Degradation of Organic Dyes using Photo-Catalytic Technique

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ABSTRCT

The present investigation is concerned to study the prepared of nano composite catalyst of titanium dioxide and carbon nanotube (TiO_2/CNT) based on photo-catalysts process. The synthesized composite catalyst was characterized by Brunauer, Emmett and Teller (BET), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), XRF and Raman Spectroscopy. Moreover, the nano composite catalyst was used as a dye to degradation of contaminated water that containing organic pollutants. The photo-catalytic degradation process was carried out at different operational parameters, (Initial concentration of hydrogen peroxide H_2O_2 of the medium, mixing speed, and flow rate for methylene blue (MB, $C_{16}H_{18}N_3SCl.3H_2O$) dye). The nano titanium dioxide / carbon nanotubes (TiO_2/CNT) composite showed greater photo-degradation activity under solar and ultraviolet (UV) lamp.

Keywords: photo-catalytic, carbon nanotubes, Titanium dioxide, Dyes degradation, nano technique.

تكسر الاصباغ العضويه بتقنية المحفز بالضوء

م.م اياد داري جعفر

قسم الهندسة الكيمياويه

الجامعة التكنولوجية

الخلا صة

يتناول البحث دراسة تحضير العامل المساعد النانوي المركب من اوكسيد التتانيوم وانابيب الكاربون(TiO_2/CNT) لعملية التحفيز بالضوء, حيث تم دراسة خصائص العامل المساعد بقياس المساحة السطحية للمركب المحضر باستخدام طريقة (BET), و تقنيات المجهر الالكتروني الماسح(SEM) , XRD, XRF ومقياس رامان. علاوة على ذلك استخدم العامل المساعد النانوي المركب لتكسير ملوثات المياه العضويه مثل الاصباغ . بعد ذلك تمت دراسة عدة عوامل مؤثرة على عملية التكسر في عملية المحفز للضوء (التركيز الابتدائي لبروكسيد الهيدروجين H_2O_2 (mg/L), وسرعة الخلط (rpm), والجريان الحجمي للصبغة والعامل المساعد (L/min)). اظهر العامل المساعد النانوي كفاءة عالية تحت تاثير اشعة الشمس والاشعة الفوق البنفسجية.

مفاتيح الكلمات: المحفز بالضوء, كاربون نانوتيوب, اوكسيد التيتانيوم , تكسر الصبغة, تقنية النانو.

INTRODUCTION

Degradation of organic pollutants and dyes such as methylene blue, bromo phenol blue, and Chicago sky blue from industrial waste water remains as a challenge because of low visible light photo catalytic activity of metal oxides and sulphides [1].

The possibility of combining heterogeneous catalysis with solar technology to achieve complete mineralization of toxic organic pollutants has received much attention [2]. Multi-walled carbon nanotubes (MWCNTs) could be considered as a good support for materials with field emission displays and photo-catalytic properties. On the other hand, a combination of Titanium dioxide (TiO_2) and MWCNT could create many active sites for the photo-catalytic degradation [3].

Advanced chemical treatment processes are used many times to achieve better treated water quality for use and also when the necessary standards are not being met with the conventional means of treatment [4].An advantage of photo-catalytic method includes low temperature, low expenses and also radically low level of energy consumption in this method [5].

Won C. O. and Ming L. C. were used the activated carbon materials and TiO_2 composites by mechanical and hydrothermal treatment while demonstrated very good performance in the photo-catalytic degradation of methylene blue [6].

The Ferrous ion and TiO_2 units were covered on the activated carbon surface and were developed through a deposition process of a sol-gel method. The Ferrous–AC/TiO_2 samples show a strong degradation and can efficiently decompose the methylene blue (MB) solution under visible light (Za-Da Meng, Kan Zhang)[7].

Sonal S., Rimi Sh., Els., a comparative photo-catalytic study of $ZnFe_2O_4$ and ($ZnFe_2O_4$/multi wall carbon nano tubes) nano composite clearly indicated the enhancement of photo-catalytic activity in ($ZnFe_2O_4$/ multi wall carbon nano tubes) nano hybrid. MB was almost 84% degraded in the presence of $ZnFe_2O_4$ photo-catalyst, while 99% degradation was observed in case of $ZnFe_2O_4$/MWCNT composite after irradiation for 5 hours in the visible light [8].

In this work, the nano composite catalyst of titanium dioxide and carbon nano tube (TiO_2/CNT) was prepared based on photo-catalysts process. The synthesized catalyst was characterized using a different analytical technique. The effect of nano photo-catalytic TiO_2/CNT composite was also evaluated by methylene blue (MB) degradation in aqueous solution under an UV lamp and solar.

EXPERIMENTAL WORK

Catalysts Preparation

Nano-TiO_2 (5 gm) was added to the aqueous Fe (NO_3) and stirred for 3 hrs. Resultant suspension was filtered and solids were washed with D.I. water until its pH reaches 7. A washed solid was dried in vacuum at 60 ^{0}C for 2 hrs to obtain yellowish TiO_2 powder loaded with Fe^{3+} ions. It was coated on substrate and used in thermal furnace as a catalytic substrate. The above prepared catalytic substrate was placed at center of quartz tube in furnace at temperature 300^0C – 800^0C. It was then catalytically (Fe^{+3}) deposited over TiO_2 surface as CNTs, **(Fig.1)**.

Catalysts Characterization

The Scanning Electron Microscopy (SEM) of carbon nanotubes and carbon nanotubes-TiO_2 composite explain the different Morphology between the two prepared samples. The SEM images of 10,000 magnifications of the prepared catalysts are shown in **(Fig.2)** than indicates that the pure carbon nanotubes and composite materials present a homogeneous distribution of TiO_2 on the CNTs. So it was considered that nano CNT-TiO_2 composites could have much more activity and show an excellent photo-catalytic activity.

The XRD (model PANalytical X'Pert pro MPD) patterns of the nano TiO_2/CNT composites were displayed in **(Fig.3)**. The patterns demonstrate the highly crystalline nature of the composites. The characteristic peaks for CNT at position of $2\Theta = 26.5°$. And you could see peak TiO_2 at $2\Theta = 43.5°$.

BET surface area was measured using a Surface Area analyzer (Q-surf 9600, USA) were used to observe the surface of the TiO_2/CNT composites is 33 m^2/gm.
From **(Fig.4)** could be observed that the XRF for pure carbon nanotubes prepared until to 98% graphite. **(Fig.5)** shows Raman spectroscopy vs Wave number (cm^{-1}) revealed invaluable insights into the purification of nanotubes. G-band (1568 cm^{-1}) corresponded to the confirmation of MWCNTs. Defect induced D-band (1350 cm^{-1}) was minimized after purifying CNTs.

Photo-catalytic degradation of dye

The photo-catalytic effect of nano TiO_2/CNT composite was evaluated by methylene blue (MB) degradation in aqueous solution under solar and UV lamp (365 nm, 1.2 Mw/cm^2). Before turning on photo-catalytic unit, the solution mixed with composite and H_2O_2 for 30 min. Then, the solution was radiated with photo-catalytic unit, **(Fig. 6**).
Sample of methylene blue (MB) solution were withdrawn at the rate of (0.5, 1, 1.5 and 2 L/ min) and concentration hydrogen peroxide H_2O_2 (200,300,400 and 500 mg/L).The agitation mixing (100, 250, 750 and 1400 rpm) with 50 mg/L from composite catalyst and pH=7 for mixture to degradation the dye.

RESULTS AND DISCUSSION

(Fig.7) shows, the Degradation of the methylene blue MB (ppm) versus UV illumination time (min) at different mixing agitation (rpm). From these figure, the prepared catalysts show the high photo-catalytic activity and degradation of methylene blue (MB). The increment of nano (TiO_2/CNT) mixing in the composite (100, 250, 500, 750 and 1400 rpm) leads to increased photo catalytic activity and degradation ability. During initial 105 minutes the high degradation at mixing speed 1400 rpm at constant (flow rate for mixture 1.5 L/min, $C_{H2O2=}$ 300 mg/L, $C_{CNT/TiO2}$= 50 mg/L and pH=7) is 0.74, the dyes were rapidly degradation in all case due to the effect of the solid nano materials.
(Fig. 8) shows, the photo-degradation ability of the samples also improved with the increment of flow meter recycles for mixture (0.5, 1, 1.5 and 2 L / min). This indicates that the increasing flow rate for mixture (MB dyes with nano (TiO_2/CNT) composite) increase degradation of methylene blue (MB) until 1.5 (L/min) is 0.74. Then increasing flow rate to 2 (L/min) the degradation of dyes is 0.69 because at 1.5 (L/min) the better flow rate to distribution in photo-catalytic reactor and when this flow, the solar energy absorbed by nano composite is very sufficient to degradation the dye.
Carbon nanotubes CNTs might accept the photo-induced electron (e-) into the conduction band of the TiO_2 particles by (UV + solar) irradiation (Eq.1). It is considered that electrons in CNTs are transferred to the conduction band in the TiO_2 particles. In this time, the electrons in conduction band might react with ($O_2^{-}\cdot$). Simultaneously, a positive charged hole (h^+) might be formed with electron transfer from valence bond in TiO_2 to CNTs (Eq.3). The positive charged hole (h^+) might react with OH^- derived from H_2O**.** with this understanding, the role played by CNTs can be illustrated by injecting electrons into TiO_2 conduction band under (UV + Solar) irradiation and triggering the formation of very reactive superoxide radical ion ($O_2^{-}\cdot$) ((Eq.2 and hydroxyl radical $OH^{\cdot}$) (Eq.4)). consequently, both radical group (superoxide radical ion ($O_2^{-}\cdot$) and hydroxyl radical ($OH^{\cdot}$)) are responsible for degradation of the organic compound as MB.

$$CNT/TiO_2 \xrightarrow{hv} CNT^+/TiO_2^- \quad (1)$$

$$CNT^{+}/TiO_{2-} + O_2 \longrightarrow CNT^{+}/TiO_2 + O_2^{-} \cdot \quad (2)$$

$$CNT^{+}/TiO_2 \longrightarrow CNT/TiO_2^{+} \quad (3)$$

$$CNT/TiO_2^{+} + (H_2O \leftrightarrow H^{+} + OH^{-}) \rightarrow CNT/TiO_2 + H^{+} + OH \cdot \quad (4)$$

Plots the variation in dye degradation against hydrogen peroxide H_2O_2 concentration in solution keeping all other parameters unchanged. Different concentrations of H_2O_2 (200,300,400 and 500 mg/L) were added to study the effect of H_2O_2 concentration on the degradation process. The rate of degradation goes on increasing with the increase in concentration of H_2O_2 and becomes maximum at 300 mg/L (Degradation of methylene blue is 0.74) and then starts decreasing with further increase in concentration of H_2O_2 (Degradation of methylene blue is 0.62, 0.45 at C_{H2O2} is 400 and 500 mg/L sequentially) .The addition of H_2O_2 may play an important role in the limitation rate of photogenerated hole-electron pairs that contribute to degradation rate MB dyes, (**Fig. 9)**. As can be seen, the degradation increases with increasing initial concentration of H_2O_2, as the formation of hydroxyl radicals is insufficient, this may explain the ability of H_2O_2 to trapping the electrons preventing the electron-hole recombination hence decrease the chance for formation of $OH^{\bullet}$ radicals on the surface of the catalyst. However, as the initial concentration of H_2O_2increases beyond a certain value (300 mg/L), the increase in decomposition rate becomes less. This is because at higher H_2O_2 concentration, more $OH^{\bullet}$is produced leading to a faster oxidation rate. However, the excess free radicals prefer to react with the excess of H_2O_2 rather than with the dye.

CONCLUSION

The synthesis and characterization of nano TiO_2/CNT composites thermally derived from CNTs by an improved oxidation method because the conductive structure of the CNT scaffolds might facilitate the separation of the photo-generated electron/ hole pairs at the CNT-TiO_2 interface leading to the faster rates of photo-catalytic oxidation. In addition, the application of anodic potentials on irradiated TiO_2/CNT composites films might result in a further enhancement. The structural variations, elemental analysis and surface morphology were investigated through preparation of TiO_2/CNT composites under ultraviolet UV and solar light irradiation. The TiO_2/CNT composite showed greater photo-degradation activity under UV and solar light irradiation. Changes of color disappearance for relative methylene blue (MB) degradation concentration under UV and solar light irradiation in the solution as a function of time was studies. The MB degradation with CNT/TiO_2 composite was carried out to observe the UV photolysis effect.

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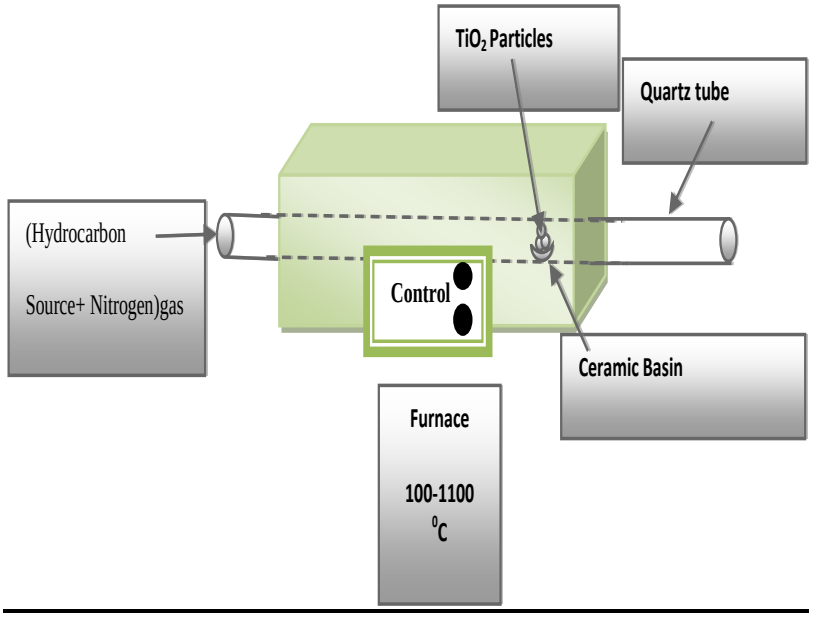

Figure (1): Carbon nanotubes deposit it TiO_2 Particles Process.

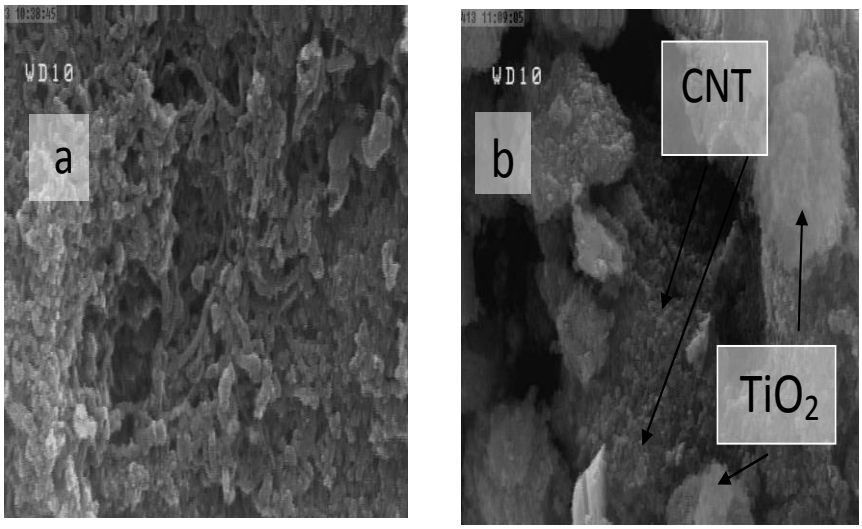

Figure (2): SEM images of the (a) functionalization of carbon nanotubes (b) Nano (CNT/ TiO_2)

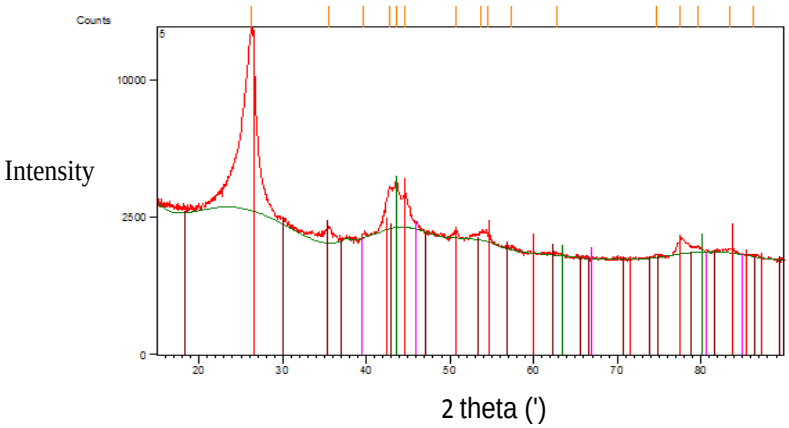

Figure (3): XRD of composite (TiO_2/ CNT)

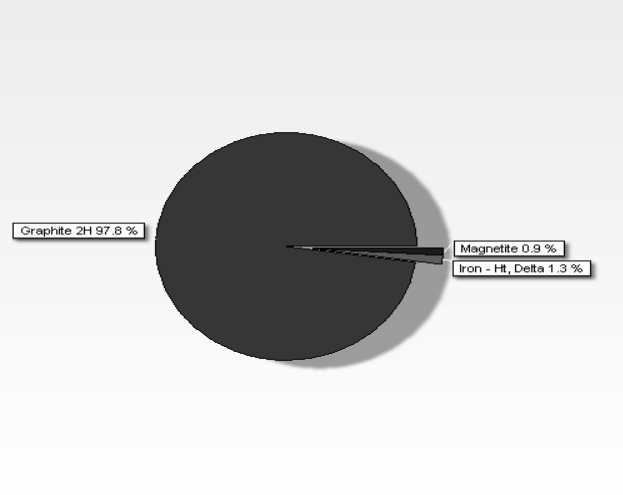

Figure (4): XRF of carbon nanotubes.

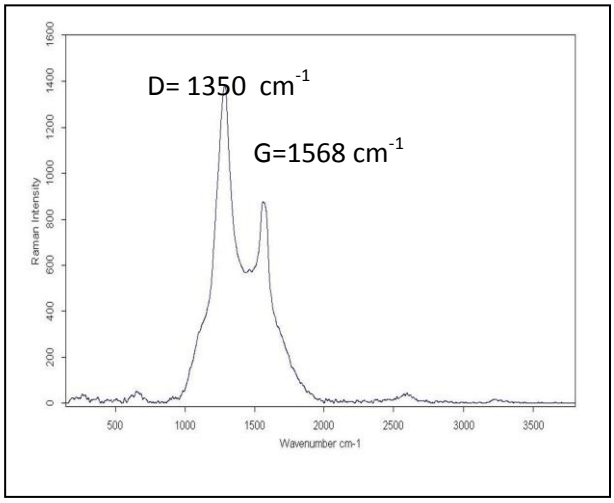

Figure (5): Raman spectra of nano composite

Figure (6): Photo-catalytic unit.

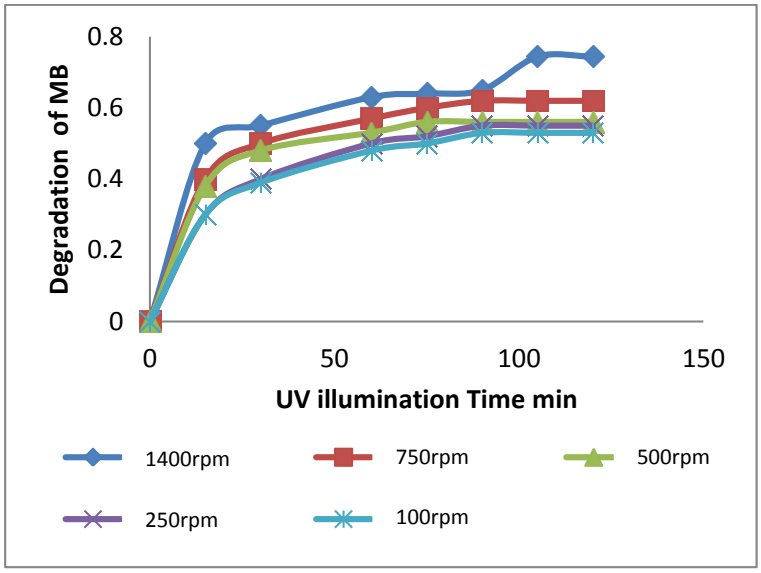

Figure (7): The Degradation of the methylene blue MB (ppm) with UV illumination time (min) at different mixing agitation (rpm) at constant C_{H2O2}= 300 mg/L and flow rate = 1.5 L/min, (pH= 7 and $C_{CNT/TiO2}$ = 50 mg/L).

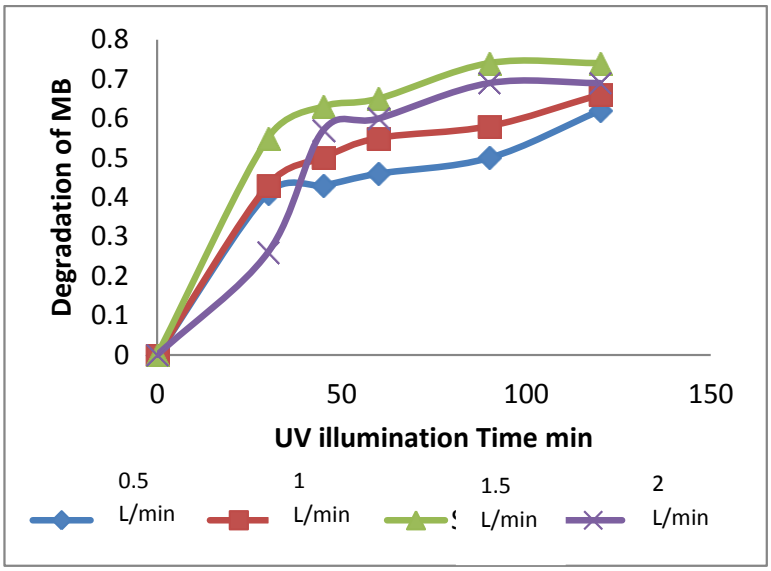

Figure (8): The Degradation of the methylene blue MB (ppm) with UV illumination time (min) at different flow rate (Liter/min) at constant C_{H2O2}= 300 mg/L and mixing agitation = 1400 rpm ,(pH=7 and $C_{CNT/TiO2}$ = 50 mg/L).

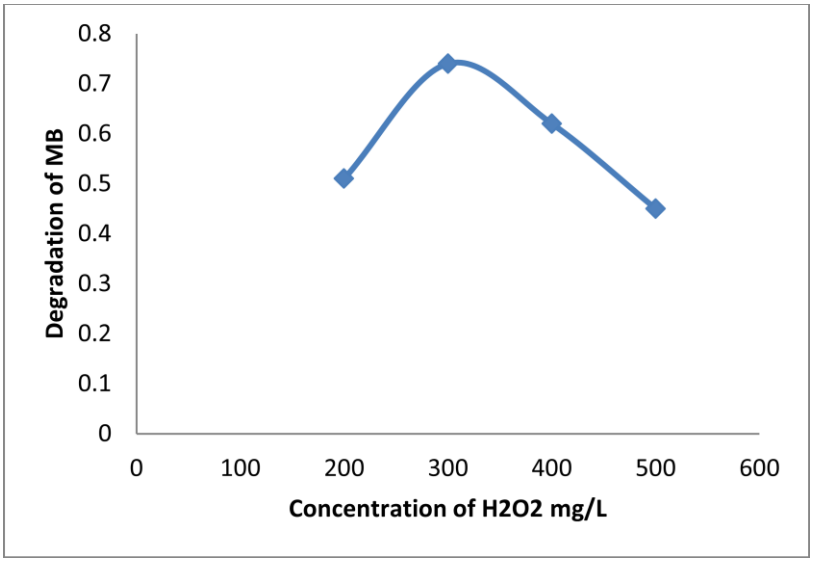

Figure (9): The Degradation of methylene blue MB (ppm) with different concentration of Hydrogen Peroxide H_2O_2 (mg/L) at constant flow rate =1.5 L/min and mixing =1400 rpm, (PH=7 and $C_{CNT/TiO2}$ = 50 mg/L).