出國報告（出國類別：論文發表）

2011 年能源、環境與可持續發展國際學術會議

服務機關：國立臺東專科學校

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派赴國家：中國上海

出國期間：**2011/10/21 ~ 2011/10/24**

報告日期：：**2011/10/22 ~ 2011/10/23**

• 摘要

十月二十一日至十月二十三日在大陸上海市舉行的 2011 國際能源、環境與永續發展研討會(The 2011 International Conference on Energy, Environment and Sustainable Development)，會議主題相當廣泛，包含：地球能源的利用、環境科學與地球永續發展等。在此次會議中，本人參與了 Progress in Environmental Science and Engineering 議題之研討，此議題延續了三天的議程，相關領域的學者於論文發表中相互討論，獲益良多，同時認識了許多相關領域的人員。

這次參加研討會發現，學術界漸漸趨向跨領域的結合且有新的研究方法也是一大重點，看到每位學者有著非凡的能力，與志同道合的同好討論問題分享心得，瞭解世界的腳步，這樣的氛圍是在令人感動，也更能體會到『聽別人的報告以及論文，同時也是讓自己增加知識最好的機會』；此外，看了許多學者們上台發表的能力，以及即時針對台下所發問的問題應答如流，更期許自己能在外語的口語翻譯及豐富的詞彙方面更加精進。

目 次

一、本文

● 目的

為提升本人學術研究水平、國際交流與結識國際相關領域學者，特參加2011 國際能源、環境與永續發展研討會(The 2011 International Conference on Energy, Environment and Sustainable Development)，共同分享學術研究成果。

● 參加會議經過

2011 國際能源、環境與永續發展研討會(The 2011 International Conference on Energy, Environment and Sustainable Development)於十月二十一日至十月二十三日在大陸上海市舉行。會議主題相當廣泛，包含：地球能源的利用、環境科學與地球永續發展等。在此次會議中，本人參與了Progress in Environmental Science and Engineering 議題之研討，此議題延續了三天的議程，相關領域的學者於論

文發表中相互討論，獲益良多，同時認識了許多相關領域的人員。

● 與會心得

此次研討會除了發表本實驗室的研究成果外，也利用空餘時間去聆聽其他學者所發表的研究論文；這次參加研討會發現，學術界漸漸趨向跨領域的結合且有新的研究方法是一大重點，看到每位學者有著非凡的能力，與志同道合的研究者討論問題分享心得，瞭解世界的腳步，這樣的氛圍更增加對自我在未來的期許。此外在上海的生活體驗亦增加了不少個人視野，無論在都市發展、創意造街與學術研究上，均是一日千里、寡目相看。最後，後學感謝學校補助註冊費，得以出國參加此國際研討會，受益良多。

● 建議

1. 對於日後參加國際會議學者的建議：出國發表研究成果前，可多準備個人及學校相關資料，俾利進

一步交流，以達學術交流之目的。

2.學校補助教師參加國際研討會是相當值得鼓勵的做法，一方面提昇教師研究能力，另一方面多與國外學者進行學術交流，才能讓本校學術研究更具國際競爭力。由於出國機票、生活費及住宿費發費甚高，從補助經費之角度來看，學校應多編列經費補助。

●其 他

無

二、附錄

- 相關資料

附錄一 論文全文

附錄二參觀活動照片

附錄一 論文全文

Study on the photocatalytic degradation of wastewater under the optimal preparation of the activated carbon supported TiO_2 thin film

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Keywords: TiO_2 thin film, Characterization, Photocatalytic degradation, Activated carbon

Abstract. Textile industries usually discharge colored effluents containing various dyes. These dyes usually contain more than one aromatic structure and they are not only difficult to be degraded biologically but also toxic. UV/semiconductor procedure, with advantages including photostability, non-toxicity, affordable price, and insolubility in water, has been studied and used. This aim of this study is to develop photocatalytic reactor with higher removal efficiency. The TiO_2 thin film was prepared by Sol-Gel method and coated on the surface of activated carbon to enhance the reaction opportunity and increase pollutants removal efficiency. Taguchi method was used to optimize preparing conditions. The results indicated that the best TiO_2 photocatalytic activity can be found when tetraisopropyl orthotitanate, isopropyl alcohol and acetic acid were mixed in the molar ratio of 1：2：8 under the calcination temperature of 500℃ for 90 minutes. Further analysis of TiO_2 thin film by SEM, ESCA and XRD, the results showed that grain size of TiO_2 was about 17 nm and crystal structure mainly was anatase. The photocatalytic reaction rate increased 15~20% when the ratio of PAC in catalyst increased > 4%. The results suggested that recovery of the composited catalyst become easy because its volume and subsiding increased.

Introduction

In recent years, many researchers are devoted to study the application of photocatalytic reaction. Among them, TiO_2 has attracted much attention because of the low price, steady and high photocatalytic activation [1-3]. However, an obvious problem, separation of photocatalyst from the reaction medium, restricted the application of heterogeneous photocatalysis. This shortcoming results in low efficiency in practical applications. In order to overcome this disadvantage, many studies have devoted the improvement for the photoactivity of TiO_2 catalyst, especial powdered catalyst. To support TiO_2 on matrixes such as activated carbon (AC), zeolites and silica, etc. is an easily applicable method for the continuous processes [4-8]. Among of them, AC is the most recommendatory use as supporting material due to its porous structure, high surface area and adsorption properties. Sol-gel method is also a common chemical approach to prepare high pure catalysts and it was modified in this study for preparing AC/TiO_2 complexes. The objectives of this study are as followings. 1) Two types of AC, granular activated carbon (GAC) and powder activated carbon (PAC), were used to prepare the optimal AC/TiO_2 complexes using Taguchi method and analyze their properties. 2) The phtotocatalytic activity of AC/TiO_2 complexes were demonstrated by the degradation efficiency of methylene blue (MB) under the certain photocatalytic conditions.

Experimental Methods/ Materials

Preparation of AC/TiO_2 Complexes. The AC/TiO_2 complexes were prepared with the modified sol-gel method using Taguchi method. The sol–gel process is one of the versatile methods to prepare high pure and nano-size materials shaped as powders or coatings. It provides a simple and easy method to synthesize nano-size photocatalysts. First, soluble TiO_2 precursor powder was prepared using a mixture of tetraisopropyl orthotitanate ($Ti(OC_3H_7)_4$) (TTIP, > 98%, Merck Co.), 2-propanol (> 99.7%, JT. Baker) and acetic acid (> 99.9%, JT. Baker). Then the mixed solutions were stirred for 24 h and dried at 105 ℃ followed by 150 ℃ for 1 h respectively. The dried gel was then pulverized into powder and calcinated in the high temperature oven. The parameters employed to control the preparation of the catalyst including 2-propanol, acetic acid (TTIP was fixed), calcinations time and calcinations temperature. The orthogonal arrays in the design of experimental method proposed by Taguchi were adopted to conduct the multiple-factor experiment. The conversion rate of MB in this experiment was employed to

identify the optimal conditions for assembly. The reactor containing AC/TiO_2 complexes was irradiated with a 365-nm UV lamp to undergo the batch photocatalytic degradation experiment. Second, the above prepared TiO_2 powder was directly mixed with GAC and PAC (JT. Baker) . The weight percentage (w/w) of TiO_2 was calculated based on the designed AC/TiO_2 ratio as followings: 95, 90, and 25. Then the mixed solutions were stirred for 1 h and dried at 105 ℃for 1 h. The AC/TiO_2 complexes prepared by this approach were assigned as GT-95, GT-90, GT-25, PT-95, PT-90 and PT-25 where G and P represent the granular activated carbon and powder activated carbon respectively.

Photocatalytic Activity Test – Methylene Blue Destruction Experiment. To evaluate the photocatalytic activities of AC/TiO_2 complexes photocatalysts activated with a photochemcal reactor (Rayonet Model RPR 100, the Southern New England Ultraviolet Company) with 360 nm irradiation for 120 min, the conversion rate of methylene blue was performed and calculated by measuring the optical absorption at a wavelength of 664 nm according to the photocatalytic degradation test described previously [9].

Results and Discussion

Optimal Preparation of Phtocatalysts using Taguchi Method. The controlling factors, which include 2-propanol (0.08, 0.16, 0.32 mol), acetic acid (0.08, 0.16, 0.32 mol), calcinations temperature (400, 500, 600 ℃)and calcinations time (90, 120, 180 min) were listed in the L_9 table. Different photocatalysts were prepared according to different combinations of controlling factors for conducting the heterogeneous photocatalytic reactions to obtain the conversion rates of MB. The MB conversion rates thus obtained were then statistically analyzed by the F test to determine the significance and variability of each factor. The variation, variance and contribution of each factor were listed in Table 1. As can be seen, among the factors, calcinations temperature had the greatest effect on conversion rate of MB in the photocatalysis system (59.41%), followed by calcinations temperature (26.18%), the amount of 2-propanol (7.89%) and finally, the amount of acetic acid (6.53%). In general, the effect of calcination temperature was more significant due to its function in removing impurities and increasing crystal strength. Table 2 shows the contributions and major effects of different parameters. The optimal preparation

condition of TiO_2 catalyst was achieved under water 2-propanol of 0.08 mol, acetic acid of 0.32 mol, (that is TTIP/ 2-proanol/ acetic acid with a molar ratio of 1:2:8), calcinations temperature of 500 °C and calcinations time of 90 min. The TiO_2 was prepared at the above optimal experimental conditions.

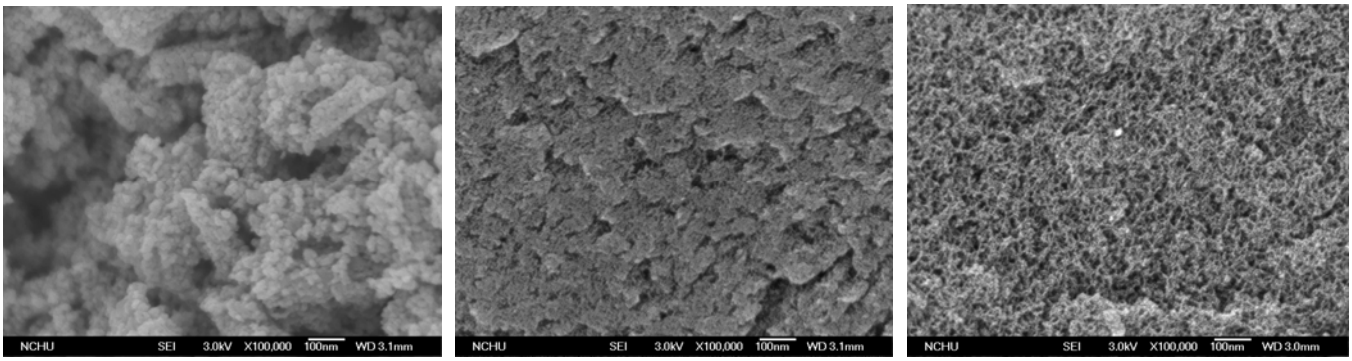
Table 1 Analysis of variables (ANOVA)

Factor	Degree of Freedom (f)	Variation (S)	Variance (V)	Contribution (%)
2-propanol (mol)	2	353.981	176.990	7.89
Acetic acid (mol)	2	293.155	146.578	6.53
Calcination Temperature (°C)	2	2666.427	1333.214	59.41
Calcination time (min)	2	1174.851	587.426	26.18

Table 2 Response of parameters in L_9 table

Factors	**2-propanol (mol)**	**Acetic acid (mol)**	**Calcination temperature (℃)**	**Calcination time (min)**
Level1	62.09	53.17	48.39	67.40
Level 2	47.45	36.66	61.99	40.46
Level 3	58.81	78.52	57.97	60.48
Main effect	14.63	41.85	13.61	26.94

Analysis of Properties of AC/TiO_2 Complexes. The field-emission scanning electron micrographs (FE-SEM, JSM-6700F, JEOL, Japan) of pure TiO_2, GAC, PAC, GT-25 and PT-25 complexes are shown in Fig.1. The Fig. 1(a) is the image of pure TiO_2 catalyst at magnification of 100,000 times. Fig. 1(b) and (c) are the images of GAC and PAC only, the porous structures were shown clearly. Fig. 1(d) and (e) are the images of GT-25 and PT-25 catalysts at magnification of 50,000 times respectively. Their structure performance on the surface of AC/TiO_2 complexes photocatalysts are similar to pure TiO_2 but more uniform and tightly. As shown in Fig. 1 (d) and (e), the particle size was about 15~20 nm.

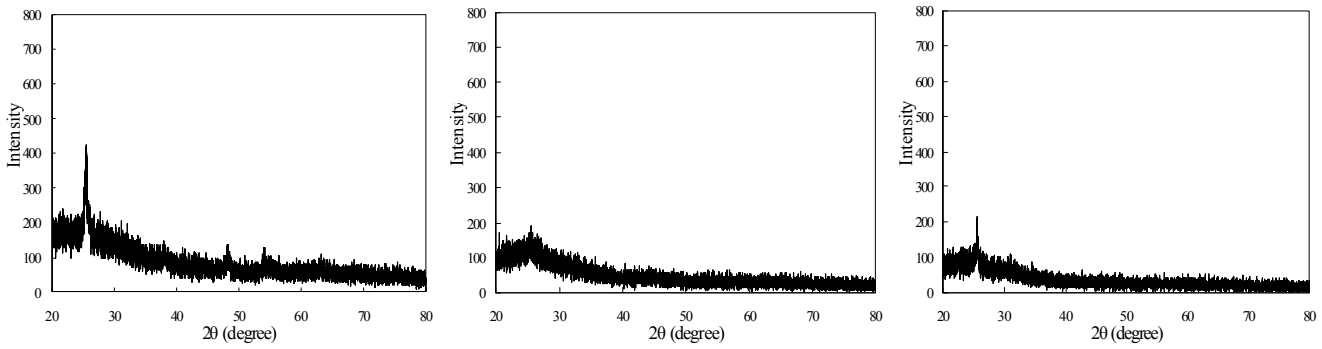


(a) the structure of pure TiO_2 (b) the structure of pure GAC (c) the structure of pure PAC

(d) the structure of pure GT-25 (magnification 50,000 times) (e) the structure of pure PT-25 (magnification 50,000 times)

Fig. 1 SEM images of TiO_2, GAC, PAC and AC/TiO_2 catalystses

The photocatalysts prepared by the modified sol-gel method were analyzed by the X-ray diffractometer (XRD, MAC MXTIII) to examine the crystals form. As illustrated in Figure 2, the main peak appears at the 2θ values of 25.4 at the scanning rate of 40.0 KV, 150 mA and 1.0 deg min^{-1}. In the JCPDS database, the three major diffraction peaks of anatase crystal structure appear at the 2θ values of 25.4, 37.9 and 48.2 (with respect to the diffraction surfaces of 101, 200 and 004, respectively). Therefore, the crystal structure of all the photocatalysts prepared in the experiment was anatase and there was no variation during preparing procedure.



(a) XRD spectra of TiO_2 (b) XRD spectra of GT-25 (c) XRD spectra of PT-25

Fig. 2 XRD spectrum of TiO_2 crystals prepared under optimal conditions

The specific areas of the photocatalysts were analyzed by Brunauer emmett teller (BET, Micromeritic ASAP 2010) and the results are presented in table 3 alone with their composition. The texture of the AC/TiO_2 complexes are highly dependent on their composition. The higher loadings of AC brought about a drastic diminution of the specific surface area as well as the pore volume.

Table 3 The specific surface area of each photocatalyst by BET analysis

Catalysts	BET（$m^2 g^{-1}$）
TiO_2	75.65
GAC	880.05
PAC	1603.81
GT-25	346.52
PT-25	1049.51

Photocatalytic Degradation Test. The photoactivity indicator of AC/TiO_2 complex were investigated by the conversion rate of MB. The 2 g AC/TiO_2 complex were used to react with the 10 ppm MB under the 3.0 mW cm^{-2}, 365 nm UV light and neglected pH for 120 min. The results are illustrated in Fig. 3 and the effect of AC/TiO_2 complex on the conversion of MB was higher than TiO_2 catalyst alone. Comparing the efficiency between PAC/TiO_2 and GAC/TiO_2, the former is also better than the latter and its effiency was up to 96 % after irradiation. Therefore, PAC/TiO_2 complexe was discussed only in the subsequent proportion experiments, These evidences

reveal that the system of AC/TiO_2 complexes has significantly high efficiency of photocatalytic degradation than TiO_2 only.

In discussion of PAC with TiO_2 at different proportion, TiO_2, PT-25, PT-90 and PT-95 were chosen in the test and the result was shown as Fig. 4. The variations in content of PAC affected the conversion of MB. As can be seen, the PAC content is higher and the conversion of MB is more efficient and the PT-25 had the greatest efficiency.

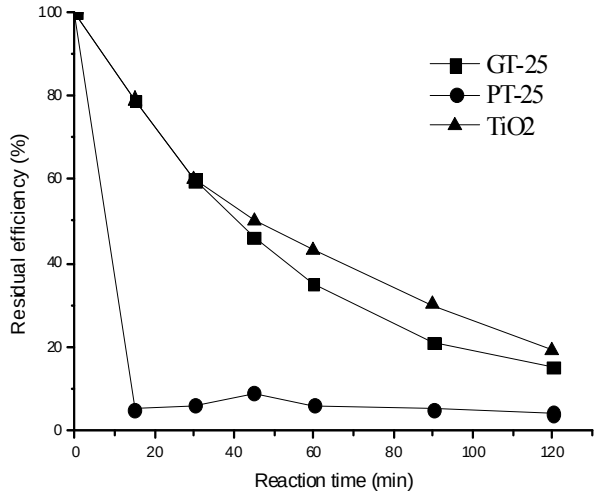


Fig. 3 Effieciency of TiO_2 and AC/TiO_2 complexes (methylene blue of 10 ppm, catalysts of 1 g L^{-1}, irradiation intensity of 3.0 mW cm^{-2}, $\lambda = 365$ nm)

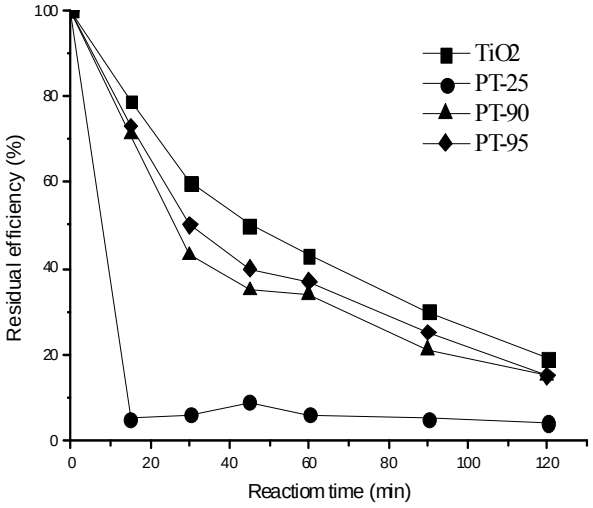


Fig. 4 Effieciency of PAC/TiO_2 complexes at different proportion

Conclusions

The activated carbons were added during preparation of TiO_2 photocatalysts using sol gel method. The particle size of AC/TiO_2 photocatalyst was about 17 nm. Under the UV irradiation, AC/TiO_2 photocatalyst enhanced MB conversion rate up to 96 %. By AC support, the photoactivity of AC was increased during the conversion of MB. It might be due to its porous structure and adsorption properties. The supported catalyst on AC has higher efficiency on the photodegradation of organic pollutants.

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附錄二 與會照片