SETSCI Conference Proceedings,
4:200-202, 2019

ISAS 2019
3rd International Symposium on Innovative Approaches in Scientific Studies
Section: Engineering and Natural Sciences
April 19 – 21, 2019, Ankara, Turkey

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING GRANULAR TiO_2

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Presentation/Paper Type: Oral / Full Paper

Abstract – The photocatalytic degredation has received a great deal of attention due to its new technology for environmental pollution. Among photocatalytic semiconductors, titanium dioxide is known as a photocatalyst for the removal of environmental contaminants. In this study, granular form of the TiO_2 (1-5mm diameter) which provided its powder was used to observe the methylene blue (MB) degradation. The purpose of this study is to investigate the reusability of granular TiO_2 (fixed as 40 gr) as a catalyst in the removal of MB by photocatalytic oxidation process for various concentration of MB (10, 20, 30, 40, 50 mg/L) and UV-irradiation time up to 60 min. Then, photocatalytic oxidation of MB using granular TiO_2 was investigated under UV irradiation. The effects of MB concentration on the color removal efficiency of the aqueous solutions were investigated. During the photocatalytic oxidation, the change in dyestuff concentration was monitored with spectrophotometer and the reaction kinetics were determined by spectrophotometric analyses. The results showed that, 87% yield was obtained using 50 mg/L MB and 40g granular TiO_2 for one hour degradation time.

Keywords – Granular TiO_2; photocatalytic oxidation; degredation; methylene blue; yield

I. INTRODUCTION

The greatest chemical materials group produced in the world is textile and painting industries. During production and usage of them, many contaminations enter to the environment [1]. From an environmental point of view, as some synthetic dyes have toxic and carcinogenic properties, they are of great concern [2]. Dyestuffs are often non-biodegradable compounds and can bring about adverse impacts on the living organisms being exposed to the contaminated water [3]. The risk of the presence of methylene blue in waste water causes harmful effects such as eye burns, nausea, vomiting and diarrhea [4]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters [5].

Several treatment technologies have been developed for the decolorization and degradation of dyes in wastewater effluents. These technologies are classified according to the principle of remediation into physical methods, such as adsorption, reverse osmosis, ultrafiltration and ion exchange, chemical methods, such as chlorination and ozonation, and biological methods, such as aerobic and anaerobic treatments. Advanced oxidation processes (AOPs) such as Fenton, photo-Fenton catalytic reactions, UV/H_2O_2 and UV/O_3 have proved to be sufficiently effective alternatives for the treatment of wastewaters containing dyes. Among them, the heterogeneous photocatalytic oxidation has received a growing attention over the last years [6].

The photocatalyst uses semiconductor metal complexes, which form a strong oxidizing environment on the surface due to the effect of UV light. Titanium dioxide, gallium phosphorus, gallium arsenic, cadmium sulfide, strontium titanate, zinc oxide, iron oxide, and tungsten oxide are the main materials which used as photocatalyst [7]. In recent years, titanium dioxide (TiO_2) has been studied intensively because of its outstanding photocatalytic activity. TiO_2 is a semiconductor material which is able to break down the organic groups and show photoactive properties when irradiation by UV light and using 5 % of daylight wavelength. TiO_2 contains main three crystal structures: anatase, rutile and brukit. Among them, anatase form of TiO_2 shows the best photocatalytic property in many applications such as self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, and photoelectrochemical conversion in in the environmental and energy fields [8,9]. However, the development of unique photocatalytic materials and their various form as granular are essential to enhance photo degradation ability especially in dye removal systems.

Because of these considerations, the aim of this study was to investigate the photocatalytic removal of methylene blue using granular TiO_2 and to investigate and reusability of granular TiO_2.

II. Materials and Method

A. Materials

TiO_2 nanoparticles (Degussa P25 (Evonik), particle size 25 nm, surface area 50 m^2/g and 80/20 anatase/rutile) was used as photocatalyst. Methylene Blue (MB) (Merck) was used as a pollutant dye. 300W-OSRAM Ultra-vitalux UV lamp was used as a UV light source. Properties of MB dye was given in Table 1.

Absorbance measurements were measured in Hach Lange DR6000 UV-Visible spectrophotometer. Mtops MS300HS magnetic stirrer was used to ensure homogeneous distribution of dyestuffs prepared at different concentrations.

B. Method

In the experimental study, 2 L of stock dye solution at a concentration of 50 mg/L was prepared for methylene blue. For photocatalytic degradation experiments, dye solutions to be used at different concentrations were prepared by diluting with ultra pure water. 40 g of granular TiO_2 was fabricated with home made granulation experiment set up. The duration of experiments for different MB concentrations was determined as 1 hour with 15 min intervals. The dye concentration was determined by taking the absorption spectra using an Hach-Lange spectrophotometer, DR6000 UV-VIS Model in the wavelength range of 200–800 nm. The highest absorbance at 665 nm was recorded for MB.

III. Results

A. UV–VIS Test of Methylene Blue

Experiments were performed with various concentrations of MB (10, 20, 30, 40, 50 mg/L) and 40 g of granular TiO_2. Fig. 1 shows the absorbance spectrum versus wavelength for MB at a fixed concentration of 20 mg/L at different time intervals. According to absorbance spectrum of the samples, maximum absorbance of all samples occurs at 665 nm wavelength.

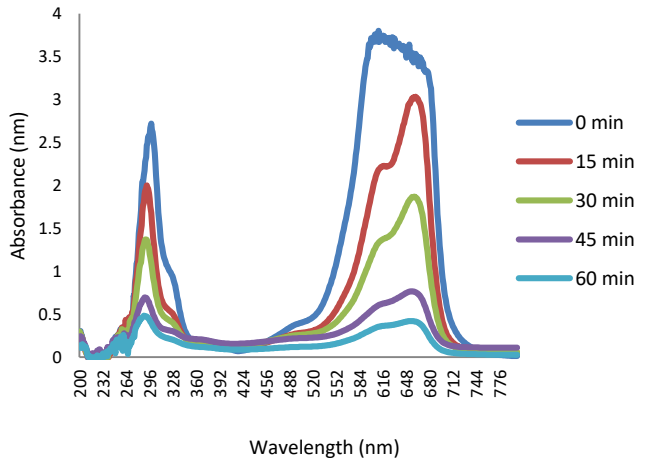
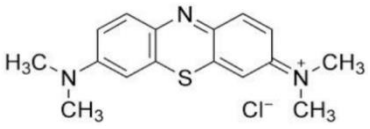


Fig. 1. Absorbance spectrum of methylene blue versus wavelength

Table 1. Chemical structure of MB.

Name	Chemical Structure	λ_{max} (nm)
Methylene blue		665

B. Effect of Initial Dye Concentration

The pollutant concentration is a very important parameter in wastewater treatment. The effects of initial dye concentrations on the photocatalytic decolorization have been investigated from 10 to 50 mg/L. The results are shown in Fig. 2 and 3. It was found that the increase in the dye concentration decreases the decolorization efficiency. Increasing the dye concentration from 10 to 50 mg/L decreases the decolorization efficiency from 100% to 87% in 60 min in the presence of granular TiO_2.

C. Determination of Reaction Kinetics

The calculated kinetic parameters of MB degradation are shown in Fig.4 and Table 2. All curves exhibited good linear correlation, and the values of correlation coefficient (R^2) were close to 1. This result indicated that the photocatalytic degradation of MB with TiO_2 catalysts followed pseudo first-order kinetics. 10 mg/L exhibited the highest reaction rate constant and hence the highest photocatalytic activity.

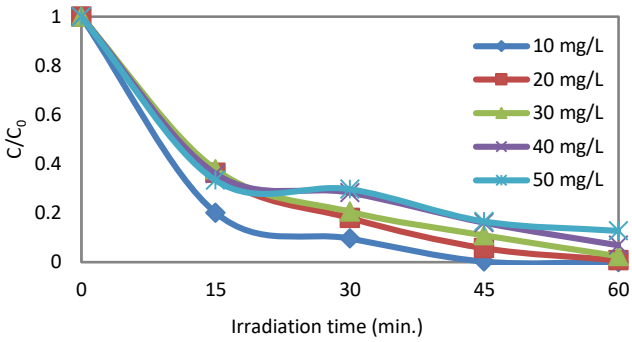


Fig. 2. The effect of initial dye concentration on photodegradation of MB by UV/TiO_2 process. (Catalyst = 40 g/100 ml)

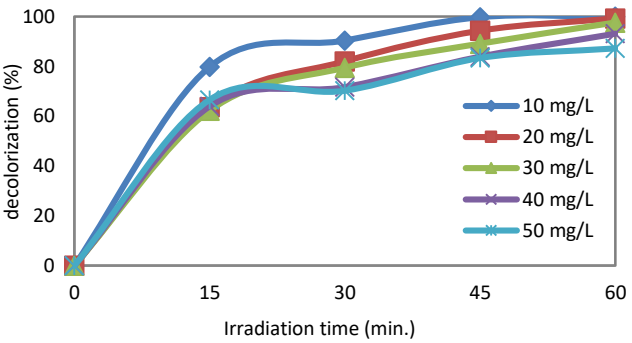


Fig. 3. Effect of initial dye concentration on decolorization of MB in the presence of granular TiO_2 (Catalyst = 40 g/100 ml)

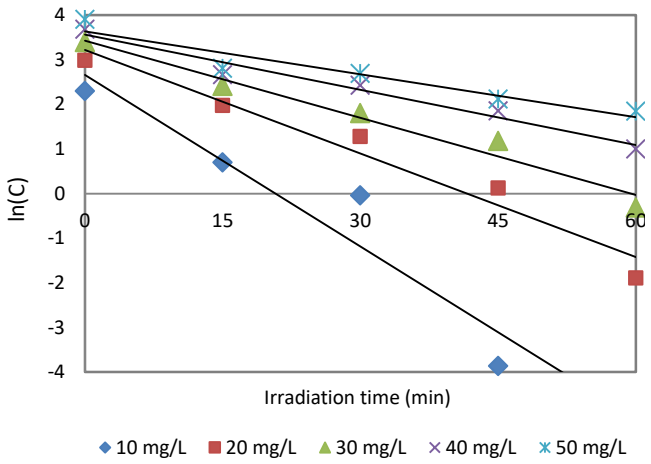


Fig. 4. The linear representation of the curves of ln(C) at different concentrations

Table 2. Pseudo-first-order kinetic parameters of MB degradation.

Sample	k	R^2
10 mg/L	0.128	0.902
20 mg/L	0.077	0.959
30 mg/L	0.058	0.973
40 mg/L	0.041	0.966
50 mg/L	0.032	0.913

IV. DISCUSSION

The results shown that the granular TiO_2 possessed excellent durability, stability and reusability. Furthermore, the ease of separating granular TiO_2 from aqueous solutions is one of the most important advantages after dye degradations. The amount of the dye adsorbed onto the catalytic surface increases with increasing dye concentration. Active sites may be covered with dyes at high dye concentration. This leads to a decreased generation of OH radicals on catalyst surface, hence reducing photocatalytic activity. On the contrary, photons easily reach to the surface of the catalyst at low dye concentrations and the formation of OH radicals will be easier.

V. CONCLUSION

From the results, it was observed that granular TiO_2 is suitable the for the removal methylene blue dye by photocatalytic degradation method. The increased initial dye concentration causes an inhibitory effect on the photocatalytic degradation yield, and it leads to a decrease in the color removal efficiency. As a result of the experiments, a yield of 87% was obtained using 50 mg/L methylene blue and 40 g of granular TiO_2 for one hour. As a results, the granular TiO_2 is the well candidate in photocatalytic applications in environment area due to its reusability and high photocatalytic stability.

ACKNOWLEDGMENT

The authors thanks to Gürbüz Research Team (GRT) researchers in Advanced Materials Laboratory for granular TiO_2 fabrication and supplying.

REFERENCES

[1] R.S. Dariani, A.Esmaeili, A. Mortezaali., S. Dehghanpour "*Photocatalytic reaction and degradation of methylene blue on TiO_2 nano-sized particles*" Optics, vol. 127, pp. 7143-7154, Sep. 2016

[2] M. Salehi, H. Hashemipour, M. Mirzaee, "*Experimental Study of Influencing Factors and Kinetics in Catalytic Removal of Methylene Blue with TiO_2 Nanopowder*" American Journal of Environmental Engineering, Jan. 2012

[3] M. Luo, D. Bowden, P. Brimblecombe, "*Removal of Dyes from Water Using a TiO2 Photocatalyst Supported on Black Sand*" Water, Air and Soil Pollution, vol. 198, pp. 233-241, March 2009

[4] E.A. El-Sharkawy, Afaf Y. Soliman, Kawthr M. Al-Amer "*Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation*" Journal of Colloid and Interface Science, vol. 310, pp. 498-508, June 2007

[5] Mohd. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, "*Adsorption of methylene blue on low-cost adsorbents: A review*" Journal of Hazardous Materials, vol. 177, pp.70-80, May 2010

[6] M.H. Abdellah, S.A. Nosier, A.H. Al-Shazly, A.A.Mubarek, "*Photocatalytic decolorization of methylene blue using TiO_2/UV system enhanced by air sparging*" Alexandria Engineering Journal, vol.57, pp. 3727-3735, Dec 2018

[7] E.Çakıroğlu, "*Titanyum Dioksit Esaslı (TiO_2) Fotokatalizör Kullanılarak Toksik Madde İçerikli Atık Suların Detoksifikasyonu*" Metallurgy and Materials Eng., Dokuz Eylul University Graduate School of Natural and Applied Sciences, Izmir, Turkey, June 2011.

[8] E.D. Sam, M. Urgen, F.Z. Tepehan, "TiO_2 fotokatalistleri" İTÜ Dergisi, Vol. 6, pp. 81-92, 2007

[9] K. Nakata, A. Fujishima, "*TiO_2 photocatalysis: Design and applications"* Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 13 (2012) 169–189