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Comparative Assessment of ZnO and TiO_2 Nano-Particles in Solar Simulated Light Mineralization of Methylene Blue in Aqueous Media

تقييم قدرة استخدام حبيبات اكسيد الزنك وأكسيد التيتانيوم في تحطيم صبغة الميثيل الأزرق في المحاليل المائية تحت ضوء مضاهي لضوء الشمس

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Abstract

Nano-powders of commercial ZnO and TiO_2 were investigated as photo-catalysts for mineralization of methylene blue (MB) in aqueous media. Comparative study was performed under solar-simulated light at room temperature and neutral conditions. Both systems showed activity and caused complete mineralization of the reacted MB molecules of low concentrations. The ZnO system showed much higher catalytic efficiency than the TiO_2 counterpart. Spectrophotometric analysis of the reaction mixture showed that up to 100% removal of MB was achieved by ZnO catalyst in 60 min, whereas the TiO_2 caused only 50% removal after the same time exposure. The UV light present in the solar simulator light (with about 5%) was responsible for mineralization of MB. Due to its higher efficiency, the ZnO system was then considered the catalyst of choice, where effects of different reaction parameters have been studied including: value of pH, temperature, light intensity, catalyst amount and MB concentration. The catalyst efficiency was measured by calculating values of turn-over number (TN), and quantum yield, after 30 min. The ZnO catalyst was isolated after reaction cessation and re-used for three times, where the catalyst retained up to 95% of its efficiency. The results show the potential value of using ZnO as a photo-catalyst for mineralization of MB in water with solar light.

Keywords: ZnO, TiO_2, Methylene Blue, Photodegradation, Water Purification.

ملخص

تهدف هذه الدراسة لتقيم قدرة حبيبات أكسيد الزنك وأكسيد التيتانيوم النانومترية على تحطيم صبغة الميثيل الازرق في المحاليل المائية. تمت هذه المقارنة باستخدام مصدر ضوئي مضاهي لضوء الشمس على درجة حرارة الغرفة وحامضية معتدلة. حيث أبدى الحفازان قدرة على تحطيم صبغة الميثيل الأزرق، الا أن أكسيد الزنك اظهر كفاءة أكبر مقارن بأكسيد التيتانيوم. التحليل الضوئي لنتائج التفاعل أظهرت التحطيم شبه الكامل ~100% للصبغة في حالة أكسيد الزنك خلال ساعة من التعرض للضوء، بينما استطاع أكسيد التيتانيوم من تحطيم 50% من الصبغة بعد التعرض لنفس الفترة من الضوء. عملية تحطيم الملوثات ناتجة عن تحفيز الحفازات بالأشعة فوق البنفسجية شحيحة التوفر في الضوء الشمسي الواصل الى الارض. تم دراسة بعض المتغيرات مثل تاثير درجة الحموضة ودرجة الحرارة وكثافة الضوء وكمية الحفاز المستخدم وتركيز صبغة الملوث على معدل ازالة الصبغة من المياه. وابدى استخدام اكسيد الزنك لعدة مرات متتالية كفاءة ثابتة نسبياً للعمل على تحطيم الملوث.

الكلمات المفتاحية: أكسيدالزنك، أكسيد التيتانيوم، الميثيل الأزرق، تحطيم ضوئي، تنقية المياه

Introduction

Extensive production of commercial products, including industrial dyes, leads to water contamination with such compounds. Textile industry is one major source of water contamination, since textile industry demands huge amounts of dyes. The annual production of industrial dyes is more than 7×10^5 tones (Spadaro, Isabelle et al. 1994). Many of such products are toxic and resistant to biodegradation (Daneshvar, Salari et al. 2003). Different methods are examined to purify waters from contaminants. Adsorption and coagulation are known, but merely uptake the toxic compounds from waste water to other media, which does not help solve problems. Traditional oxidation processes such as ozonation and chlorination are only effective in destroying specific classes of dyes (Ganesh, Boardman et al. 1994). Such methods are costly and may yield additional problems. Advanced oxidation processes

(AOPs) have been considered as an effective technology in treating water organic contaminants. AOPs involve catalysis with semiconductors surfaces (TiO_2, ZnO, ZrO_2, V_2O_5, WO_3, Fe_2O_3, SnO_2, CdSe, GaAs, GaP and sulphides like CdS and ZnS) and a suitable radiation source. TiO_2 and ZnO powders are widely used in such technologies. For this purpose, both systems are being examined in a comparative manner.

Zinc oxide is a non-hazardous, stable, abundant, and low cost compound. ZnO has a high band gap (3.2 eV) which demands UV light (<390 nm). ZnO nano-powder was investigated as a catalyst in photo-degradation of organic contaminants in water under UV light (Sakthivel, Geissen *et al.* 2002; Daneshvar, Salari *et al.* 2004; Evgenidou, Fytianos *et al.* 2005; Navarro, Fenoll *et al.* 2009; Ren, Yang *et al.* 2010; Fu, Han *et al.* 2012; Pawar and Lee 2014). TiO_2 has been extensively investigated in photo-degradation applications. Like ZnO, TiO_2 is stable under photo-electrochemical applications, non-toxic, abundance, and high oxidizing power. TiO_2 is more widely investigated in photo-degradation application than ZnO under UV applications (Tang, Zhang *et al.* 1997; Choi, Hong *et al.* 2000; Xu and Langford 2001; Chen, Lu *et al.* 2007; Yogi, Kojima *et al.* 2009; Gupta, Jain *et al.* 2012).

For effective AOP technique, solar light should be used rather than UV lamps. However, solar light involves mostly visible and infrared radiations, which pushed many people to use sensitizers in order to activate TiO_2 and ZnO under solar light processes. Unfortunately, sensitization leads to other difficulties namely cost and sensitizer stability concerns (Cho, Choi *et al.* 2001; Bae and Choi 2003; Sirimanne, Jeranko *et al.* 2003; Zhou, Zhang *et al.* 2006; Hilal, Majjad *et al.* 2007; Zhang, Chen *et al.* 2008; Zyoud, Zaatar *et al.* 2010; Chowdhury, Moreira *et al.* 2012). This work aims at a totally different strategy. As solar light that reached earth involves ~5% UV radiations, we wish to use such UV light in mineralizing organic contaminants, one of which is the widely used MB dye.

For this purpose both ZnO and TiO_2 nano-powders have been chosen as catalysts in photo-degradation MB using solar simulator lamp which involves ~3% UV. If any of these systems showed significant activity under solar simulated light, it will then be more effective under natural solar light that contains higher UV ratio (MacLaughlin, Anderson et al. 1982).

MB is a heterocyclic aromatic chemical dye with a molecular formula $C_{16}H_{18}N_3SCl$. Its molecular structure and molecular absorption spectrum are shown in Figure (1). MB dye is widely used by industries for different purposes. MB may cause many poisoning symptoms (Oliveira, Franca *et al.* 2008). For these reasons it was chosen here. Furthermore, MB is easy to analyze spectrophotometrically.

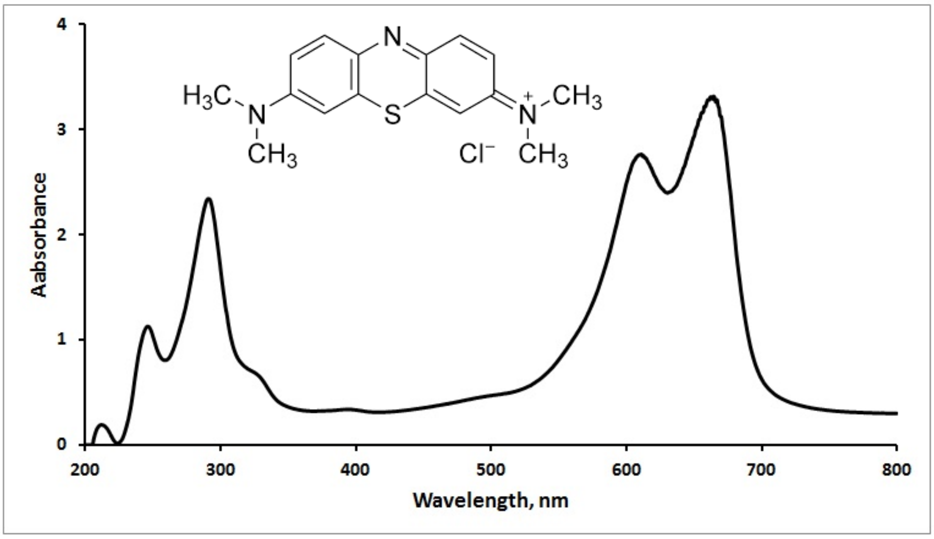

Figure (1): Molecular structure and electronic absorption spectrum for MB.

1. Experimental

Methylene blue, TiO_2 (Anatase, describe) and ZnO (description) were all purchased from Merck. Other common chemicals were obtained from the local market. A 400 W Osram Tungsten Halogen lamp was used as a source for solar simulated light. The lamp spectrum is a bell curve that resembles solar light with little UV radiation (~3%). A light-meter (model lx-102) from Lutron was used to measure the radiation intensity at the reaction mixture surface. A Shimadzu UV-1601 spectrophotometer was used to measure remaining methylene blue concentration using calibration curves.

The catalytic experiment was typically conducted as follows: A 100 mL of MB solution of known concentration was placed in a thermo-stated 250 mL beaker. Certain amount of ZnO or TiO_2 was added. The mixture was magnetically stirred in dark for 30 min to calculate the amount of adsorbed MB on the catalyst particle surfaces. The beaker was then exposed to the light source. A specific amount of mixture was withdrawn from the solution every 15 min, centrifuged (5000 rpm for 5 min) and spectrophotometrically analyzed for remaining MB concentration at 670nm.

2. Results and discussions

ZnO and TiO_2 were investigated here in mineralization of MB using solar simulator lamb. A number of control experiments were performed. In one experiment using either ZnO or TiO_2 catalysts, a cut-off filter (400 nm or shorter) was used which indicates that photo-degradation reaction is due to the UV radiations. In another experiment the catalysts were used in the dark no loss of contaminant, other than adsorption of fixed amount (~3.5 ppm) onto catalyst, was observed. Exposure of contaminant solution, in the presence of a catalyst, to solar simulated light, showed continued lowering in contaminant concentration with time. The loss in contaminant concentration is due to complete mineralization of the reacted molecules. No other organic compounds resulted from the reacted MB molecules. This was confirmed by spectrophotometric analysis of the reaction mixture, as described below.

The effect of type of catalyst system has been studied as described below. Effects of other factors, such as pH, contaminant concentration and catalyst amount are also discussed. Catalyst efficiency was understood in terms of TN and QY measured after 30 min reaction time.

2.1. Effect of catalyst type

ZnO and TiO_2 catalyst systems were studied. Figure (2) shows that more MB was removed in case of ZnO more than in case of TiO_2, keeping all other reaction conditions the same. The Figure shows that the ZnO catalyst caused more than 90% removal of the MB in 30 min. Only about 30% of MB was removed by TiO_2 catalyst in 30 min.

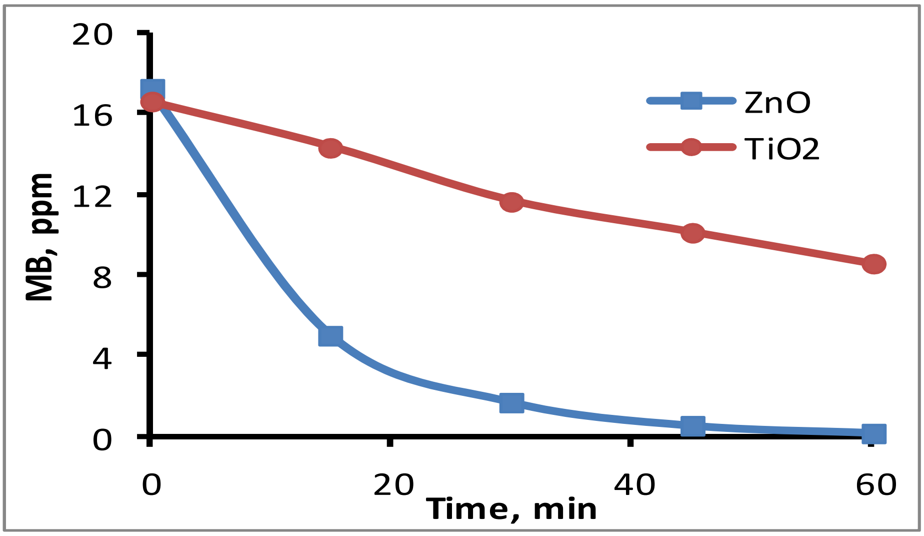

Figure (2): Profiles describing MB removal from aqueous solution (100 mL, 20 ppm) using different types of nano-powder catalyst (0.1 g). Reactions were conducted using 19 mW/cm^2 at 30 ^{o}C under neutral conditions.

All reacted MB molecules were totally mineralized into CO_2, H_2O and other inorganic nitrogen and sulfur compounds. Complete MB removal occurred in the ZnO system, and no organic molecules were detected after reaction completion in 60 min. Figure (3) shows gradual MB color disappearance with reaction progress.

The absence of electronic absorption bands in the range 200-350 nm, typically known for phenyl groups in different organic compound, confirms complete removal of such stable organic compounds.

Furthermore, the continued loss of absorption bands in the range 500 – 700 nm confirms the continued disappearance of the stable azo group in MB, Figure (4).

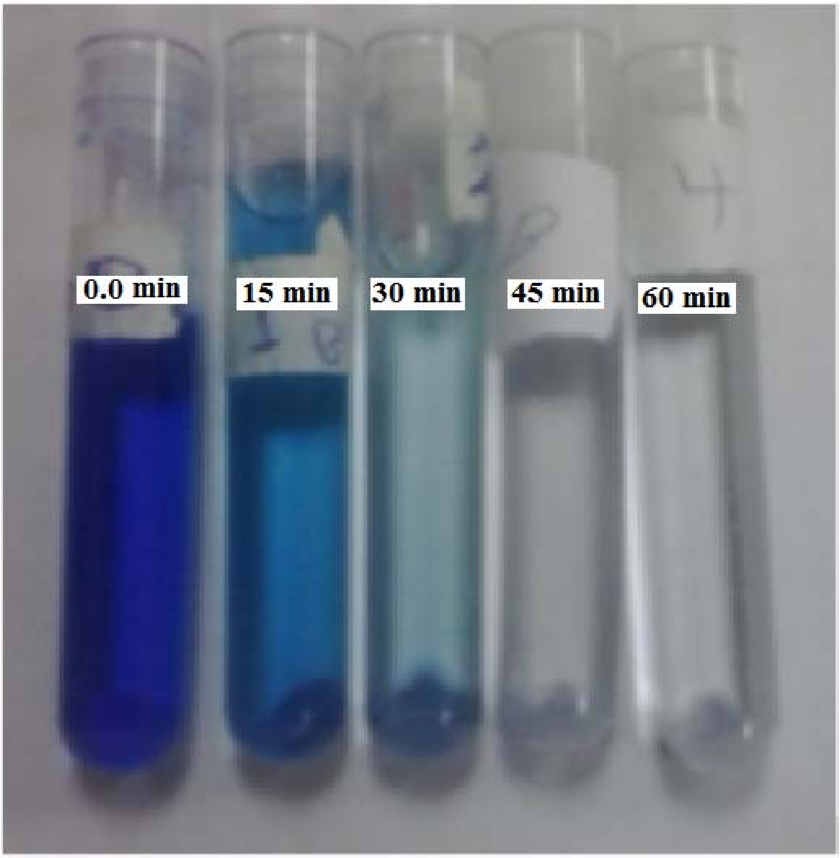

Figure (3): Photographic image showing color disappearance for MB aqueous solution during photo-degradation reaction with ZnO.

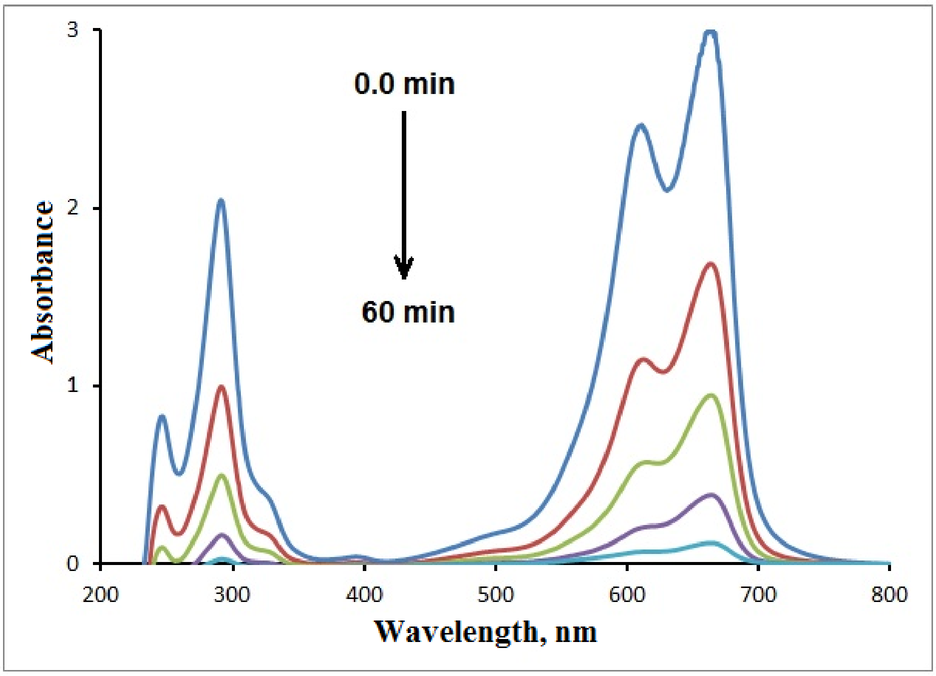

Figure (4): Electronic absorption spectra measured for MB aqueous solution during photodegradation reaction with ZnO.

The results indicate that the ZnO system was more effective, in photo-degradation of MB, than the TiO_2 system. This difference is not due to particle size or surface area differences, since both systems have comparable particle sizes and relative surface areas. The reason is due to higher sensitivity of ZnO to absorb UV tail that occurs in the solar simulated light. The higher absorptivity of the ZnO towards the UV radiation is well documents in earlier reports (Hilal, Nour *et al.* 2009; Hilal, Al-Nour *et al.* 2010; Catano, Valencia et al. 2012; Fatin, Lim *et al.* 2012). For these reasons, this study was restricted to the use of ZnO system rather than the TiO_2 hereinafter.

3.2 Effect of pH

The effect of pH on the photo-degradation rate of MB was studied. Natural waters normally have 6-8 pH range (Greenberg, Clesceri *et al.*

1992), and it is necessary to investigate efficiency of ZnO under such conditions to emulate natural water conditions. The amphoteric nature of ZnO also necessitates the study of pH. The OH groups at the ZnO surface are affected by the pH value (Degen and Kosec 2000; Omar, Aziz *et al.* 2014). The MB molecules are also affected by pH as well. The intermediate oxidizing species (•OH, $O_2{\bullet}^-$, H_2O_2 and $HO_2{\bullet}$) that are expected to occur during the photocatalytic process are also affected by the pH value (Zepp, Faust et al. 1992; Chang, Hsieh *et al.* 2008). The zero point charge of ZnO is 9.0, above which the ZnO surface is negatively charged.

The pH effect was studied under three values, namely acidic (pH 3), neutral and basic (pH 10.4) media. Figure (5) shows that the photo-degradation rates in basic and neutral media are higher than in acidic medium. In basic media, ~95% of MB was photo-degraded after 30 minute, ~70% in neutral media, and ~25% in acidic media. The basic solution (pH~10.4) showed highest T.N. and Q.Y. values, followed by neutral solution. The neutral solution showed nearly complete photo-degradation of MB after 60 minute of irradiation. Values of T.N. and Q.Y. are presented in Table (1). The fact that the under neutral conditions the ZnO showed soundly high efficiency is an added value for using the ZnO system, since natural waters commonly have pH close to 7.

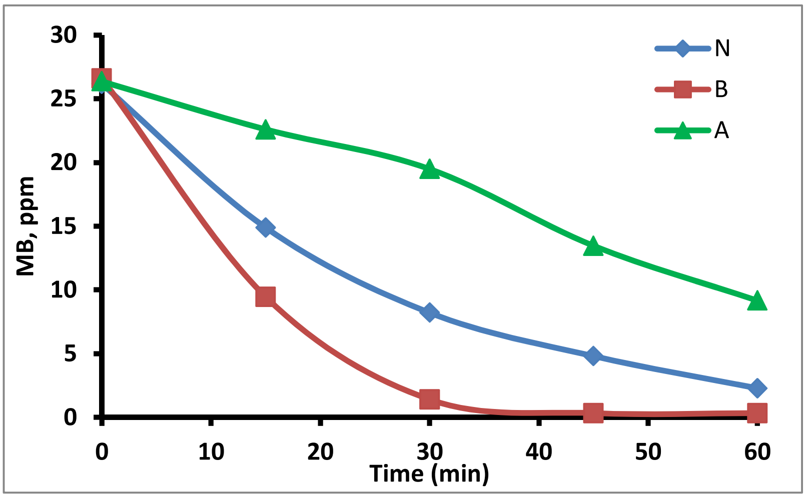

Figure (5): Photodegradation profiles of MB (100 mL of 30 ppm, 30°C, 19 mW/cm^2) at different pH values.

3.3 Effect of light intensity

The effect of light intensity on methylene blue photo-degradation was studied. Two different light intensities (19.0 and 1.9 mW/cm^2) were investigated. Experiments were conducted on MB solutions (100, 10 ppm) using 0.10 g ZnO powder. Figure (6) shows the photo-degradation reaction profiles for MB with time for the two different illumination intensities. About 95% mineralization occurred within about 30 min of illumination in case of higher radiation intensity. In case of lower illumination intensity, up to 55% mineralization occurred in 30 min. Table (1) summarizes these results. The TN value was higher with higher illumination intensity, which is not unexpected. This is because more photons are used and more electrons are excited in the catalyst nanoparticles. The value of QY is higher for the lower light illumination experiment. Again this is also expected. The number of incident photons exceeds the number catalyst particles. Therefore, only certain number of photons is necessary to excite particles, and other photons are in excess. The results suggest that the ZnO catalyst is useful even under low illumination intensities that may occur in nature.

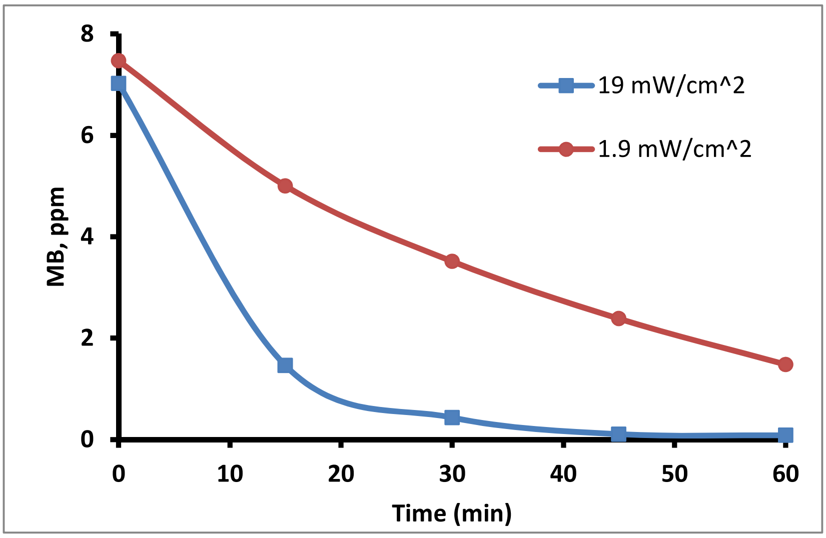

Figure (6): Photodegadation profiles of MB (100 mL of 10 ppm, 30°C, 19 mW/cm^2) under different illumination intensity.

3.4 Effect of catalyst amount:

The effect of ZnO amount on the photo-degradation of MB was investigated, as shown in Figure (7). Table (1) summarizes the results of Figure (7). After 60 min of irradiation, 99% of MB was mineralized when using 0.20 g of zinc oxide. When using 0.1 g of catalyst, 92% MB was mineralized. 78% photo-degradation occurred when using 0.05 g catalyst. Table (1) shows that the values of the QY increases with higher catalyst amount. With more particles, higher total surface area and higher number of catalyst sites are expected which increases the overall activity

Despite these results, the values do not accurately describe the effect of catalyst amount on its relative efficiency. The TN value decreased with increasing ZnO amount, as shown in Table (1). This means that the relative efficiency of the catalyst is lowered by increasing catalyst loading. This is attributed to the fact that increasing the catalyst amount allows more particles to exist at the top of the reaction mixture. Small amount of photons are thus allowed to penetrate through the reaction mixture, which lowers the fraction of unused catalyst particles in mixture. Therefore, the relative catalyst efficiency is lowered by increasing the catalyst amount. These results are consistent with earlier report (Hilal, Nour et al. 2009; Zyoud and Hilal 2009; Hilal, Al-Nour et al. 2010; Zyoud, Zaatar et al. 2010; Zyoud, Zaatar et al. 2011). Collectively, the results encourage using less amounts of catalyst in future water purification.

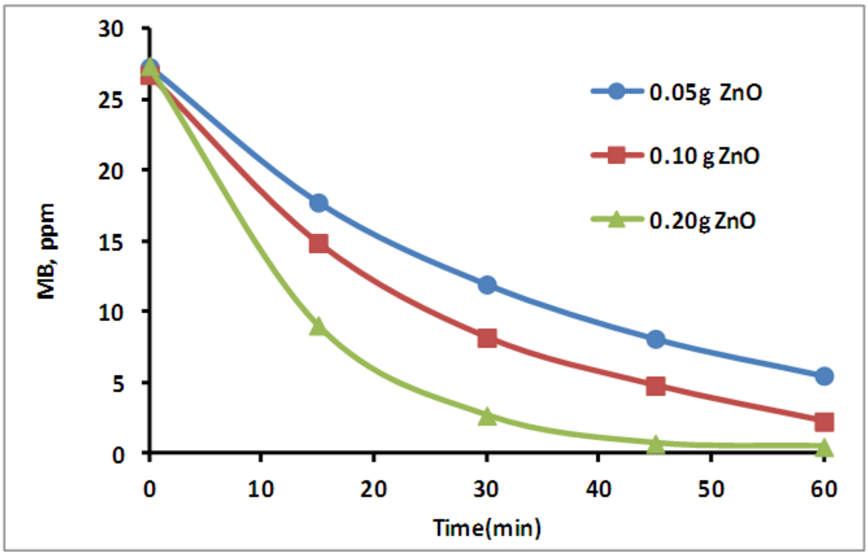

Figure (7): Photodegradation profiles of MB (100 mL of 30 ppm, 30^{o}C, 19 mW/cm^2) using different amounts of ZnO.

3.5 Effect of MB concentration

The effect of MB concentration on the photo-degradation rate was studied. The photo-degradation reaction profiles with time for different contaminant concentrations are shown in Figure (8). In case of lower contaminant concentrations (10 or 20 ppm) complete mineralization occurred in 60 min. In case of higher concentrations, 91%, 85%, 71%

degradation occurred for the 30, 40 and 50 ppm concentrations, respectively. Despite the lowering in removal percentage with higher contaminant concentration, the average reaction rate increased. Values of both T.N. and Q.Y. increased with higher contaminant concentrations. The results indicate that ZnO nano-powder is a suitable catalyst photo-degradation of MB over a wide range of concentrations. The results also indicate complete safe removal of MB from water in relatively short times, in support of our earlier study on different systems (Hilal, Al-Nour *et al.* 2010; Zyoud, Zaatar *et al.* 2010).

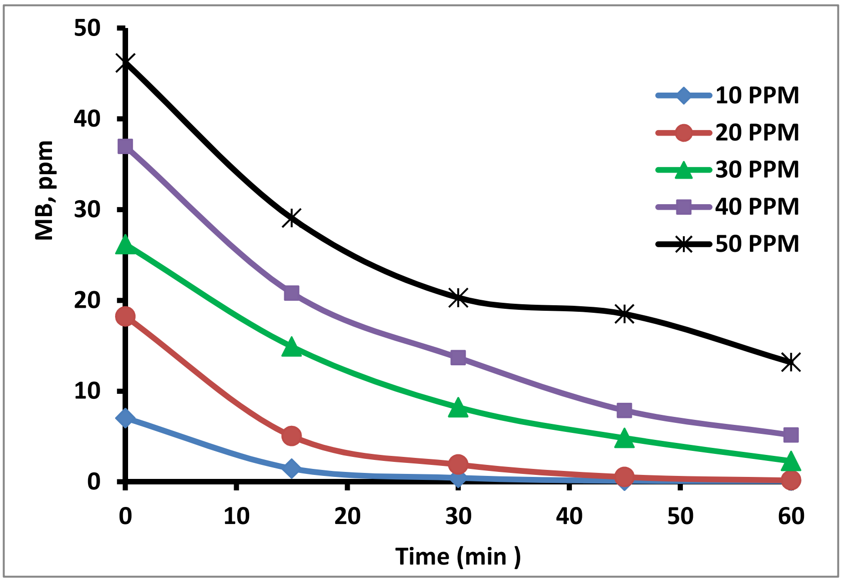

Figure (8): Photodegradation profiles of different MB concentrations (100 mL, 0.1g ZnO, 30°C 19.0 mW/cm^2).

3.6 Reuse experiment

The ZnO catalyst stability, in photo-degradation of MB in aqueous solutions, on reuse was investigated. The ZnO catalyst powder was isolated from the reaction mixture after reaction completion by decantation and reused for fresh MB solutions, for three uses. Figure (9) shows the photo-degradation reaction profiles for aqueous MB (100 mL, 30 ppm) in neutral solutions using first catalyst, recovered and second recovered ZnO powders. No observable loss in catalyst efficiency was observed on reuse. After 60 minutes about 95% of methylene blue was photo-degraded in the tree reuse experiments. The slightly lower value for the second recovered catalyst is presumably due to loss of traces of the catalyst during recovery. The results indicate the value of using ZnO catalyst in mineralizing MB contaminant in aqueous solution under mild conditions of pH and temperature, and the ability to recover it for several times.

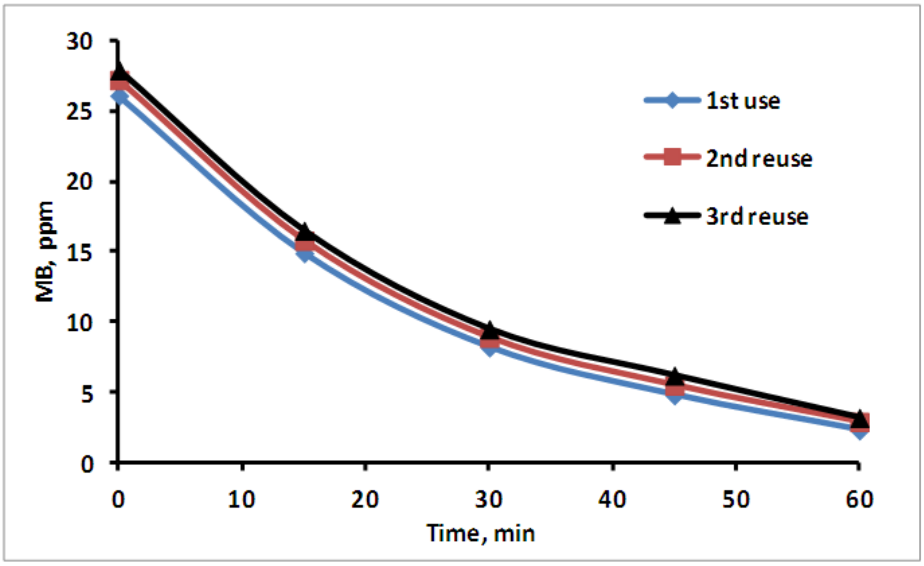

Figure (9): ZnO powder (0.10 g) were added to 100 mL (30 ppm) methylene blue.

Table (1): QY and TN values calculated after 30 min of irradiation.

<table>
<tr><th colspan="6">Comparison between catalyst type on photodegradation 100 mL, 10 ppm MB, using 19.0 mW/cm^2 light</th></tr>
<tr><td></td><td colspan="2">ZnO</td><td colspan="3">TiO_2</td></tr>
<tr><td>Q.Y</td><td colspan="2">0.01968</td><td colspan="3">0.0115</td></tr>
<tr><td>T.N</td><td colspan="2">0.00141</td><td colspan="3">0.00082</td></tr>
<tr><th colspan="6">Effect of light intensity on the photodegradation 100 mL, 10 ppm MB, at 30^oC, pH 7.</th></tr>
<tr><td></td><td colspan="2">19.0 mW/cm^2</td><td colspan="3">1.9 mW/cm^2</td></tr>
<tr><td>Q.Y</td><td colspan="2">0.01968</td><td colspan="3">0.0685</td></tr>
<tr><td>T.N</td><td colspan="2">0.00141</td><td colspan="3">0.00050</td></tr>
<tr><th colspan="6">Effect of catalyst amount on the photodegradation rate of 100mL, 30 ppm MB, at 30^oC, pH 7, and 19.0 mW/cm^2 light.</th></tr>
<tr><td></td><td colspan="2">0.05 g</td><td colspan="2">0.10 g</td><td>0.20 g</td></tr>
<tr><td>Q.Y</td><td colspan="2">0.03381</td><td colspan="2">0.03989</td><td>0.06485</td></tr>
<tr><td>T.N</td><td colspan="2">0.00486</td><td colspan="2">0.00287</td><td>0.00233</td></tr>
<tr><th colspan="6">Effect of contaminant concentration on the photodegradation 100 mL, 30 ppm MB, at 30^oC, pH 7, and 19.0 mW/cm^2 light.</th></tr>
<tr><td></td><td>10 ppm</td><td>20 ppm</td><td>30 ppm</td><td>40 ppm</td><td>50 ppm</td></tr>
<tr><td>Q.Y</td><td>0.01968</td><td>0.04670</td><td>0.03989</td><td>0.05716</td><td>0.06064</td></tr>
<tr><td>T.N</td><td>0.00141</td><td>0.00336</td><td>0.00287</td><td>0.00411</td><td>0.00436</td></tr>
<tr><th colspan="6">Effect of pH on the photo-degradation of 100 mL, 30 ppm MB, at 30^oC, pH 7, and 19.0 mW/cm^2 light.</th></tr>
<tr><td>pH</td><td colspan="2">3</td><td colspan="2">7.4</td><td>10.4</td></tr>
<tr><td>Q.Y</td><td colspan="2">0.01332</td><td colspan="2">0.0400</td><td>0.0606</td></tr>
<tr><td>T.N</td><td colspan="2">0.00096</td><td colspan="2">0.0029</td><td>0.0044</td></tr>
</table>

4 Conclusion

Both TiO_2 and ZnO nano-powders can be used as catalysts for solar mineralization of methylene blue contaminant. The ZnO showed higher catalyst efficiency and can be used to completely photo-degrade methylene blue in water under a range of working conditions. The ZnO catalyst can also be recovered and reused multiply without noticeably losing its efficiency. The results indicate the possibility of using ZnO in purifying natural waters contaminated with methylene blue industrial dye.

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