Photocatalytic Degradation using a Nanocomposite of Multi-walled Carbon Nanotubes and TiO_2 Nanoparticles

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Abstract

Multi-walled carbon nanotubes (MWNTs) with titanium dioxide (TiO_2 -P25) were synthesized by simple dipping and evaporation method. This method was used for synthesis of different ratios of titanium dioxide loaded on MWNTs (P25/X%MWNT, where X=0.25, 0.5 and 1). Experimental results also proved that MWNT/ TiO_2 nanocomposites display relatively higher photocatalytic activity than TiO_2 for the photocatalytic degradation of Cobalamin. The enhancements in the activity for the nanocomposites in the existence of MWNTs or synergetic effect were explained to be related to the increasing of the surface area of synthesized composites and the transition of the excited electron from conduction band (CB) of TiO_2 to the surfaces of MWNTs leading to reducing the recombination of formed electrons and holes.

Keywords: MWNT, P25-TiO_2, composite, Cobalamin degradation, adsorption.

الخلاصة

الكاربون النانوي الانبوبي متعدد الجدران مع ثاني اوكسيد التيتانيوم حضر باستخدام طريقة التحميل . هذه الطريقة استخدمت لتحضير نسب مختلفة من التيتانيوم المحمل على تراكيز مختلفة من الكاربون النانوي الانبوبي متعدد الجدران وهي 0.25, 0.5, 1% من الكاربون النانوي متعدد الجدران الى ثاني اوكسيد التيتانيوم.النتائج بينت ان المتراكبات المحضرة بينت زيادة في الفعالية الضوئية للتيتانيوم بوجود الكاربون النانوي الانبوبي مقارنتا مع ثاني اوكسيد التيتانيوم لوحده والتي اختبرت لتفاعل الازاله اللونيه للكوبل امين . زيادة الفعالية كانت مرهونه بزيادة نسبة الكاربون في المتراكب .زيادة الفعاليه بوجود الكاربون النانوي الانبوبي فسرت على اساس زيادة المساحة السطحية للمتراكب المحضر وقدره الكاربون النانوي على مسك الالكترون المثار من حزمة التوصيل مما يقلل من نسب اعادة اتحاد الالكترون المثار مع الفجوة الموجبة الشحنة.

الكلمات ألمفتاحيه: الكاربون النانوي متعدد الجران, ثاني اوكسيد التيتانيوم, متراكب, تحطيم الكوب لامين, امتزاز.

Introduction

A composite material can be defined as an attempt to create new material by a combination of two materials or more that produces new characteristics in better properties as compared with those of the individual components used alone (Zeleska, 2008). Most synthesis composites are made by combined two materials only, one is the matrix which represents the higher ratio, and surrounds with other material, which is called the reinforcement within binds for important reason, this produces development process to achieve a reduction in product development time, production costs, enhance the activities, suitable for different conditions and quality defects (Hambali *et al.*, 2009). One of the most important Binary composites in the last twenty-four years is semiconductors composites with carbon material such as active carbon (Arana, 2003), black carbon(Gong *et al.*, 2011), graphene (Tan *et al.*, 2013), Fullerene (Oh *et al.*, 2007), carbon nanotubes (CNTs) (Wen *et al.*, 2013). This study deals with binary composite which consists of carbon nanotubes (CNTs) with TiO_2. Carbon nanotubes (CNTs) are rare structure materials which consist of carbon atoms band with each ether within sp^2 hyperdization, forming graphene layers wraps to forming tubular figure(Chae and Lee, 2014). Carbon nanotubes can be classified into three types which are single walled carbon nanotubes (SWNTs), few walled carbon nanotubes (FWCNTs), and multi walled carbon nanotubes (MWNTs) (Kenan *et al.*, 2013). The mainly methods which commonly depend on the synthesis of carbon nanotubes include arc discharge (Muhammad and Rafigue, 2011), chemical vapor deposition (Grebenykov *et al.,* 2008), and laser ablation (Scott *et al.*, 2011), With the development on synthesis technology process of CNT, the coast of CNTs has reduced significantly(Wilson *et al.,* 2012; Oh, 2009). which encourages using it in many applications with different types of semiconductors such as hydrogen production (Liao *et al.,* 2012), removed of pollutant (Kuo, 2009), full cell (Annamalai and Tao, 2013) and solar cell (Kongkan *et al.,* 2007). titanium dioxide (TiO_2) is an n-type semiconductor material with the range of band gap from 3 eV to 3.2 eV (Szlachetko et al., 2014) which represent one of the main disadvantages of TiO_2 because the most used photocatalyst with specific requires excitation with UV light due to its wide band gap (Yin *et al.*, 2010). Many methods are used to reduce this problem one of them is represent by Doping metal such Pt, Pd, Au, and Ag (Chen *et al.*, 2010) or nonmetal elements, such as nitrogen, sulfur, and also carbon, have been investigated to increase photocatalytic activity of TiO_2-based materials(Asahi *et al.,* 2001; Ohno *et al.*, 2004; Huang *et al.,* 2008).

All of these methods aim to increase the activities of TiO_2 by using the principle of composite. The collection process for MWNTs with TiO_2 in new composite depends on many causes: one of them suggests that carbon nanotubes behave as a semiconductor supports because of their combination of physiochemical properties which include excellent conductance, high abilities for adsorption, (Wang *et al.*, 2005). A similar literature has shown that the activities of TiO_2 increased due to abilities of CNTs to decrease TiO_2 crystalline grain and particle sizes(Lee et al., 2007), or increased in the activity of the particles because the direct interaction between CNTs and TiO_2 reduces the recombination of (h+/e-) (Yao *et al.,* 2008). generally, It is believed that the change on activities can be related to the TiO_2–CNTs bonding which can be formed through some physic/chemical interactions such as Vander Walls interaction . The coupling out situ effect of P25 with MWNTs has been shown to provide a synergistic effect which can enhance the overall reaction of photocatalytic degradation. In this work TiO_2 was tested to facilitate enhancement in activity out situ by using a specific type of titanium dioxide, which is P25 and consists of two phases 80% Anatase and 20% Rutile, with three percentage ratios of multi walled carbon nanotubes MWNTs. The activity of the synthesis composite was measured by making a degradation of Cobalamin ($C_{63}H_{88}CoN_{14}P$). Cobalamin is vitamin B12, commonly known as a complex compound of an organometallic species which is distinguished by the cobalt atom in a Corrine ring (Quaroni *et al.,* 1995).

2-Chemicals

The MWNTs, used in this study were purchased from Aldrich. According to the product specifications, the two compounds were fabricated by a chemical vapor deposition method. While the MWNTs 95% carbon nanotubes had a mode diameter of 5.5. TiO_2 sample was purchased from Degussa, Germany (TiO_2-P25) and the CyanoCobalamin purchased from Sigma with purities of more than 98.5%.

3- Preparation of Binary composite

TiO_2/carbon binary composites were prepared by a simple evaporation method. First, the MWNT was treated with mixture of acid HNO_3/H_2SO_4 (1/3) to activate the surfaces in order to exist in an ultrasonic system for 7h (Kevin *et al.,* 2011) washing and drying at 100^{o}C. Different ratios of activated carbon nanotubes were dispersed in water in a 200-mL beaker and sonicated for 20 min. Commercial TiO_2 powder

(Degussa P25; Anatase and Rutile mixture (8:2) with a BET area of. 50 m^2/g) was added to the suspension at ratios of 0.25, 0.50, and 1.00% (MWNT:TiO_2) during sonication . The mixed suspension was filtered by using a vacuum evaporator (the Rota vapor re121 BUSHI 461 water Bath) at 45 °C to accelerate the evaporation of the water. After the water evaporation, the composite was dried overnight in an oven at 104 °C to avoid any physicochemical change in the carbon materials that occurs at higher temperatures in the presence of oxygen.

4- Measuring the activity of the composite

The photocatalytic activities of the P25, and x%MWNT/P25 (x=0.25, 0.50, 1.00) were determined by the decomposition of the Cobalamin in an aqueous solution under UV light with light intensities of 1.3 m W/cm^2. The catalysts (175m g) were suspended in 100 mL of Cobalamin solution with a concentration of 40 ppm in a glass vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium among the photocatalyst, the Cobalamin and the atmospheric oxygen, which was then considered as the initial concentration. The light irradiation of the reactor was done for 60 min and the removal of the dispersed powders through a centrifuge. The clean transparent solution was analyzed using a UV–Vis spectrophotometer. The spectra (300-700 nm) for each sample were recorded and the absorbance was determined at the characteristic wavelength at 550 nm.

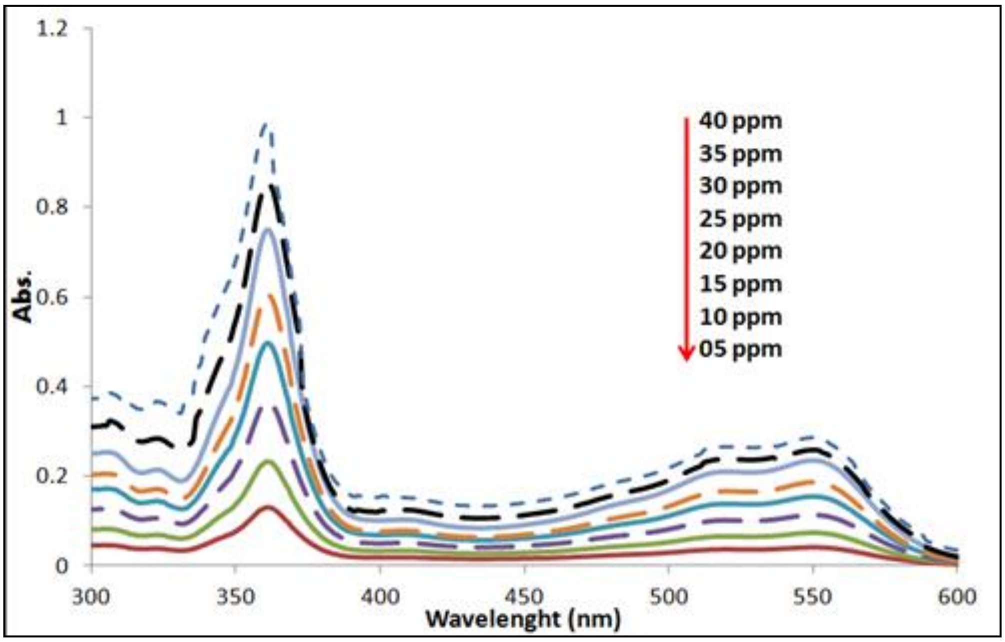

Figure 1. Spectrum of the UV-vis spectroscopy for Cobalamin with different concentrations.

The decolorizing processes of Cobalamin in existence of pare P25 and with three types of synthesis composite as a photocatalyst shows clear changes in activity for synthesis composites. The decolorizing activity of P25 increases greatly in the existence of MWNTs, which enhance the adsorption for a synthesis composite more than P25 alone within the range of this work which is presented in Fig 8.

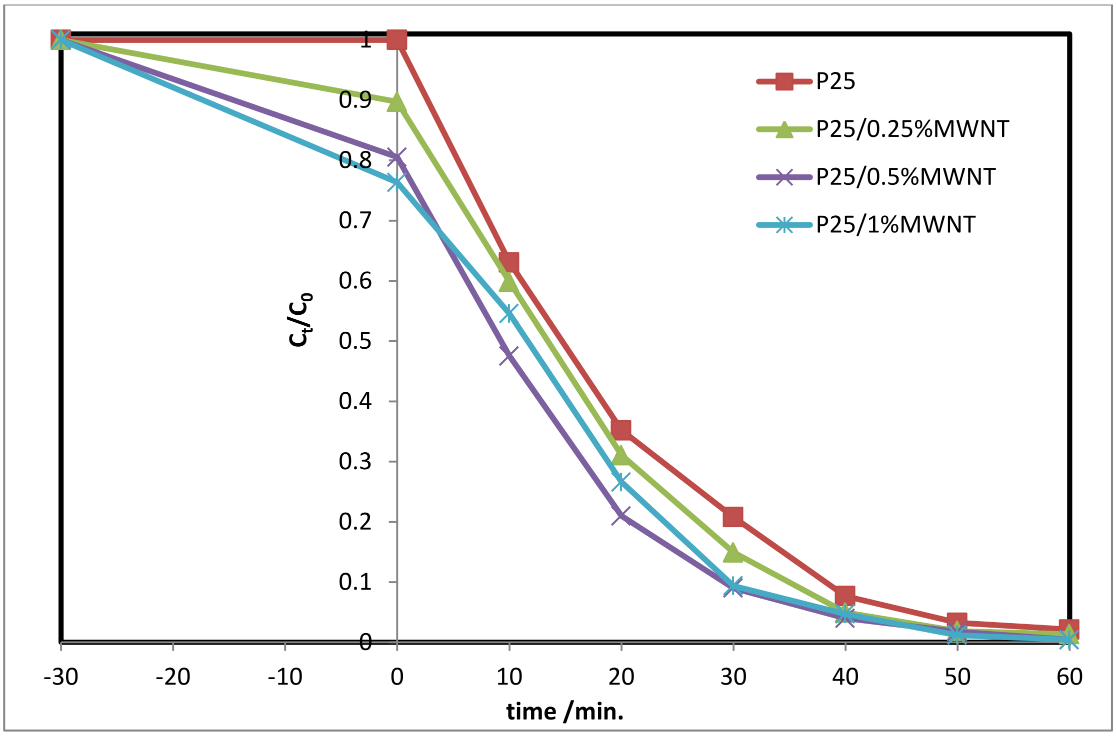

Figure 2. Degradation reaction for (175mg) pare P25 ,0.25%MWNT/P25, 0. 5%MWNT/P25 and 1%MWNT/P25 with 40 ppm Cobalamin at 298K in existence of O_2 gas and light intensities of 1.3 m W/cm^2.

The photodegradation experiments by the UV irradiation of the Cobalamin solutions follow the pseudo-first-order kinetics with respect to the concentration of dyestuff in the bulk solution (C):

$$-\frac{dC}{dt} = K_{app}\, C$$

When making an integration for this equation and by using the same restriction of C = C_0 at t = 0, and C_0 being the initial concentration in the bulk solution before starting the light reaction), thus the equation becomes.

$$\ln\left(\frac{C_0}{C}\right) = K_{app}\, t$$

where K_{app} is the apparent reaction rate constant. A plot of ln (C_o/C_t) versus t for Cobalamin degradation with different composite of MWNT/TiO_2 photocatalysts is presented in Fig. 2. The value of K_{app} can be obtained directly from the slopes of the respective linear curves in Fig 3. Comparing the K_{app} for the photodegradation of Cobalamin with P25 and the three types of composite, the photolysis of Cobalamin without a catalyst shows that the sources of illumination did not make any photolysis for Cobalamin.

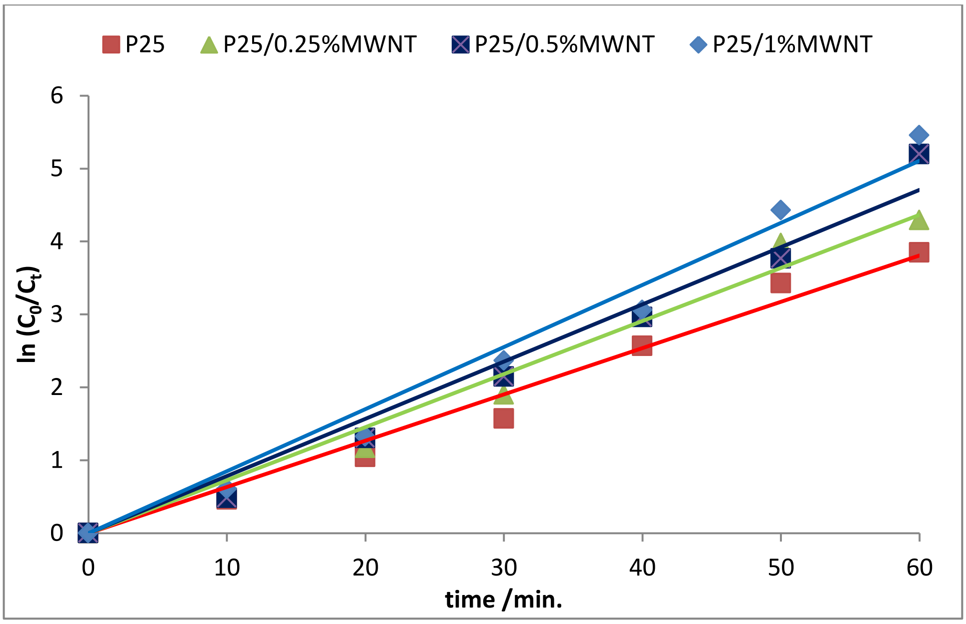

Figure 3. Rate constant for the degradation reaction of different ratios (175mg) MWNT/P25, and pare P25, with40ppm Cobalamin at 298K in the existence of O_2 gas and light intensities of 1.3 mW/cm^2.

Table 2. Summary of the UV- light photodegradation of Cobalamin on three ratios composites of MWNT/P25 .

Sample	$C_{0\ ppm}$	k s^{-1}	R	TOC_{8h}
P25	≈ 40	0.064	1.00	79.12
P25/0.25%MWNT	35.89	0.072	1.12	83.14
P25/0. 5%MWNT	31.14	0.078	1.21	87.48
P25/1%MWNT	32.21	0.085	1.32	90.37

The synergy factor (R) is expressed as the following equations

$R = k_{app}$ (CNT/P25)/ k_{app} (P25)

When k_{app} (CNT/P25) , k_{app} (P25) refers to the apparent rate constant for the decolonization in the existence of the composite and P25 respectively (Claudia *et al.*, 2008). From the results above it can be seen that the MWNTs exist causing an increase in decolonization rate, which is attributed to two reasons the first was the increase in ability of the adsorption for P25 with the existence of MWNTs in the composite, which was clearer with 1%MWNTs as compared with pare P25. The existences of MWNTs within the P25 matrix caused a new creation of a kinetic synergetic effect for the process of photodegradation more than the P25 without MWNTs because of the physical properties of the adsorption for this types of carbon nanotubes which reduces the concentration of Cobalamin in a dark reaction before a light reaction as shown in Fig. 7, table 1 shows the value of adsorption at the equilibrium in the dark reaction which represents a starting point for the decolonization process with three compounds.

The synergetic effects on Cobalamin removal for the three percentage of MWNTs in the composite which is used in this study indicates an increase in the activity of the binary composite, thus may be correlated to the UV- vis light absorption spectra and also the change in adsorption for the composite. at the same time the increases in activity did not continue for the high ratios of MWNTs because the shielding effect which reduces the amount of UV-light which can be absorbed by composite due to reducing the penetration for light to the TiO_2 surfaces (Khan *et al.*, 2013). A proposed mechanism for the enhanced photocatalysis of the MWNT/P25 composites is shown schematically in Fig. 4.

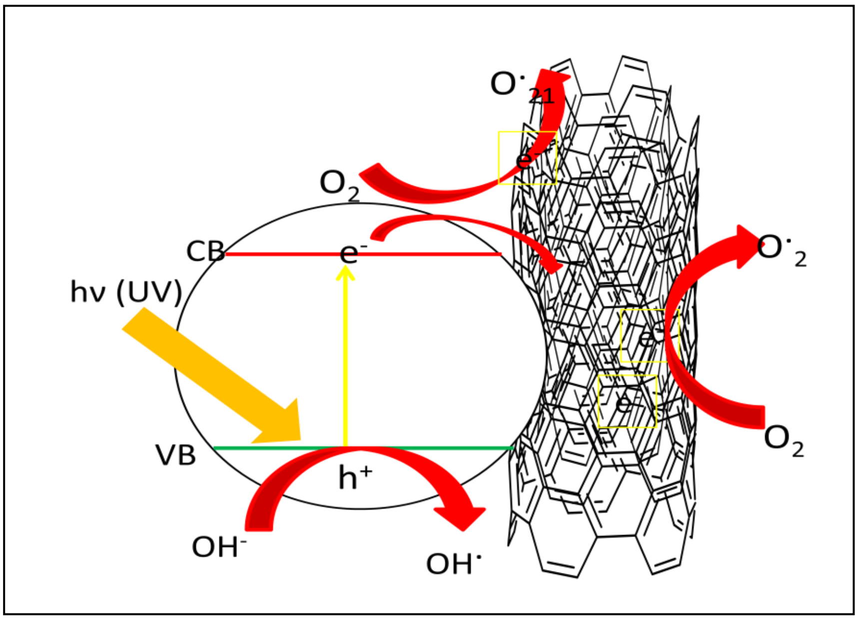

Figure 4. Schematic of a proposed model for the MWNT/P25 mechanisums.

Under UV illumination electrons are excited from the valances band to the conduction band of the P25, which leads to the formation of positive hole h^+ in the valance band and a negative charge in conduction band e^- . The state of the two active sites in the absences of MWNTs was that most of these two charges will recombine quickly while losing most sites which may react chemically, only <1% of the electrons and the hole will react (Li *et al.*, 2007) .The band gap for P25 is about 3.18 e V (Valencia *et al.*, 2010) while the band gap for the MWNTs which o.5 eV (Bickley *et al.*, 1991), thus when the MWNTs attached to the surfaces of the P25, the excited electrons in the conduction band of the P25 will be transferred to the surfaces of the CNTs which will allow for their separation, and will prevent or at least reduce the recombination process and separation for the charges (Robel *et al.*, 2005).

The last process will lead to an increase in the live time for the hole which forms $OH^•$ in high concentrations and at the same time the excited electrons will react with the O_2 gas to form superoxide. The addition of small percentage of MWNTs to the semiconductors increases changes in conductivity (Xu *et al*., 2010) which explains the changes in activity for the P25 when different ratios of MWNTs are added to form binary composites, and also causes them to reduce the particle size of the binary composites which leads to the enhanced photocatalytic activity.

To test the ability of the used synthesis composite many times, the three types of composite were tested three times which show a good efficiency for the recycling, of the photocatalysts

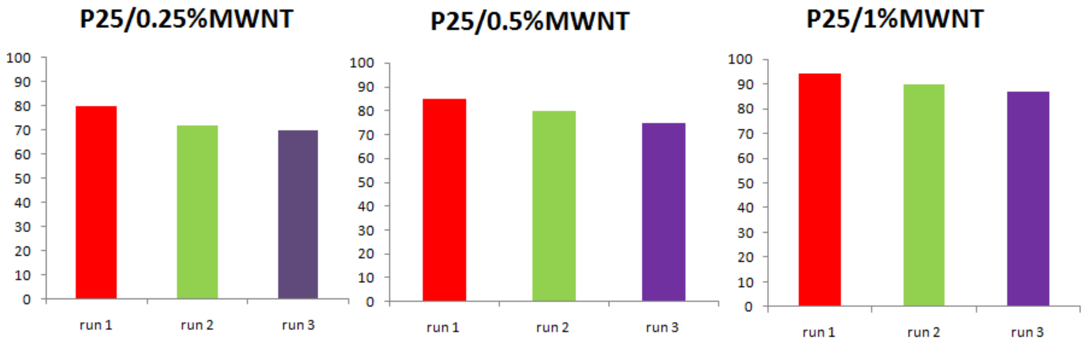

Figure 5. The efficiency of three composite to reused three times.

5-Conclusions

The coupling effect of the adsorption/photocatalitc which accrued between the carbon nanotubes by using the MWNTs with TiO_2 represents the key for the high efficiency of decolonization and the process of mineralization for Cobalamin. This study demonstrates that the charge transfer is very sensitive and affected by the percentage of carbon nanotubes and at the same time the increase in the ability of the new synthesis composite on the adsorption as compared with a pristine semiconductor is not considered the only condition that enhances the effectiveness of its existence, but with a property of good conductivity certainly gives a clear variation in potency, thus MWNTs appears more able to enhance the activities of P25 as compared with pare P25.

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