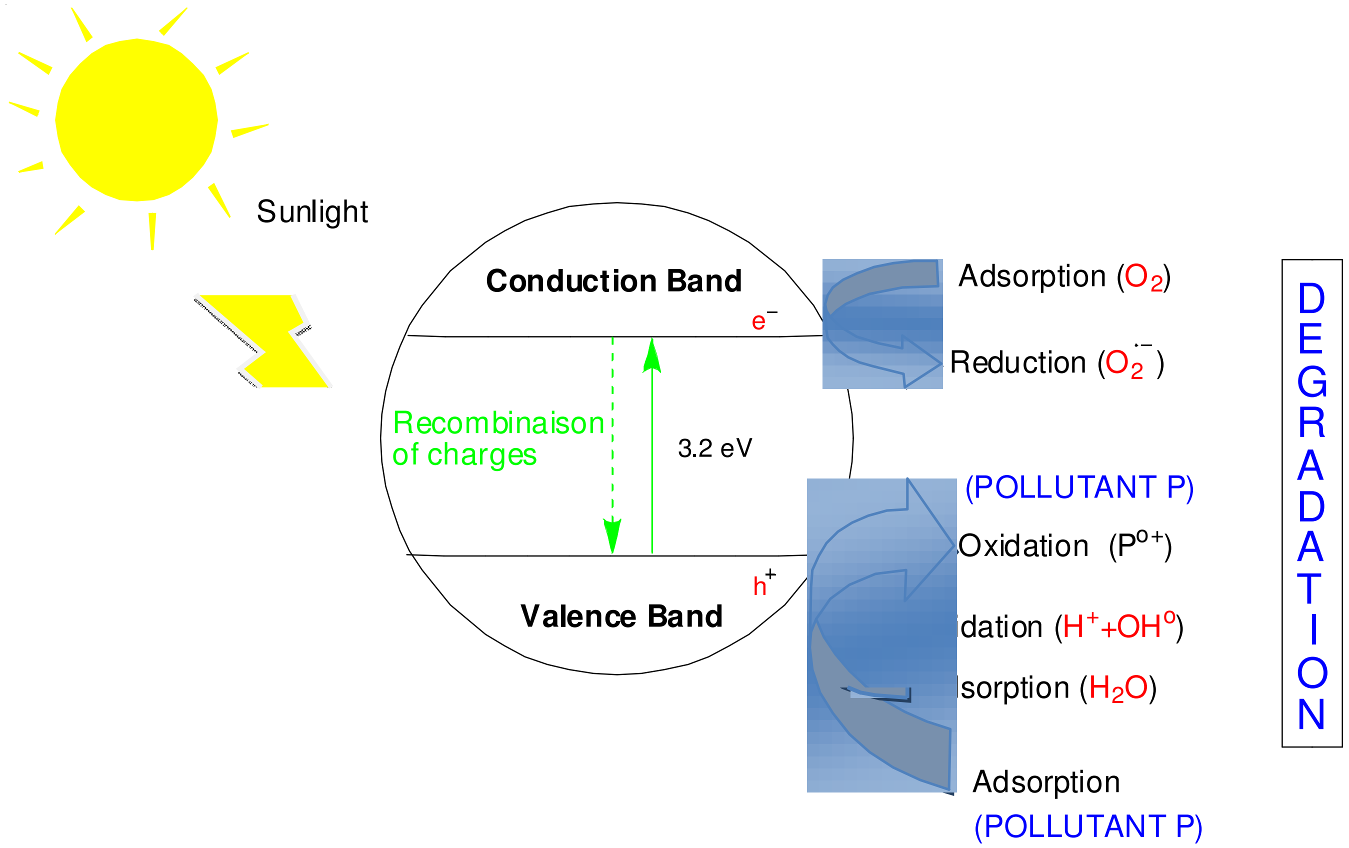
Keywords: Solar, Photocatalytic reactions, Cobalamin, Titanium dioxide, Zinc oxide, Decolorization efficiency.

INTRODUCTION

Sunlight is commonly used as a source for photocatalytic degradation of organic pollutants because it is safe, free and has a wide range of electromagnetic radiation[1,2]. Solar spectra contain about 4 % of ultraviolet light[3]. It is possible in solar photocatalytic degradation process to complete mineralization of toxic organics. It is also possible to remove and recover toxic metals. It is by sunlight catalyst can be activated and from other applications of solar photocatalysis disinfection of drinking water may be included without the use of chlorine, but by using a UV transparent solar collector[4-6]. Solar disinfection of water (SODIS) is a simple and low cost technique used for disinfection of drinking water by placing the infected drinking water in transparent containers and exposing to direct sunlight. This technique can be enhanced in the existence of semiconductors[7-9].

The removal of color from wastewater is more important than the removal of other colorless chemicals[10,11]. The products resulted from the degradation process should be non-toxic or at least less toxic than the degraded original compound[12,13]. The energy captured by plants from sunlight leads to the process which leads to the oxidization of water by oxygen reducing carbon dioxide. In other words, the oxidation of water and the reduction of CO_2 are achieved by solar energy[14,15]. Since sunlight is the available natural energy source, it can be used for the irradiation of semiconducting materials[16,17]. Heterogeneous photocatalysis is a method used for the degradation of various types of organic pollutants in water and wastewater[18,19]. Different types of semiconductors such as TiO_2, ZnO, CdS and ZnS and irradiation source 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[20,21]. In the illumination of an oxide semiconductor, usually different types of titanium dioxide anatase or rutile produce photo excited electrons (e^-) and positive charged holes (h^+). The complete degradation of many organic pollutants occurs through one of the mechanistic pathways as follows:

Heterogeneous photocatalysis uses atmospheric O_2 as oxidant because of having the properties to scavenger the electrons from the conduction band and may cause complete degradation, detoxification and mineralization of the cobalamin[22,23]. Heterogeneous photocatalysis is an important technology to destruct the organic pollutants including organic reactive cobalamin leading to the total mineralization[24,25].



Scheme-I: General mechanism of the photocatalysis on semiconductor particle

Semiconductor used as catalyst in heterogeneous reaction are characterized by an electronic band structure in which the highest occupies energy band called valence band (vb) and the lowest empty band in zero Kelvin is called conduction band (cb). The two layers are separated by a band gap that is the region of forbidden energies in a perfect crystal. When a photon has the energy equal or higher than the band gap energy which promoting an electron from valance band to conduction band for a semiconductor particle surface, this electron promoted from the valance band to the conduction band leaving positive hole (h^+) in the valance band. These electrons and hole pairs can be recombined on the surface or in the bulk of the particle in a few nanoseconds and the energy is dissipated as heat or can be trapped in surface states where they can react with donor or acceptor species adsorbed or close to the surface of the particle[23].

The idea of this work was derived from the announcement of Nine Sigma 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 absorbent surfaces. The aim of this study was to investigate the photocatalytic decolorization of cobalamin in aqueous suspensions of TiO_2 and ZnO under solar irradiation.

EXPERIMENTAL

The measurements of specific surface area Brunaure-Emmett-Teller (B.E.T) of ZnO and TiO_2 (DegussaP25), were carried out employing a micrometrics automate 23 instrument. The gas mixture used in all experiments was 70 % helium and 30 % nitrogen gas. Samples were heated to 150 °C for 1 h to clean the surface from adsorbed organic compound and water. The nitrogen gas adsorption and desorption isotherms at 77 K were measured using a Quantachure Autosorb 3B after the sample were vacuum dried at 200 °C over night.

Photocatalytic reactions: Different types of photocatalytic reactors were experimented in this work. Irradiations 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 titanium dioxide or zinc oxide containing cobalamin in beaker, under magnetic stirring, were irradiated in light of wavelength 365 nm. In all experiments, the required amount of the catalyst was suspended in 100 cm^3 of aqueous solution of cobalamin. After illumination, 2 mL was taken from the reaction suspension, centrifuged at 4,000 rpm for 15 min in an 800 B centrifuge and filtered for two times to remove the particles. The second centrifuge was found necessary to remove fine particle of the titanium dioxide or zinc oxide. After the second centrifuge, the absorbance at the maximum wavelength of the cobalamin was measured with UV-visible spectrophotometer at 298.15 K.

The apparatus used for photocayalytic reaction is shown in Fig. 1. The lamp was positioned perpendicularly above the beaker. The mercury lamp was allowed to warm up for 3 min to ensure a stable light intensity before commencing a reaction. This system is consists four platforms, so a set of 4 experiments could be carried on at the same time.

The apparatus used of solar reactor is shown in Fig. 2.

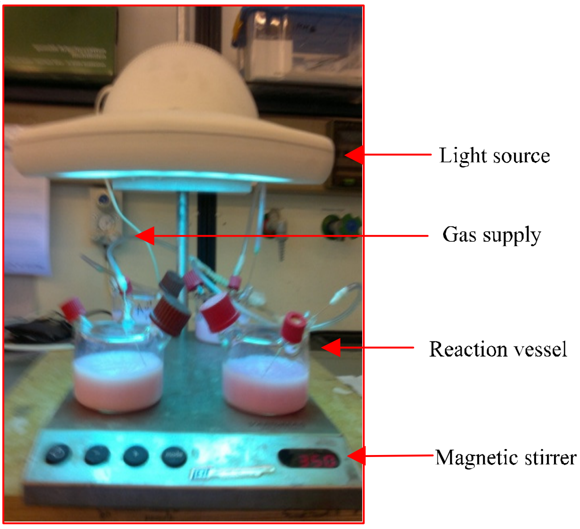


Fig. 1. Photocatalytic reactor

Fig. 2. Solar reactor

RESULTS AND DISCUSSION

The measurements of specific surface areas of the catalyst were analysized by Brunauer-Emmett-Teller method based on the nitrogen adsorption/desorption isotherm. Increase in the rate of degradation with increase in amount of catalyst is due to availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst then hydroxyl radicals and super oxide ions (O_2^-) are increase. In these experiments used [ZnO, TiO_2 (DegussaP25)] and measured by using B.E.T method. The results listed in Table-1 show that the surface area of different types of catalyst under the experimental condition temperature equal to 393.15 K and the gas pressure range between 1.1-1.2 bar[23].

TABLE-1
SURFACE AREA OF ZnO AND TiO_2

Type of catalyst	Measured surface area /(m^2g^{-1})	Standard surface area /(m^2g^{-1})
Zinc oxide(ZnO)	5.78	7.11
TiO_2 DegussaP25	48.11	50

Effect of solar radiation: The influence of solar light on the decolorization of the cobalamin was studied at various time intervals as shown in Fig. 3. From these results it is found that the photodecolorization of cobalamin increased with increasing solar light intensity .The maximum degradation (99 %) of cobalamin was observed [concentration of cobalamin 40 ppm and 350 (mg/100 mL) ZnO] and maximum degradation (96 %) of cobalamin was observed pconcentration of cobalamin 40 ppm and 175 (mg/100 mL) TiO_2]. In Iraq intense sunlight is available almost throughout the year and hence solar light could be effectively used for photocatalytic decolorization of pollutants in wastewater[26].

The result given in Fig. 3 shows the relationship between photodecolorization efficiency (PDE) and irradiation time for catalyst in presence of solar radiation. These results indicate that the photodecolorization efficiency increased with increasing solar light intensity. One of possible explanation for such behavior is that the electron-hole formation is predominant and hence, electron-hole recombination negligible. However, at lower light intensity, electron-hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the percentage degradation of cobalamin[27-30].

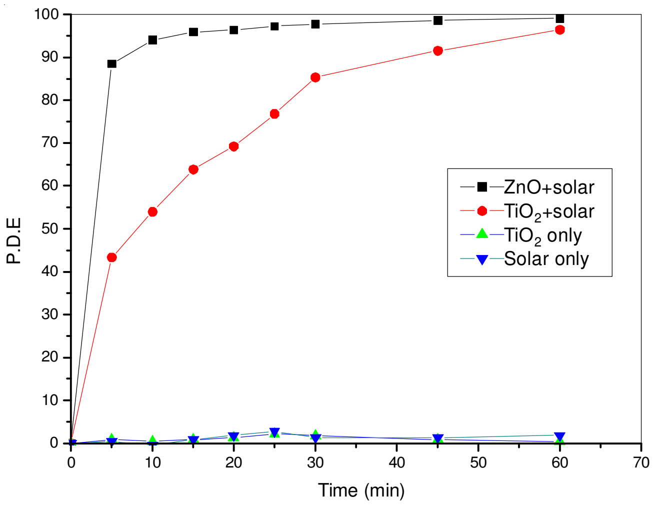


Fig. 3. Photodecolorization efficiency with irradiation time by using solar radiation

Effect of addition of [H_2O_2] for TiO_2 (DegussaP25): Hydrogen peroxide (H_2O_2) plays an important role in the production of hydroxyl radicals. In these experiments TiO_2 (DegussaP25) was used as photocatalyst to degrade of cobalamin in the aqueous suspensions under the determined experimental condition, light intensity equal to 1.3 mW cm^{-2}, solution pH equal to 7.8, temperature equal to 298.15 K , TiO_2 (DegussaP25) concentration 175 (mg/100 mL) and initial cobalamin concentration of 40 ppm. The effect of using different concentration of hydrogen peroxide (H_2O_2) in the range between (0.1-4) mmol L^{-1} are shown in Fig. 5. The results in Fig. 5 show that the rate constant of reaction increases with increase of the hydrogen peroxide concentration. Fig. 4 shows the UV-visible absorption spectra of cobalamin at different concentrations of H_2O_2 by TiO_2 (DegussaP25)[31].

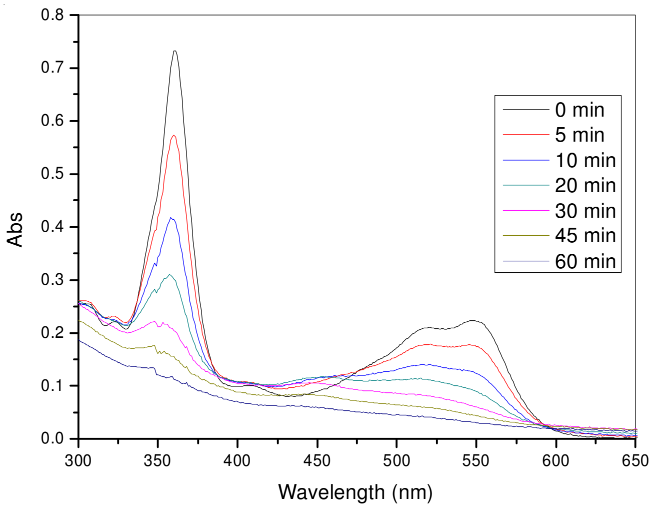


Fig. 4. UV-visible absorption spectra of cobalamin at (0 mmol L^{-1} H_2O_2)

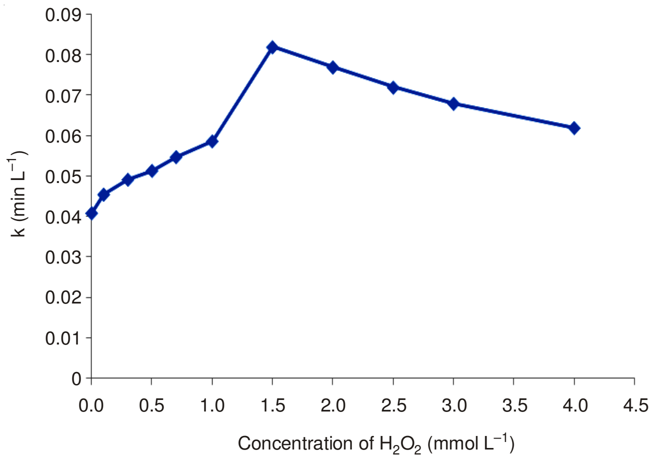


Fig. 5. Effect of addition of $[H_2O_2]$ on rate constant by TiO_2 (DegussaP25)

The effect of addition of H_2O_2 on the decolorization rate was studied for photocatalytic decolorization of the cobalamin. The results plotted in Fig. 5 show that the decolorization rate increases with the increase of concentration of H_2O_2 from 0.1 to 1.5 mmol/L, becomes maximum at 1.5 mmol/L and then $^{\bullet}OH$ starts decreasing from 1.5 to 4.0 mmol/L with increase in the concentration of H_2O_2[32].

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

$$H_2O_2 + e^{-}_{cb} \longrightarrow {}^{\bullet}OH + OH \quad (1)$$

$$H_2O_2 + {}^{\bullet}O_2 \longrightarrow {}^{\bullet}OH + OH \quad (2)$$

At high concentration of hydrogen peroxide H_2O_2 the photocatalytic processes decrease because of its hydroxyl radical scavenging effect, according to the following equations[33].

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (4)$$

Recovery of titanium dioxide: Titanium dioxide is regarded as friendly of environment, because we can reuse it more times. The results in Fig. 6 show the relationship between the photodecolorization efficiency (PDE) with number of recovery for the surface of TiO_2 (DegussaP25) under the experimental conditions, initial cobalamin concentration of 40 ppm, solution pH equal to 7.8, light intensity is equal to 1.3 $mWcm^{-2}$, TiO_2 (DegussaP25) concentration 175 (mg/100 mL) and the temperature equal to 298.15 K. The first column gives a maximum of photodecolorization efficiency % and then slight decreases[34].

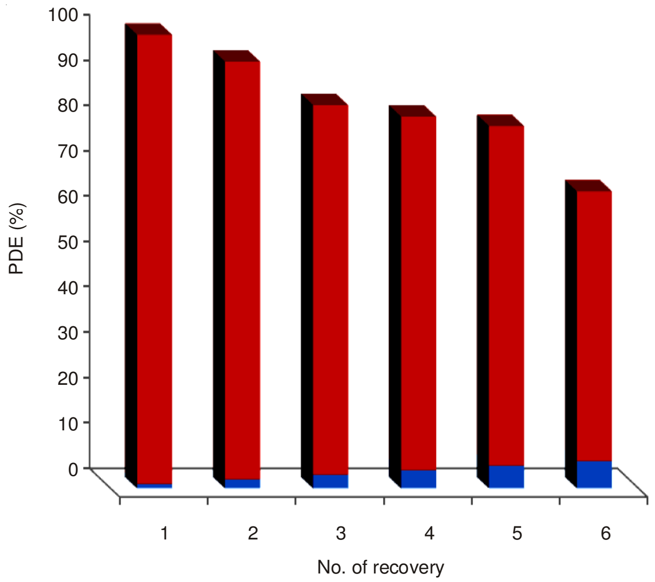


Fig. 6. Number of recovery for TiO_2 (DegussaP25)

Conclusion

Investigation of the photocatalytic decolorization of cobalamin under different experimental conditions led to the following conclusions:

- The existence of catalyst and lights is essential for photocatalytic degradation of cobalamin.
- Solar photocatalytic treatment is an efficient technique for decolorization of cobalamin through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time.
- Visible light/ZnO and visible light/TiO_2 systems could be efficiently used for photodegradation of cobalamin. The results indicate that the degree of photodegradation of cobalamin was obviously affected by different parameters. The complete removal of color could be achieved in a relatively short time of about 10 min, when ZnO was used under solar irradiation.
- The procedure used in this research can be used as an efficient technology for solar photocatalytic degradation of the cobalamin under natural weathering conditions.

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