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Research Article

Photocatalytic Degradation of Indoor Air Pollutants by Pt-TiO_2

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Titanium dioxide (TiO_2) has been extensively studied with regard to its application as the physical sunblock in sunscreen or other cosmetic products, as well as in environmental remediation processes. In this study, the Taguchi method was applied to determine the optimum gaseous DCM (dichloromethane) by Pt-TiO_2 with different Pt contents. An orthogonal array (L32) experimental design that allows for the simultaneous investigation of the variations of six parameters (light source, catalyst type, initial concentration, retention time, photointensity, and relative humidity) was employed to determine the optimum levels. The value of photointensity was not at a confidence interval. According to the response values and an analysis of variance (ANOVA), an experimental result of 34.7 as the optimum condition is forecast. Although the predetermination of 34.7 is not equal to the experimental value, it is contained within the 90% confidence interval (25.8, 43.6).

1. Introduction

Titanium dioxide (TiO_2) has been extensively studied with regard to its application as the physical sunblock in sunscreens or other cosmetic products and in environmental remediation processes because of its high degree of photocatalytic activity, chemical stability, nontoxicity, and commercial availability. Heterogeneous photocatalysis over UV-illuminated semiconductors constitutes a very promising technique for air purification [1–3]. However, the valence band holes and conduction band electrons, which are produced with the UV irradiation, easily recombine and liberate light or heat, which are responsible for low degradation efficiency [4]. In order to enhance degradation efficiency, modifications of TiO_2 have been conducted with metal or nonmetal substances [5, 6].

In contrast, an excessive metal deposition on TiO_2 has an inhibitory effect on contaminant degradation [7]. In degradation experiments, many factors affect degradation efficiency. The use of an orthogonal array to design the experiments and the S/N ratio (signal-to-noise ratio) to analyze experimental data has allowed designers to simultaneously study the effect of multiple control factors on the average quality characteristic and variance, both quickly and economically. Thus, within the process of the experiment, although using only a few experimental runs, an equally full factorial experiment can be created to obtain the optimum synthesis parameter [8–10].

In this study, the Taguchi method was applied to determine the optimum gaseous DCM (dichloromethane) by Pt-TiO_2 with different Pt contents. DCM is used as a solvent in paint strippers and removers (30%), in adhesives (20%), as a propellant in aerosols (10%), as a solvent in the manufacture of pharmaceuticals and drugs (10%), in chemical processing (10%), as a metal cleaning and finishing solvent (10%), and in urethane foam blowing (5%) [11]. However, due to health concerns, the usage of DCM as an extraction solvent in food products and coffee has declined greatly over the years 12. An orthogonal array (L32) experimental design that allows for the simultaneous investigation of the variations of six parameters (light source, catalyst type, initial concentration, retention time, photo intensity, and relative humidity) was employed to determine the optimum levels. The percent of residual removal was transformed into an accurate signal-to-noise ratio (S/N ratio) for "the smaller-the-better" (SB) response. The initial concentration was found to be the most effective factor for promoting DCM removal, followed by retention time and relative humidity. A light source of

UV/LED, catalyst type of 0.005 wt%, initial concentration of 50 ppmv, retention time of 100 s, and relative humidity of 0% were the best conditions as determined by the Taguchi method.

2. Materials and Methods

2.1. Preparation of Photocatalyst Film. The photocatalytic deposition reported by Chen et al. [5] was modified in this study. For Pt/ TiO_2 preparation, an aqueous TiO_2 suspension (P-25) (25 mg L^{-1}) containing methanol and a predetermined amount of hexachloroplatinic acid ($H_2PtC_{16} \cdot 6H_2O$) was irradiated with a 13.3 W cm^{-2} mercury UV lamp using an APUV-12F lamp for 8 hr. N_2 gas was purged through the suspension prior to UV irradiation to remove any oxygen. Dioctyl sulfosuccinate of 0.02 g L^{-1} was subsequently used as a dispersing agent and stirred vigorously in the mixed solution for more than 8 h. A quartz tube (22 mm I.D., 25 mm O.D., and 500 mm length) was then impregnated with the mixed solution for about 1 min before it was taken out and air-dried. Then, the coated quartz tube was calcined at 300°C for 2 hr.

2.2. Characterization of Catalyst. The catalysts were characterized by X-ray diffractometry using a computerized X-Ray Diffractometer (Japan, Cu Ka radiation, 1.54056 nm). High-resolution Transmission Electron Microscope (HR-TEM) images were obtained by means of a JEOL-3010 device with 300 kV accelerating voltage, and the amounts of Pt content were ascertained using an inductively coupled plasma-optical emission spectrometer, ICP/OES (Perkin Elmer, Optima 2000DV).

2.3. Orthogonal Array and Experimental Factors. The aim of this investigation was to determine the optimum process conditions for the removal of gaseous DCM from synthetic gas. The effect of the experimental parameters on the removal of DCM and the levels determined in line with the preliminary tests are given in Table 1. The orthogonal array experimental design method was chosen to determine the experimental plan, L32 (21 × 45), as shown in Table 2, as it was the most suitable for the conditions being investigated: one parameter with two levels and five parameters with four levels. The performance of the Pt/ TiO_2 photocatalyst was assessed in the reactor for treating DCM. This study used an annular photocatalytic reactor (APR) to assess the performance of the catalysts, since it was simple and easy to operate under different operational conditions. The APR schematic and experimental apparatus were described schematically in our previous work [12].

3. Results and Discussion

3.1. Characterization of Catalysts. Catalyst structures were indicated by X-ray diffractometer (XRD). As Figure 1 shows, the XRD pattern of the Pt/ TiO_2 catalyst was essentially the same as that of the TiO_2 sample. The absence of diffraction lines of the Pt phase on the Pt/ TiO_2 catalyst indicated that

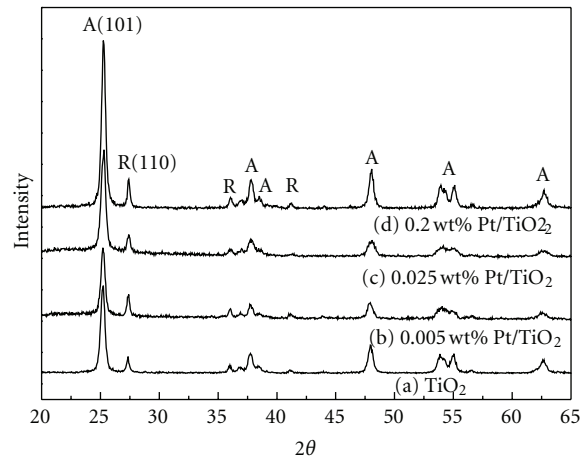


Figure 1: XRD patterns of pure TiO_2 and Pt- TiO_2.

the platinum was well dispersed; the amount of doped Pt was less than 5.0%. The high dispersion degree was also cofirmed by the HR-TEM image of the TiO_2 and Pt/ TiO_2 in Figure 2, in which a clear lattice image of TiO_2 and Pt particles on TiO_2 are evident. The lattice constant of anatase and rutile of the *C* axis in the crystal were 3.61 and 2.59 Å, respectively. The lattice constant was not influenced by the doped Pt. The size of the Pt particles was determined to be about 3 nm. The amount of doped Pt was determined by ICP. The result showed that the actual doping was as had been expected.

3.2. Determination of the Optimal Removal Conditions. On the basis of the Taguchi method, the percent of DCM removal was selected as a response variable, and the experimental data were transformed into the S/N ratio. In order to conduct an analysis of the relative importance of each factor more systematically, an analysis of variance (ANOVA) was applied to the data. The results of various runs were performed by ANOVA, as shown in Table 3. The data showed that the contributions of the six factors, that is, light source, catalyst type, initial concentration, retention time, photointensity, and relative humidity, were 7.38%, 10.23%, 26.77%, 19.78%, 4.57%, and 13.83%, respectively. It was apparent that, of the selected factors, initial concentration had the major influence on the reduction of gaseous DCM. The set mean S/N ratio for each level of the factors was calculated. The data from Table 3 shows the $(S/N)_{SB}$ response graph (see Figure 3) for the removal of DCM. The higher average $(S/N)_{SB}$ response represents the best level of each factor and was interpreted as the optimized removal efficiency. Therefore, the optimum treatment conditions were light source of UV/LED, catalyst type of 0.005 wt%, initial concentration of 50 ppvm, retention time of 100 s, and relative humidity of 0%.

In this situation, the predicted value of the response parameter S/N is calculated as follows:

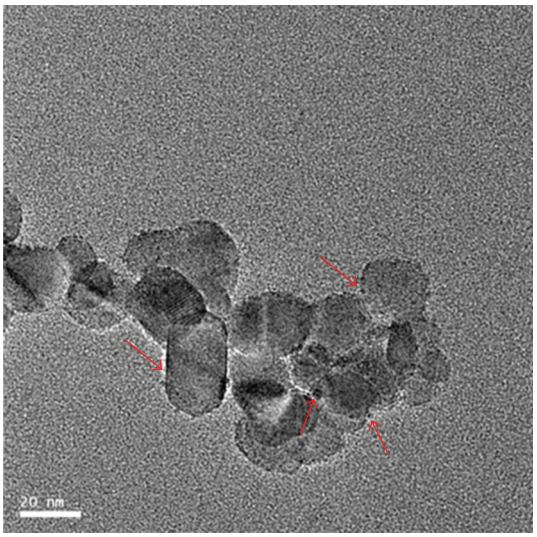
$$\overline{T} = \frac{1}{N}\sum_{i=1}^{32}\eta_i. \quad (1)$$

Table 1: Parameters and their values corresponding to their levels to be studied in experiments.

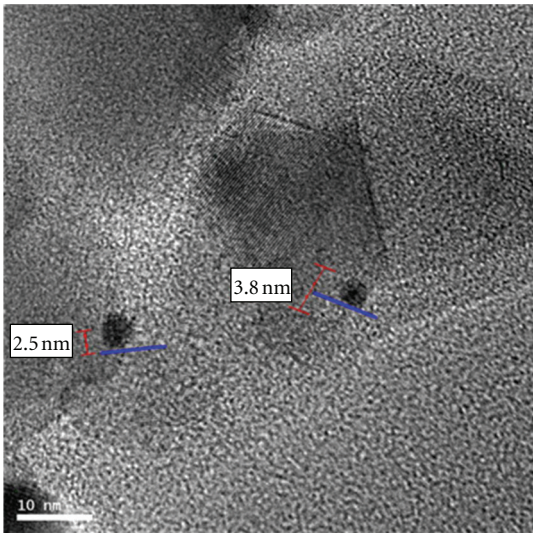
Control factor	Level			
	1	2	3	4
(A) Light source	UV	UV/LED	—	—
(B) Catalyst type	TiO_2	0.005 wt.% Pt/TiO_2	0.025 wt.% Pt/TiO_2	0.2 wt.% Pt/TiO_2
(C) Concentration (ppmv)	50	100	200	300
(D) Retention time (sec)	40	60	80	100
(E) Photointention (Mw cm^{-2})	1.55	1.62	2.1	2.4
(F) Relative humidity (%)	0	5	15	45

Table 2: Experimental layout using the L32 orthogonal array and experimental results for photocatalytic oxidation.

Exp.	Factor levels						C/C_0			S/N$_i$
	A	B	C	D	E	F	Exp. 1	Exp. 2	Exp. 3	
1	1	1	1	1	1	1	0.40	0.48	0.42	7.2
2	1	1	2	2	2	2	0.62	0.64	0.68	3.7
3	1	1	3	3	3	3	0.72	0.73	0.70	2.9
4	1	1	4	2	4	4	0.79	0.77	0.78	2.2
5	1	2	1	1	2	2	0.27	0.34	0.35	9.9
6	1	2	2	2	1	1	0.17	0.18	0.20	14.7
7	1	2	3	3	4	4	0.27	0.37	0.32	9.8
8	1	2	4	2	3	3	0.43	0.40	0.35	8.0
9	1	3	1	2	3	4	0.50	0.55	0.53	5.6
10	1	3	2	1	4	3	0.76	0.75	0.74	2.5
11	1	3	3	2	1	2	0.74	0.67	0.76	2.8
12	1	3	4	3	2	1	0.33	0.40	0.37	8.7
13	1	4	1	2	4	3	0.37	0.40	0.49	7.5
14	1	4	2	1	3	4	0.88	0.86	0.89	1.1
15	1	4	3	2	2	1	0.42	0.31	0.48	7.8
16	1	4	4	3	1	2	0.81	0.86	0.76	1.8
17	2	1	1	2	1	4	0.62	0.63	0.61	4.2
18	2	1	2	3	2	3	0.52	0.54	0.50	5.6
19	2	1	3	2	3	2	0.83	0.90	0.84	1.3
20	2	1	4	1	4	1	0.75	0.70	0.73	2.7
21	2	2	1	2	2	3	0.01	0.01	0.01	40.0
22	2	2	2	3	1	4	0.32	0.45	0.26	9.0
23	2	2	3	2	4	1	0.47	0.38	0.44	7.3
24	2	2	4	1	3	2	0.76	0.81	0.72	2.3
25	2	3	1	3	3	1	0.01	0.01	0.01	40.0
26	2	3	2	2	4	2	0.01	0.10	0.10	22.0
27	2	3	3	1	1	3	0.86	0.81	0.86	1.5
28	2	3	4	2	2	4	0.96	0.93	0.96	0.5
29	2	4	1	3	4	2	0.12	0.08	0.18	17.5
30	2	4	2	2	3	1	0.01	0.02	0.05	29.4
31	2	4	3	1	2	4	0.90	0.91	0.94	0.8
32	2	4	4	2	1	3	0.77	0.87	0.90	1.4



(a)



(b)

Figure 2: TEM images of (a) pure TiO_2, (b) Pt- TiO_2.

Predicted value for the S/N is

$$\mu_{S/N} = \overline{T} + \left(A2 - \overline{T}\right) + \left(B2 - \overline{T}\right) + \left(C1 - \overline{T}\right) + \left(D4 - \overline{T}\right) + \left(F1 - \overline{T}\right). \quad (2)$$

Confirmation testing is a necessary and important step in the Taguchi method, and a confirmation test must be carried out at the end of an optimization study. A confirmation test was conducted for the photodegradation of DCM without

Table 3: Pooled ANOVA table for the regular analysis.

Factor	SS	DOF	Contribution	Var	F	Confidence level
A	248.9	1	7.38%	248.9	6.35	97.6%
B	344.8	3	10.23%	114.9	2.93	93.2%
C	902.5	3	26.77%	300.8	7.68	99.8%
D	666.6	3	19.78%	222.2	5.67	99.2%
E	154.1	3	4.57%	51.4	1.31	69.3%
F	466.2	3	13.83%	155.4	3.97	97.1%
Error	587.7	15	17.43%	39.2	—	—
Total	3370.8	31	100.00%			

Note 1: At least 90% confidence level.
Note 2: SS: the sum of squares total; DOF: degrees of freedom; Var: variance; F: variance between/variance within.

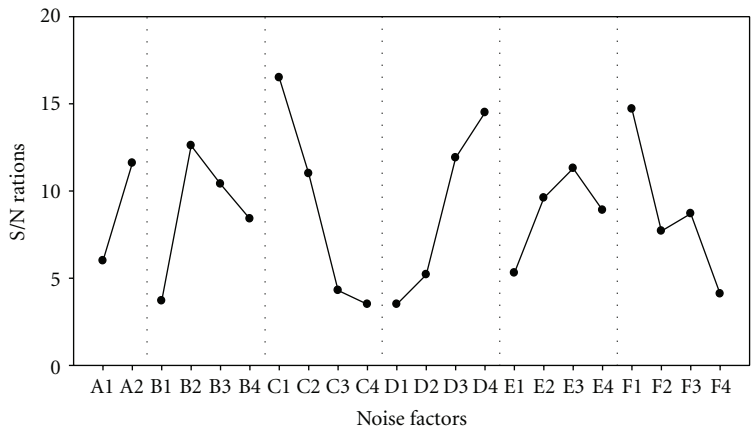


Figure 3: $(S/N)_{SB}$ graphical illustration of the response to each factor.

repetition at the optimum setting of the process parameters. The 90% cofidence interval of the confirmation test (CI) was calculated using

$$\mathrm{CI} = \sqrt{F_{\alpha;1,\nu_2} \times \mathrm{MSE} \times \left[\frac{1}{n_{\mathrm{eff}}} + \frac{1}{r}\right]}. \quad (3)$$

So, the predicted optimal range (for confirmation runs of one test) was

$$\begin{gathered} \widehat{\mathrm{SN}} - \mathrm{CI} \le \mu_{\mathrm{Confirmation}} \le \widehat{\mathrm{SN}} + \mathrm{CI} \\ 25.8 \le \mu_{\mathrm{Confirmation}} \le 43.6, \end{gathered} \quad (4)$$

where $F_{\alpha;1;\nu 2}$ is F value of the significant level of α; MSE, merge all variance; n_{eff}, effective observations; r, test times.

The confirmation test indicated that 40 values for the photodegradation DCM was within the acceptable limits. Under these conditions, the efficiency of treated VOCs reached a maximum in the process of photodegradation DCM from the indoor environment.

4. Conclusions

In this study, Pt-TiO_2 was prepared by photocatalytic deposition. The lattice constant of TiO_2 was not influenced by the doping. The size of the Pt particles was determined to be about 3 nm. The amount of doped Pt was determined by ICP. The result showed that the actual doping was the same as had been expected. To optimize the operational factors of DCM photodegradation, the Taguchi method was employed. A light source of UV/LED, catalyst type of 0.005 wt%, initial concentration of 50 ppvm, retention time of 100 s, and relative humidity of 0% were the best conditions for the degradation of gaseous DCM. Although the optimum relative humidity was determined to be 0%, the water vapor is present inevitably. A steam trap was suggested to apply to combine both the experimental and practice conditions for the practical application.

Acknowledgment

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References

[1] R. M. Alberici and W. F. Jardim, "Photocatalytic destruction of VOCS in the gas-phase using titanium dioxide," *Applied Catalysis B*, vol. 14, no. 1-2, pp. 55–68, 1997.

[2] J. M. Coronado, M. E. Zorn, I. Tejedor-Tejedor, and M. A. Anderson, "Photocatalytic oxidation of ketones in the gas phase over TiO_2 thin films: a kinetic study on the influence of

water vapor," *Applied Catalysis B*, vol. 43, no. 4, pp. 329–344, 2003.

[3] A. G. Kontos, A. Katsanaki, T. Maggos et al., "Photocatalytic degradation of gas pollutants on self-assembled titania nanotubes," *Chemical Physics Letters*, vol. 490, no. 1–3, pp. 58–62, 2010.

[4] Y. Chen, J. C. Crittenden, S. Hackney, L. Sutter, and D. W. Hand, "Preparation of a novel TiO_2-based p-n junction nanotube photocatalyst," *Environmental Science & Technology*, vol. 39, no. 5, pp. 1201–1208, 2005.

[5] H. W. Chen, Y. Ku, and Y. L. Kuo, "Effect of Pt/TiO_2 characteristics on temporal behavior of o-cresol decomposition by visible light-induced photocatalysis," *Water Research*, vol. 41, no. 10, pp. 2069–2078, 2007.

[6] Q. Li and J. K. Shang, "Composite photocatalyst of nitrogen and fluorine codoped titanium oxide nanotube arrays with dispersed palladium oxide nanoparticles for enhanced visible light photocatalytic performance," *Environmental Science & Technology*, vol. 44, no. 9, pp. 3493–3499, 2010.

[7] J. Mo, Y. Zhang, Q. Xu, J. J. Lamson, and R. Zhao, "Photocatalytic purification of volatile organic compounds in indoor air: a literature review," *Atmospheric Environment*, vol. 43, no. 14, pp. 2229–2246, 2009.

[8] Y. L. Kuo, T. L. Su, F. C. Kung, and T. J. Wu, "A study of parameter setting and characterization of visible-light driven nitrogen-modified commercial TiO_2 photocatalysts," *Journal of Hazardous Materials*, vol. 190, no. 1–3, pp. 938–944, 2011.

[9] M. P. Elizalde-González and L. E. García-Díaz, "Application of a Taguchi L16 orthogonal array for optimizing the removal of acid orange 8 using carbon with a low specific surface area," *Chemical Engineering Journal*, vol. 163, no. 1-2, pp. 55–61, 2010.

[10] M. N. Chong, B. Jin, C. W. K. Chow, and C. P. Saint, "A new approach to optimise an annular slurry photoreactor system for the degradation of Congo Red: statistical analysis and modelling," *Chemical Engineering Journal*, vol. 152, no. 1, pp. 158–166, 2009.

[11] M. T. Holbrook, "Methylene chloride," in *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 16, pp. 371–380, John Wiley & Sons, New York, NY, USA, Online edition, 2003.

[12] C. M. Ma, Y. W. Lee, G. B. Hong, T. L. Su, J. L. Shie, and C. T. Chang, "Effect of platinum on the photocatalytic degradation of chlorinated organic compound," *Journal of Environmental Sciences*, vol. 23, no. 4, pp. 687–692, 2011.