광촉학반응을 이용한 메틸오렌지의 탈색

이 태 규, 김 동 형, 김 경 남, 오 정 무
한국에너지기술연구소, 태양에너지응용연구팀

Heterogeneous Photocatalytic Bleaching of Methyl Orange

Tai K. Lee, Dong H. Kim, Kyung N. Kim, Chungmoo Auh
Applied Solar Energy Lab, Korea Institute of Energy Research

Abstract

This work was performed to investigate the photocatalytic decolorization of waste water from textile industries. Methyl orange was used as a target dye with suspended Hombikat TiO2 photocatalyst with a recirculating annular photoreactor. 1 wt % Pt-doped Hombikat thin film tubular reactor with parabolic reflector also was usedin this experiment. The pH effect and flow rate effect on photobleaching of 0.012 g/l methyl orange solution. AtpH=3 colour of methyl orange was completely bleached in 30 min with a 20 W UV lamp.

1. Introduction

It has been known that semiconducting photocatalyst along with an appropriate wavelength of light is a prerequisite for the complete decomposition of toxins present in water. Semiconductors can act as sensitizers for light-induced redox processes due to their electronic structure consisting of a filled valence band and an empty conduction band. Electron (e_{CB}) / hole (h_{VB}^{+}) charge pairs are generated within the photocatalyst particle following the absorption of photons with an energy exceeding the semiconductor bandgap energy.

In this work we aimed at investigating the photocatalytic bleaching of methyl orange in the presense of Hombikat TiO_2 and Pt-doped Hombikat,

respectively. Azo dyes are mostly used in textile industry, and are certainly contained in effluents discharging from the textile industries. Due to the stability of modern dyes, conventional biological treatment is sometimes ineffective for decolorizing the textile dye waste streams. Methyl orange is one of typical azo dyes, and its colour and structure strongly depend on pH. Therefore effort has been directed toward investigating the effect of pH and flow rate on the photobleaching rate of methyl orange with TiO_2 powder and Pt-doped TiO_2 in the aqueous solution using two different types of recirculating photoreactor.

2.Experimental

Hombikat UV 100 TiO_2 powder was provided by ISFH of Germany. Its lattice was proved to be anatase by XRD, and surface area is higher than 250 m^2/g . The primary particle size is less than about 10 nm.
Reagent-grade $H_2PtCl_6 nH_2O$ (n=4.8 or 6) has been used to deposit platinum islands on Hombikat. In this experiment reagent-grade methyl orange has been selected as a model compound for photocatalytic bleaching.
In order to prepare Pt-loaded TiO_2, initially exact amount of $H_2PtCl_6 nH_2O$ was taken regarding mass ratio to TiO_2, and dissolved into ethanol(EtOH). This platinic acid-EtOH solution and Hombikat were then mixed with deionized water and stirred vigorously. The water employed in all preparations and experiments was purified by a Milli-Q/RO system resulting in a resistivity higher than 18.2 MΩcm. And then this mixed slurry solution was dried at 80 °C in air for 24 hr. Finally heat treatment was carried out at 300 °C in air for 1 hr.
Two different recirculating photoreactors have been employed; an annular photoreactor and a parabolic trough tubular photoreactor. 1 g / l of Hombikat or Pt-doped Hombikat powder was loaded as photocatalyst. The slurry was recirculated through a reactor by means of a peristaltic pump during illumination. Only one 20 W UV lamp mounted down the center of the reactor and provided illumination to the suspension for an annular reactor in Fig.1. A recirculation reservoir was placed on a magnetic stirring plate, and provided inlet ports for oxygen sparging at the flow rate

of 30 ml/min during run. Fig. 2 shows the recirculating parabolic trough tubular reactor coated with 1 wt % Pt-doped Hombikat TiO_2 photocatalyst. Parabolic reflecting material of the concentrator is optical mirrors. Its aperture area is 0.3 m^2, and focal length and spot size are about 30 cm and 1.25 cm, respectively. Volume of borosilicate tubular reactor is about 60 cm^3. Total 900 cm^3 of feed solution was circulated during illumination provided from 600 W halogen lamps or UV Osram lamps. Oxygen sparged during each run.

Initial concentration of methyl orange solution was 0.012 g/l. Since the absolute concentrations of methyl orange after photoreaction were unknown, dye degradation rates were quantified by measuring the absorbance using UV-VIS spectrometer at 465 or 509 nm wavelegnths.

If the pH of methyl orange solution was in the range of 3-5, the colour became reddish and the absorbance was measured at 509 nm. However, if the pH of methyl orange solution in the range of 7-11 then colour was orange and the absorbance was measured at 465 nm.

3. Results and Discussion

3.1 Effect of pH

As mentioned previously, since colour and structure of methyl orange strongly depend on pH, pH plays an important role in photobleaching of methyl orange as illustrated in Fig. 3. Increasing initial pH value from 3 to 7.5 decreased bleaching rate but at pH=9.1 bleaching rate increased. However, bleaching rate decreaded again at initial pH = 11. The results with an annular reactor also can be summarized as follows ;

pH = 3.0 ; Ao = 0.83	A(40min) = 0.006	A/Ao = 0.007
pH = 5.6 ; Ao = 0.542	A(70min) = 0.049	A/Ao = 0.09
pH = 7.5 ; Ao = 0.567	A(70min) = 0.087	A/Ao = 0.153
pH = 9.1 ; Ao = 0.921	A(50min) = 0.182	A/Ao = 0.198
pH = 11 ; Ao = 0.979	A(50min) = 0.432	A/Ao = 0.441

3.2 Effect of flow rate

The effect of flow rate on the bleaching rate was investigated by utilizing a

parabolic trough tubular reactor and the initial pH of methyl orange solution was 3. During one experimentation flow rate was swithched three times from 490 cc/min to 270 cc/min and then to 90 cc/min. The inner wall of tubular reactor was coated with 1 wt % Pt-doped Hombikat and Osram UV lamp was used. As shown in Fig. 4 it was observed that the change in bleaching rate of methyl orange is negligible. It is also seen that the slope of absorbance-illumination time curve, dA/dt = 0.002, and is almost constant. Results show that flow rate does not affect the beleaching rate for the recirculating photoreactor under this experimental conditions.
Fig. 5 also shows the effect of flow rate on the bleaching rate but inital pH = 9.2. It was also observe that the effect of flow rate was marginal.

3.3 Effect of photoreactor and photon source

Osram UV lamp(Fig.4) and halogen lamp(Fig.6) have been utilized to irradiate the parabolic trough tubular reactor. For both cases the initial concentration of methyl orange was 0.012 g/l, pH = 3 and flow rate was 460 cc/min. Results are summarized as follows ;

Ao = 0.605 A(135 min) = 0.362 ; Osram UV lamp

Ao = 0.606 A(210 min) = 0.364 ; halogen lamp

It is observed that decolourization reaction rate with hallogen lamp is much slower than that with Osram UV lamp.

3.4 Effect of platinum doping

Fig. 7 shows the result of the photobleaching rate of methyl orange with an annular photoreactor in the presense of 1 wt % Pt-doped Hombikat. It is shown that the bleaching ratio has been significantly enhanced compare with the result of undoped Hombikat in Fig. 3. It has been validated from this result that an appropriate platinization on TiO_2 helps decolourization in water phase by retarding $e_{CB}^- - h_{VB}^+$ recombination.

4. Summary

The results reveal that photocatalytic bleaching of effluents from textile industries is one of the promising waste water treatment technologies.

The photobleaching of methyl orange was significantly enhanced by the Pt-doped TiO_2 photocatalyst. Also thin film photoreactor can be utilized without loosing activity for photobleaching of dye. At pH=3 colour of methyl orange was completely bleached in 30 min with an annular reactor and a 20 W UV lamp. It can be concluded that photocatalytic treatment of waste water from textile industries is promising technology for the practical use.

Acknowledgement

The authors acknowledge the financial support of Ministry of Science and Technology. We wish to thank Dr. D. Bahnemann and Mr. M. Lindner of ISFH, Germany for supplying materials and valuable assistance for performing measurement.

References

1. M. Anpo, H. Nakaya, S. Kodama, Y. Kubokawa, K, Domen, and T. Onish, *J. Phys. Chem.*, 90,p 1633 (1986).
2. R. W. Matthews, *J. Phys. Chem.*, 91,p 3328 (1987).
3. C. Kormann, D. W. Bahnemann, and M. R. Hoffmann, *Environ. Sci. Technol.*, 25,p 494 (1991).
4. T. K. Lee, D. H. Kim, S. H. Cho, and C. P. Auh, *J. Korean Solar Energy*, 12,p 10 (1992).
5. C. S. Turchi and D.F. Ollis, *J. of Cat.*, 119,p 483 (1989).
6. D. Bahnemann, Photocatalytic formation of sulfur-centered radicals by one-electron redox processes, in C. Chatgilialoglu and K. D. Asmus, Sulfur-centered Reactive Intermediates in Chemistry and Biology(NATO-ASI Series), Plenum Press, London, NewYork (1990).
7. J. Fritz and G. Schenk, Quantitative Analytical Chemistry, Allyn and Bacon, Inc. (1966).
8. D.F. Ollis, C. Hsiao, L. Budiman, and C. Lee, *J. of Cat.*, 88,p 89 (1984).

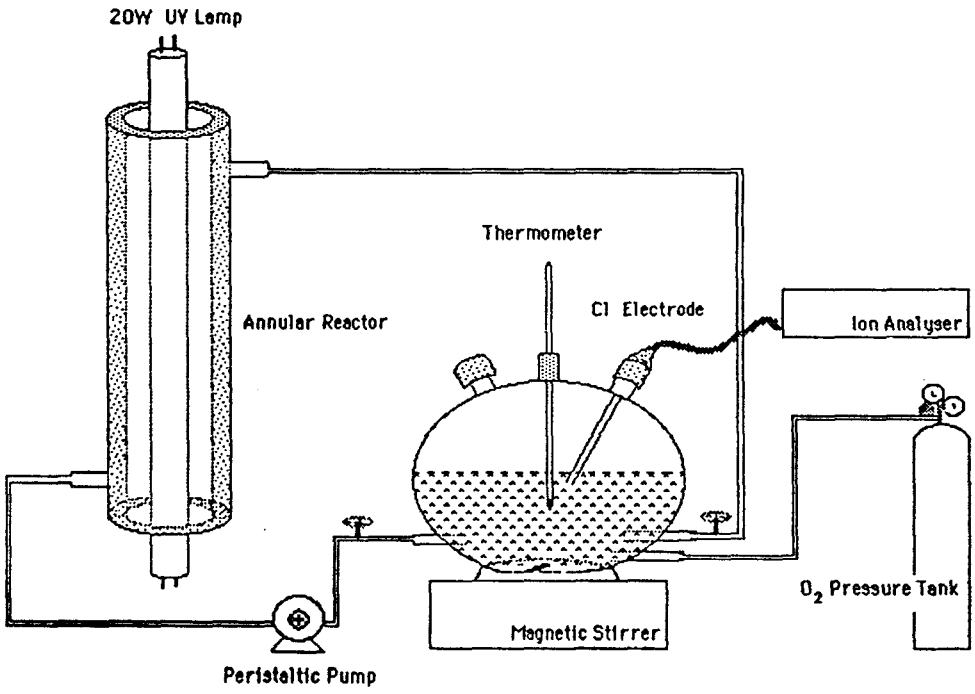

Fig. 1 The annular photoreactor.

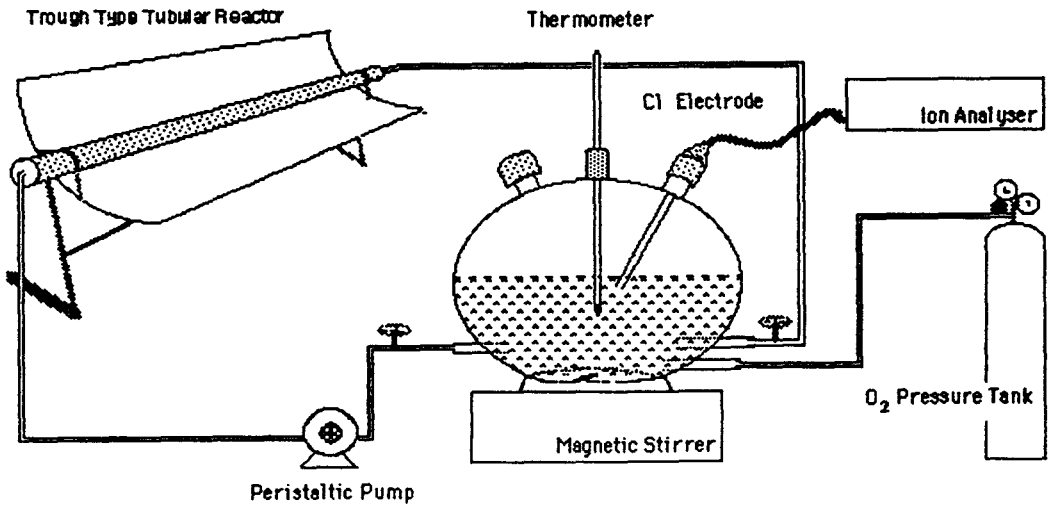

Fig. 2 The parabolic trough tubular photoreactor.

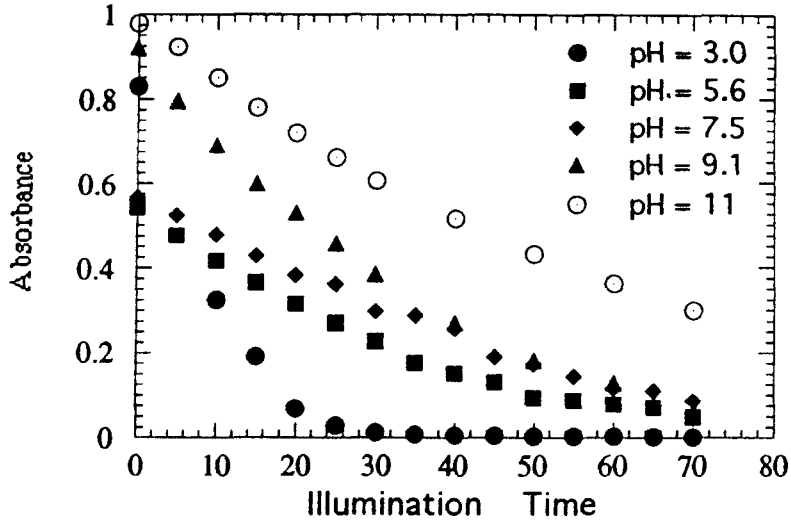

Fig. 3 The effect of pH on bleaching rate of methyl orange (0.012 g/ l MO, 1 g/l Hombikat, 20 W UV lamp, flow rate = 490 cc/min, continous O_2 sparging, cold water HX).

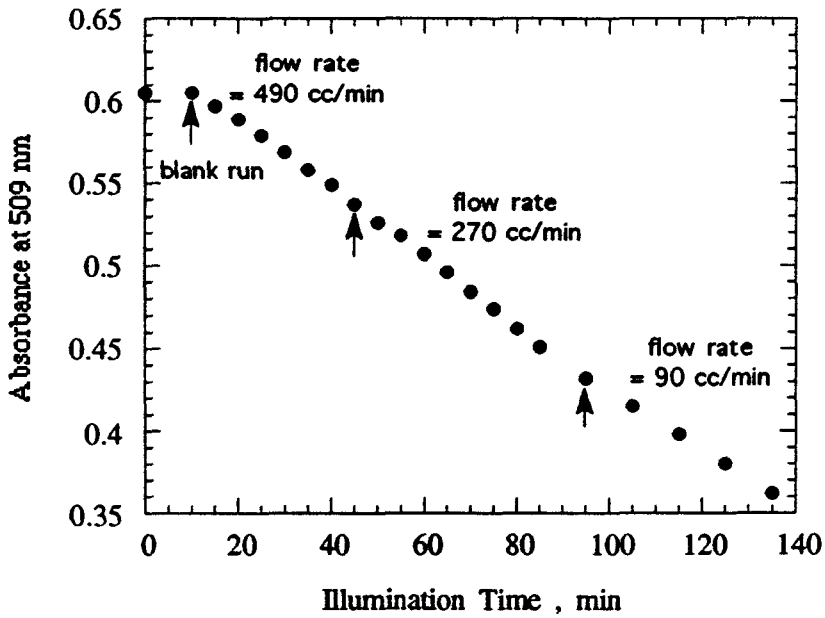

Fig. 4 The effect of flow rate on bleaching rate of methyl orange (0.012 g/ l MO, 1 g/l Hombikat, pH = 3, Osram UV lamp, continous O_2 sparging, cold water HX).

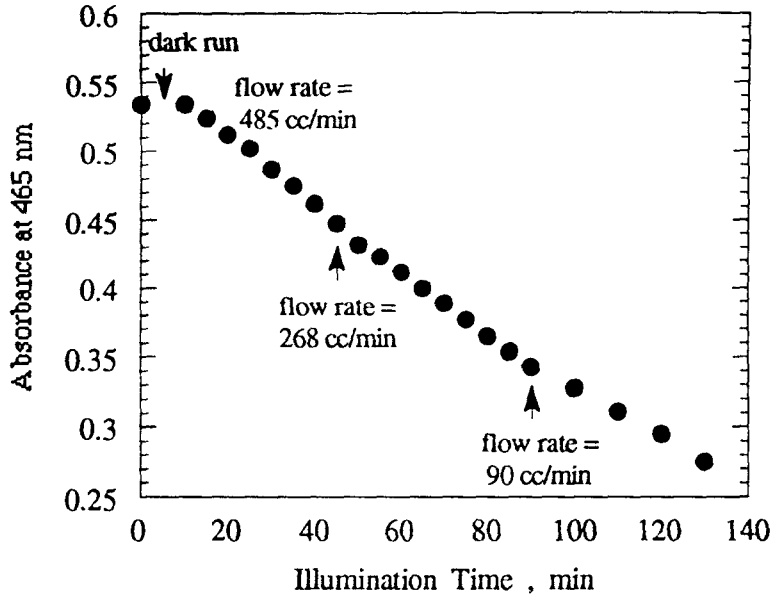

Fig. 5 The effect of flow rate on bleaching rate of methyl orange (0.012 g/ l MO, 1 g/l Hombikat, pH = 9.2, Osram UV lamp, continous O_2 sparging, cold water HX).

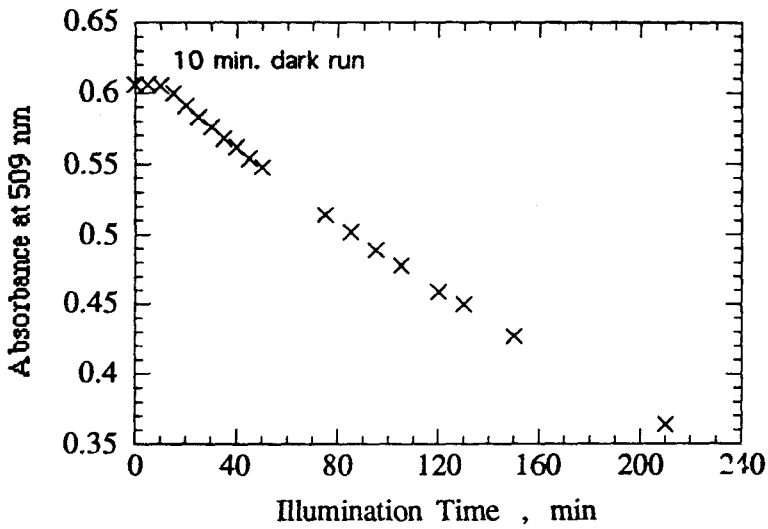

Fig. 6 Absorbance as a function of illumination time (0.012 g/ l MO, 1 g/l Hombikat, pH = 3, halogen lamp, flow rate = 490 cc/min, continous O_2 sparging, cold water HX).

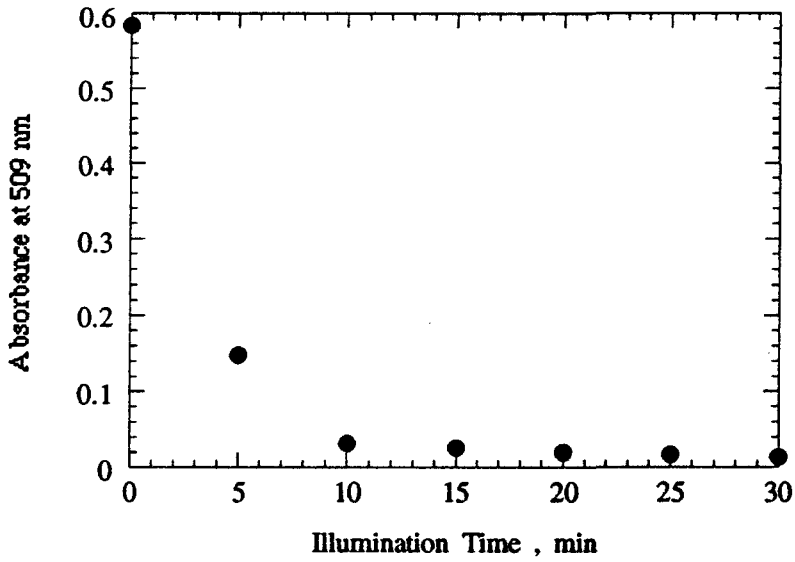

Fig. 7 Absorbance as a function of illumination time (0.012 g/ l MO, 1 g/l Pt-doped Hombikat, pH = 3, annular reactor, flow rate = 490 cc/min, continous O_2 sparging, cold water HX).