International Journal of Modern Chemistry, 2015, 7(1): 45-53

Modern Scientific Press

International Journal of Modern Chemistry **ISSN: 2165-0128**

Journal homepage: www.ModernScientificPress.com/Journals/IJMChem.aspx *Florida, USA*

Article

Photocatalytic Degradation of Methylene Blue by Modified Nanoparticles Titania Catalysts

Ahmed H. Hattab*, Awad I. Ahmed, S. M. Hassan, A. A. Ibrahim

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

* Author to whom correspondence should be addressed; E-Mail: ahmadhamdi79@yahoo.com

Article history: Received 3 March 2015, Received in revised form 5 April 2015, Accepted 1 May 2015, Published 6 May 2015.

Abstract: A series of titania loaded with different content of MCM-41 (1wt%-7wt%) were prepared by impregnation method using titanium iso-propoxide as precursor for titania and tetraethoxysillane (TEOS) as a precursor for MCM-41. MCM-41/TiO_2 samples were calcined at 150, 250, 400 and 600^oC, the photocatalytic activity of the TiO_2 loaded with MCM-41 was then investigated in the degradation of methylene blue (MB) using UV/visible light. The results show that the titania loaded with MCM-41 has higher photocatalytic activity than pure titania. The kinetic of MB degradation was first order reaction.

Keywords: Titania, MCM-41, Photocatalytic degradation, TiO_2, Methylene Blue.

1. Introduction

Photocatalytic oxidation is one of the most new pollution treatments and is widely applied to water and air purification [1]. Titania (TiO_2) is a wide band-gap semiconductor with a large number of applications in catalysis, photovoltaic's, optoelectronics, self-cleaning glass, pigments and many others [2]. In recent years photocatalytic processes using titania have been used for important problems of environmental interest like purification of water and air [2, 3]. Titania has attracted a great deal of attention since it has high photocatalytic activity and physicochemical stability [4, 5]. The basic

principle of TiO_2 photocatalysis in presence of water and oxygen under illumination with solar light is as follows: after excitation with light of an energy higher than the band gap (e.g. 3.2 e.V for anatase), two of holes (h+) and electrons (e−) are formed, which can either recombine inside or on the surface of titania or react with adsorbed electron donors (e.g. hydroxide ions) or acceptors (e.g. oxygen). The resulting hydroxyl radicals $OH^{\bullet}$ and superoxide ions $O_2^{-\bullet}$ are known to be an oxidizing agents able to oxidize organic compounds [6-10]. However, the widespread use of titania was impaired by some flaws of its structure, agglomeration easily happing during the synthesis process and wide band gap (3.2 e.V) which requires ultraviolet irradiation for photocatalytic activation [7].

Since the discovery of the periodic mesoporous molecular sieves of the M41S family by researchers at Mobil in 1992 a new area in inclusion chemistry has begun. It is now obvious that morphological control and structure of mesoporous silica are very important for different applications, MCM-41, one of the members of the M41S family [11], has a well-defined array of uniform hexagonal mesoporous with high internal surface area, exhibiting great potential applications as the supports of titania. It has been reported that incorporation of titania into MCM-41 framework gives unique photocatalytic activity [12- 14].

Firstly, uniform ordered channels of mesoporous materials, such as MCM-41 can control the particle size of titania and efficiently prevent particles from agglomeration [15]. Secondary, one of the primary requirements for a good catalyst is to have a high surface area, ordered mesoporous silica materials, possess high surface area as well as high number of active sites for certain reactions. MCM-41 can be used as high surface area materials for dispersing titania nanoparticles [16-19].

Also, support materials with high surface area and good acidic properties adsorb organic pollutants near to the active sites that results in enhanced photocatalytic degradation rate, moreover the photocatalytic efficiency is also increase by decreasing the electron-hole recombination, facilitating the interfacial charge transfer from the surface of the photocatalyst to the substrate [20].

In recent work, the nano-sized MCM-41 was synthesized and used as a support for titania loading. In order to examine the photocatalytic activity of the prepared samples, photocatalytic degradation was tested on the degradation of Methylene Blue.

2. Experimental

2.1. Synthesis of MCM-41 Catalyst

Pure silica MCM-41 (Si-MCM-41) was synthesized according to the original method that proposed by Beck et al. [21]. Cetyltrimethyl ammonium bromide (CTAB) as template was dissolved in amount of distilled water in presence of ammonia solution. Addition of ammonia results in a sufficiently basic solution (pH 13.0-14.0) to initiate the formation of silicate anions. Once fully

dissolved, the silica source, tetraethoxysillane (TEOS), was added drop-wise to the mixture with vigorous stirring at room temperature. At higher tetraethoxysillane loading, a thick white paste is formed. The product was filtered, washed with distilled water and dried in air at 120ºC. The mole composition of the gel mixture was CTAB: TEOS: Ammonia: H_2O are 0.22: 1.04: 1.39: 44.4 respectively. The sample was calcined in air at 550º C for 6 h period with rate of 5°C per minute.

2.2. Synthesis of MCM-41/TiO_2

MCM-41/TiO_2 was prepared using titanium (IV) isopropoxide (TIP) as titanium source, ethanol as solvent and calcined MCM-41 as prepared before. Calcined MCM-41 suspended in ethanol then titanium (IV) isopropoxide was dropped wise with vigorous stirring for 1 hour after that 10 ml of distilled water was added until complete precipitation of TiO_2 with stirring for 2 hours at 25ºC. The MCM-41 contents were taken to be 1, 2, 3, 5 and 7 wt%. The product was filtered using rotary at 80º C to evaporate ethanol. The resultant is calcined in muffle at 150º C, 250º C, 400º C and 600º C.

3. Results and Discussion

3.1. Photocatalytic Degradation of Methylene Blue

3.1.1. Effect of MCM-41 content

By increasing MCM-41 contents, the catalytic activity increases until 3wt% of MCM-41 then decreases at 5wt% and 7wt%. Fig. 1 shows the irradiation time of methylene blue (10 mg/L) by different contents at 250ºC. All samples were reach to equilibrium after 1.5 hour and the best degradation was with 3wt% MCM-41/TiO_2, which degraded 93.8% of methylene blue after 1 hour.

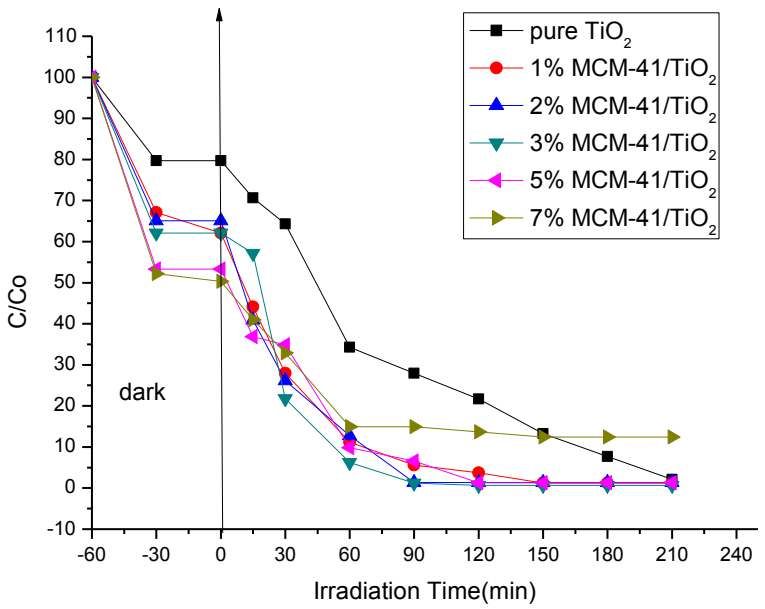

Fig. 1. Irradiation time for methylene blue by different MCM-41 content on TiO_2

3.1.2. Effect of Calcination Temperature

The samples were calcined at different calcination temperature 150ºC, 250ºC, 400ºC and 600ºC, the results show that the calcination at 250^{0}C has given the best results in all MCM-41 content on TiO_2 as showing in Fig. 2.

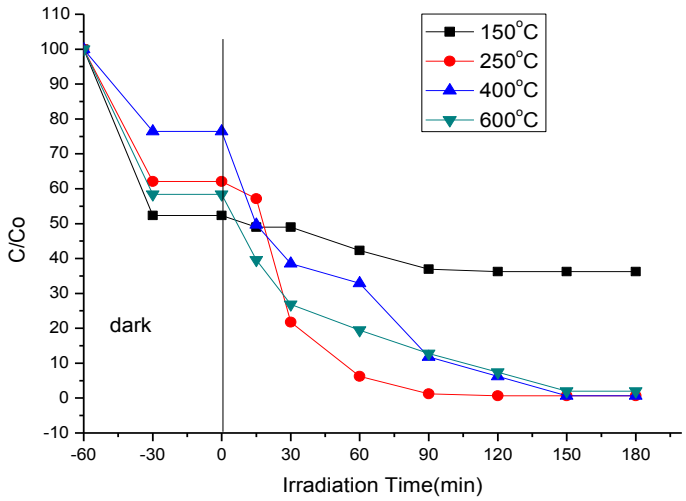

Fig. 2. Irradiation time for methylene blue by 3wt% MCM-41 content on TiO_2 on different calcination temperatures

3.1.3. Effect of catalyst weight

A different amount of catalyst were taken and it was clearly that by increasing the amount of catalyst the photocatalytic degradation activity increases as shown in the Fig. 3. One gm/L of the catalyst was used to avoid the ineffective excess of catalyst and to obtain the best weight using for photocatalytic degradation [22, 23].

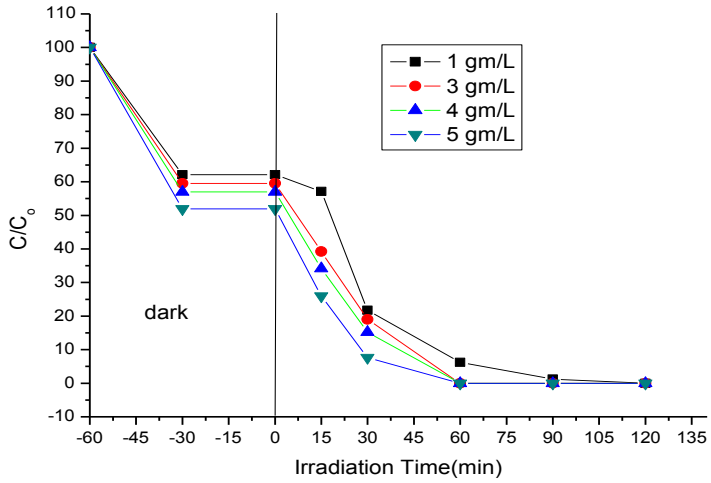

Fig. 3. Irradiation time for Methylene Blue by 3% MCM-41 content on TiO_2 in different amount of catalyst

3.1.4. Effect of initial concentration of MB

It is well known that the initial concentration of the dyes playing very important role in photodegradation of organic pollutants [22]. The photocatalytic degradation rate decreases with increasing initial concentration, due to the lifetime of hydroxyl radicals formed is very short (only a few nanoseconds), they can only react at or near the location where they are formed [23].

The initial MB concentration C_o were varied from 10 mg/L to 30 mg/L and with 1 gm/L of 3% MCM-41/TiO_2 as shown in Fig. 4.

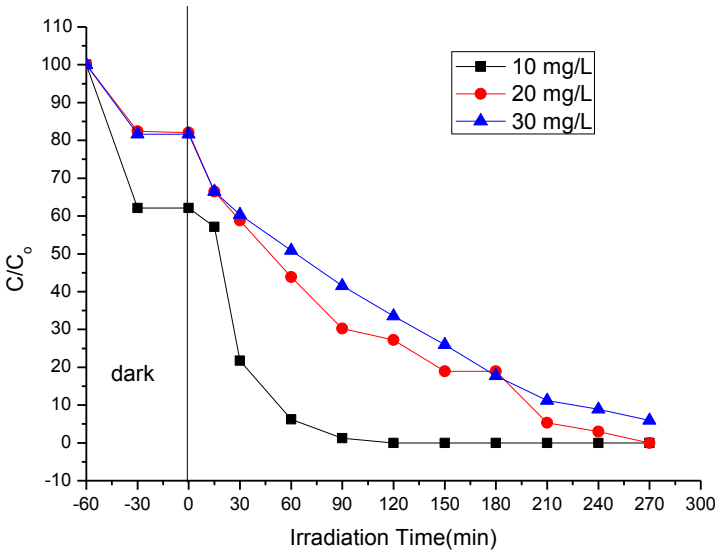

Fig. 4. Irradiation time for methylene blue by 3% MCM-41 content on TiO_2 in different initial concentration of dye

4. Kinetic Study

The kinetics study of photocatalytic degradation of methylene blue was investigated for modified MCM-41/TiO_2 systems.The loss of methylene blue was observed as a function of irradiation time and data were fitted to a first-order rate model, (Equation 1).

$$\ln (C_t / C_0) = - k t \quad (1)$$

Where C_0 and C_t are the concentration of MB at irradiation times 0 and t and k is a first-order rate constant (min^{-1}). For methylene blue, first order reaction was found to have maximum value of R^2 as compared to the second order. This means that the pseudo-first order kinetic of dye removal is acceptable for photocatalytic processes as showing in Fig.5 and 6. R^2 and k values are shown in Table 1 and 2 for photocatalytic degradation of methylene blue [24-27].

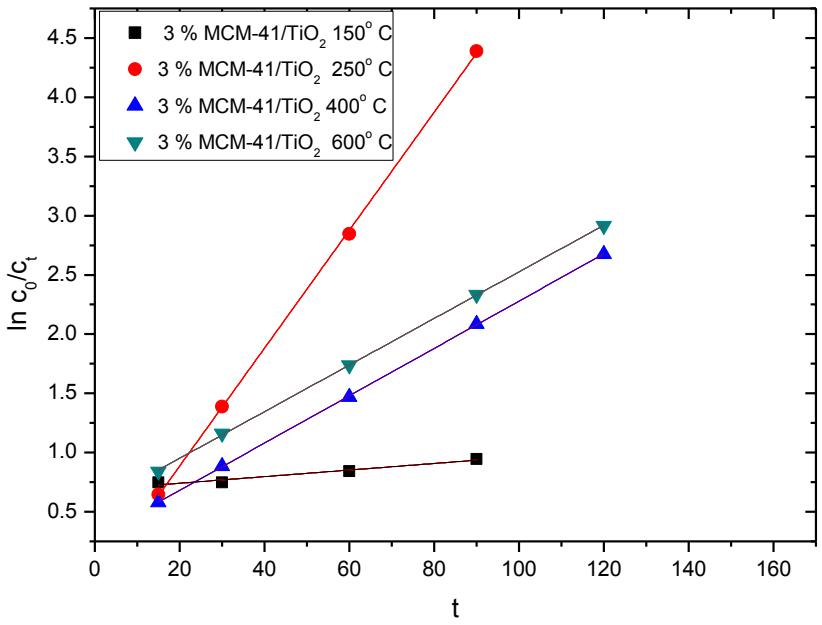

Fig. 5. Kinetics of photodegradation of methylene blue by different calcination temperature of 3 wt% MCM-41 content on TiO_2

Table 1. R^2 and k values for photodegradation of methylene blue by different calcination temperatures of 3% MCM-41 content on TiO_2

Calcination temp. for 3%MCM-41 on TiO_2	**R^2**	**k (min^{-1})**
150°c	0.94201	0.00278
250°c	0.99977	0.04979
400°c	0.99993	0.01997
600°c	0.99984	0.01968

Table 2. R^2 and k values for photodegradation of methylene blue by different content of MCM-41 on TiO_2

MCM-41 content on TiO_2 at 250°c	**R^2**	**c (min^{-1})**
Pure TiO_2	0.99907	0.01197
1% MCM-41	0.99976	0.02410
3% MCM-41	0.99977	0.04979
7% MCM-41	0.99991	0.01223

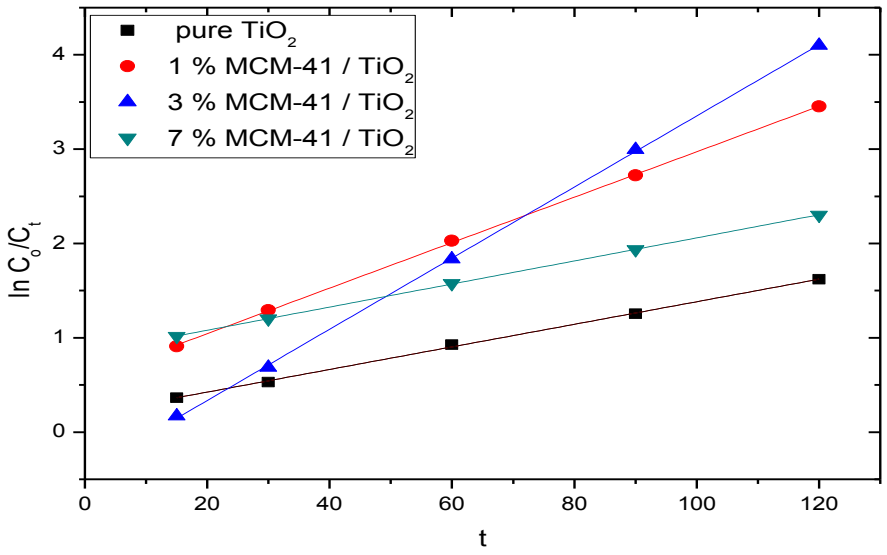

Fig. 6. Kinetics of photodegradation of methylene blue by different content of MCM-41 on TiO_2

5. Conclusion

In summary, the MCM-41/TiO_2 samples were prepared using MCM-41 as support for titania. The prepared samples were calcined at different calcination temperatures. The photocatalytic activity of MCM-41/TiO2 system was tested with methylene blue and the degradation reached to 99.4% after 90 min for 3wt% MCM-41/TiO_2 calcined at 250^{o}C. The photocatalytic degradation follows the first-order kinetic.

Reference

[1] C. Chawengkijwanich, S. Chiarakorn, W. Tongon. Visible light responsive Ag/TiO_2/MCM-41 nanocomposite films synthesized by a microwave assisted sol–gel technique. *Superlattices and Microstructures*, 2014, 69:108-121.

[2] C.L. Bianchi, E. Ghedini, G. Cruciani, M. Ongaro, M. Signoretto, V. Trevisan. TiO_2–MCM-41 for the photocatalytic abatement of NOx in gas phase. *Applied Catalysis B: Environmental*, 2010, 95:130-136.

[3] M. Abyaneh, N. Lihitkar, R. Pasricha, S, Gosavi, S. Kulkarni, V. Samuel. Titania nanoparticles synthesis in mesoporous molecular sieve MCM-41. *Journal of Colloid and Interface Science*, 2007, 314:310-316.

[4] B. Youn, C. Woo, H. Lee, S. Kim, S. Oh, Y. Sung. Photocatalytic Oxidation of Gaseous Formaldehyde on TiO_2: An In Situ DRIFTS Study. *Topics in Catalysis*, 2005, 35:255.

[5] C. Gao, C. Li, J. Bao, J. Ding, S. Sun, Z. Qi. Photodegradation of rhodamine B in aqueous solution via SiO_2@TiO_2 nano-spheres. *Catalysis Letters*, 2010, 137:239-246.

[6] D. Stephan, P. Wilhelm. $ZnFe2O_4$-TiO_2 Nanoparticles within Mesoporous MCM-41. *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, 185:19-25.

[7] A. Tang, H. Yang, J. Jin, Y. Deng. TiO_2 photocatalyst for water treatment applications, the *Scientific World Journal*, 2012, 8.

[8] S. Lee, S. Park. Recent developments in photocatalytic water treatment technology: A review. *Journal of Industrial and Engineering Chemistry*, 2013, 19:1761-1769.

[9] Bo Jin, C. Chow, C. Saint, M. Chong. Synthesis of TiO_2/Al-MCM-41 Composites with Coal-Measure Kaolin and Performance in Its Photocatalysis. *Water Research*, 2010, 44:2997.

[10] Q. Wu, S. Li. Bandgap modulation of TiO_2 and its effect on the activity in photocatalytic oxidation of 2-isopropyl-6-methyl-4-pyrimidinol. *Materials Sciences and Applications*, 2011, 2:14-19.

[11] E. Beyers, G. Mihai, V. Meynen. Synthesis structural characterization and photocatalytic activity of Ti-MCM-41 mesoporous molecular sieves. Journal of Porous Mater, 2009, 16:109-118.

[12] B. Zhu, J. Zou, L. Wang, M. Zhang, X. Zhang, Z. Mi. Isomerization of Norbornadiene to Quadricyclane Using Ti-Containing MCM-41 as Photocatalysts. *Catalysis Letters*, 2008, 124:139–145.

[13] S. Anandan. Photocatalytic effects of titania supported nanoporous MCM-41 on degradation of methyl orange in the presence of electron acceptors. *Dyes and Pigments*, 2008, 76:535-541.

[14] F. Lefebvre, J. Basset, W. Lian, X. Fu, X. Wang. Structure preparation and photocatalytic activity of titanium oxides on MCM-41 surface. *Journal of Catalysis*, 2006, 238:13-20.

[15] C. Du, H. Yang, Y. Deng. Synthesis and optical properties of mesoporous MCM-41 containing doped TiO_2 nanoparticles. Transition metal oxide loaded MCM catalysts for photocatalytic degradation of dyes, *Colloids and Surfaces A: Physicochemistry Eng. Aspects*, 2009, 339:111-117.

[16] B. Venugopal, D. Jyothi, G. Madras, P. Deshpande, S. Chandrasekaran. Transition metal oxide loaded MCM catalysts for photocatalytic degradation of dyes. *Journal of Chemistry Science*, 2012, 124:385-393.

[17] A. Aboul-Gheit, A. Szegedi, J. Valyon, M. Miha´lyi, R. El-Salamony, S. Abdel-Hamid, S. Mahmoud. Mesoporous Ti-MCM-41 materials as photodegradation catalysts of 2,4,6 trichlorophenol in water. *Journal of Mater Science*, 2011, 46:3319-3329.

[18] D. Wu, Q. Chen, W. Shi, Y. Sun, Y. Xu. Visible-light-responsive Ag–Si codoped anatase TiO_2 photocatalyst with enhanced thermal stability. *Materials Chemistry and Physics*, 2011, 125:825-832.

[19] E. Vaschetto, G. Eimer, K. Sapag, M. Crivello, S. Casuscelli, V. Elı´as. Synthesis and Photocatalytic Activity of Titania-Loaded Transition Metal-Modified MCM-41 Molecular Sieves. *Top Catalysis*, 2011, 54:277-286.

[20] K. Zare, M. Enhessari, M. Mozaffari, M. Sadjadi. Effects of $NiTiO_3$ nanoparticles supported by mesoporous MCM-41 on photoreduction of methylene blue under UV and visible light irradiation. *Superlattices and Microstructures*, 2010, 47:685-694.

[21] E. Reddy, L. Davydov, P. Smirniotis. Synthesis characterization and photocatalytic activity of titania loaded Cd-MCM-41. *Catalysis Letters*, 2002, 79:1-4.

[22] R. Matthews. Photooxidation of organic impurities in water using thin films of titanium dioxide. *Journal of Physical and Chemistry*, 1987, 391:328-3333.

[23] A. Sclafani, F. Miano, G. Martra, L. Marchese, L. Palmisano, M. Schiavello, V. Augugliaro. Photocatalytic degradation of nitrophenols in aqueous titanium dioxide dispersion. *Applied Catalysis*, 1991, 69(1):323-340.

[24] A. Soliman, E. El-Sharkawy, K. Al-Amer. Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation. *Journal of Colloid and Interface Science*, 2007, 310:498–508.

[25] H. Hashemipour, M. Mirzaee, M. Salehi. Experimental Study of Influencing Factors and Kinetics in Catalytic Removal of Methylene Blue with TiO_2 Nanopowder. *American Journal of Environmental Engineering*, 2012, 1:1-7.

[26] C. Chawengkijwanich, N. Grisdanurak, P. Klankaw, S. Chiarakorn. TiO_2-MCM-41 Thin Film Photocatalyst Prepared from Rice Husk Silica under Room Temperature. *Journal of Materials Science and Engineering*, 2011, A1:488-495.

[27] A. Houas, C. Guillard, E. Elaloui, H. Lachheb, J. Herrmann, M. Ksibi. Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental*, 2001, 31:145–157.