CHAPTER 7

A STUDY OF THE EFFECT OF ENVIRONMENTAL PARAMETERS ON GR/Fe^{3+}–TiO_2 PHOTOCATALYST AND THE PRACTICAL USE OF GR/Fe^{3+}–TiO_2 PHOTOCATALYST FILM FOR FORMALDEHYDE REMOVAL

7.1 Introduction

Formaldehyde (HCHO) is considered as a major indoor air pollutant causing serious health problems in human such as the irritation of respiratory tract, headache, fatigue and thirst (Sekine, 2002). HCHO is commonly released from household products, burning and building materials (Ao, et al., 2004). In the case of the emissions of HCHO inside vehicles, the use of ethanol-blended fuels and biodiesel blends also emits HCHO to the environment (Pang et al., 2008 and Peng et al., 2008). It has been reported that the concentration of HCHO inside vehicle at 65 °C was higher than 1000 ppbV (Schupp et al., 2005). Previously, our group has reported enhancing the photocatalytic activity of TiO_2 co-doping of graphene–Fe^{3+} ions formaldehyde removal. The results show that graphene/Fe^{3+}–TiO_2 (GR/Fe^{3+}–TiO_2) exhibits larger photocatalytic activity than that of TiO_2, Fe^{3+}–TiO_2 and GR–TiO_2 and GR/Ag_2S–TiO_2 photocatalysts as shown in Table 7.1.

Table 7.1 Degradation efficiency (%) of photocatalysts at optimal condition of GR, Fe^{3+} and Ag_2S dopants for formaldehyde removal

Sample	Degradation efficiency (%)	
	UV	Visible light
TiO_2	21.50	12.52
GR–TiO_2 (1:50)	26.76	12.56
GR/Fe^{3+}–TiO_2 (0.12 wt% Fe^{3+})	50.31	24.95
GR/Ag_2S–TiO_2 (5.6 wt% Ag_2S)	27.26	15.20

The degradation efficiency (%) of photocatalyst for gaseous HCHO removal under UV irradiation was about 54–80% under humidity levels in the range of 2100–2200 ppmV (Ao, et al., 2004). In the batch reactor, the maximum degradation efficiency of gaseous HCHO under UV irradiation was around 35–80% when the initial concentration was set at 7000 ppmV (Boonamnuayvitaya and Photong, 2009). The study of the photocatalytic degradation of gaseous HCHO under outdoor sunshade irradiation by using glass chamber reactor has been reported. The initial concentration of gaseous HCHO was set around 5500–4200 ppmV. It was obvious that the degradation efficiency performed in the range of 30–85%. However, other environmental conditions such as temperature, relative humidity (%RH), visible light intensity and intensity of UV did not report (Kaewtip, et al., 2012a). It was noted that degradation efficiency of HCHO in the presence of the photocatalyst depended on the environmental parameters. For example, initial concentration of HCHO, relative humidity (%RH) and light intensity (Jo, et al., 2001 and Liu, et al., 2008a). Thus, the understanding of the effects of environmental parameters on photocatalytic degradation (PCD) process is essential for indoor air cleaning technology Owing to the small number of studies on the effects of initial concentration of HCHO, RH and light intensity on PCD process, the aim of this chapter is to evaluate the effects of initial concentration of HCHO, RH and light intensity on GR/Fe^{3+}–TiO_2 photocatalyst by using glass chamber reactor. All studied parameters were monitored under dark condition and visible light in order to understand the effects of environmental conditions for the practical use of GR/Fe^{3+}–TiO_2 for indoor and car interior air purification.

In this section, the experiment was set to two paths: a study of the effect of environmental parameters on GR/Fe^{3+}–TiO_2 photocatalyst and the practical use of GR/Fe^{3+}–TiO_2 photocatalyst film for formaldehyde removal. A glass chamber reactor was used as simulated car interior environmental conditions. Briefly, for the first path, the environmental conditions (initial concentration of HCHO, relative humidity (%RH) and visible light intensity) in the glass chamber reactor was various under room temperature (25 °C). For the second path, the initial concentration of HCHO was fixed around 670 ± 90 ppmV. The glass chamber reactor was placed to outdoor sunshade irradiation. The change of initial concentration of HCHO, relative humidity (%RH), visible light intensity, intensity of UV and temperature was measured.

7.2 Results and discussion

7.2.1 Optical property of prepared GR/Fe^{3+}–TiO_2 film

The transparency of the photocatalytic film was about 80–90% in the visible light region as shown in Figure 7.1. The decrease in transmission of photocatalyst film (<400 nm) can be observed because of the absorption of TiO_2 photoexcitation process (Kaewtip, et al., 2012a). In addition, the transparency of GR/Fe^{3+}–TiO_2 photocatalyst film is also reduced because of the large visible light adsorption of graphene (Low and Boonamnuayvitaya et al., 2013a).

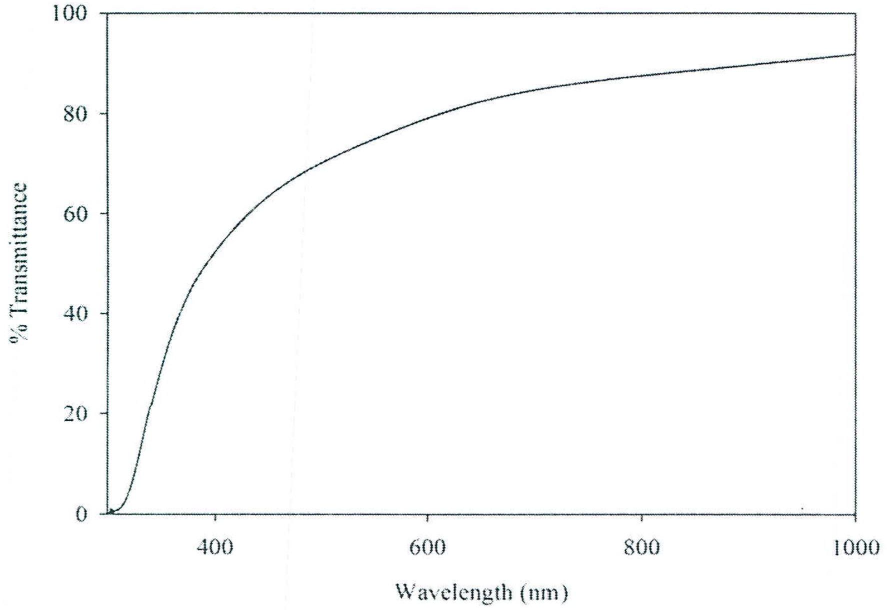

Figure 7.1 Optical property of photocatalyst film.

7.2.2 Effect of HCHO initial concentration

The effect of initial concentration of HCHO on the photocatalytic activity was investigated as shown in Figure 7.2. The plot of HCHO concentration versus visible light irradiation time shows that HCHO was continuously degraded using GR/Fe^{3+}–TiO_2 photocatalyst under visible light irradiation. The degradation rate constant and degradation efficiency for HCHO removal was evaluated as shown in Table 7.2.

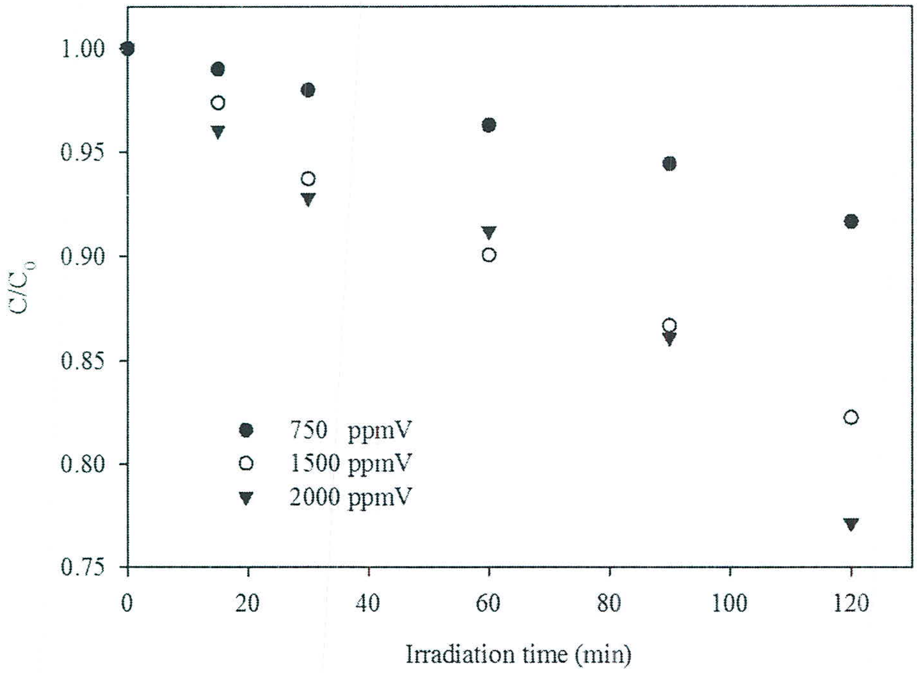

Figure 7.2 Effect of HCHO initial concentration on photocatalytic activity.

Table 7.2 Degradation efficiency (%) and apparent rate constant (k_{app}) at various HCHO concentrations.

C_0 (ppmV)	Degradation efficiency (%)	k_{app} (min^{-1})	r^2
750	8.3	0.7×10^{-3}	0.989
1500	17.7	1.7×10^{-3}	0.988
2000	22.8	2.2×10^{-3}	0.996

According to the rate law, rate is proportional to the initial concentration. Therefore, the degradation rate constants of HCOH increase with increasing initial HCHO concentration leading to higher degradation efficiency. This phenomenon may be attributed to the increase in collision frequency of HCHO to catalyst surface resulting in an enhanced photocatalytic activity (Liang et al., 2012).

7.2.3 Effect of relative humidity

The adsorption efficiency of photocatalyst films at various %RH in the dark condition is as follows: 30 (12 ± 0.1 %) > 60 (9 ± 0.2 %) >> 80 (1 ± 0.2 %) %RH. HCHO adsorption efficiency of photocatalyst is continuously decreased with increasing relative humidity because of the saturated water adsorption on the surface of photocatalyst. The photocatalytic degradation of HCHO at various %RH conditions was shown in Figure 7.3. In Table 7.3, the maximum photocatalytic degradation of HCHO can be observed at low %RH (30% RH). However, the degradation efficiency of HCHO decreased from 14.1 to 3.1% when the RH was increased from 60 to 80 %RH. In addition, the experimental results of the HCHO removal at different %RH show that the degradation rate of HCHO at 30 and 60%RH is greater than that of 80 %RH. The apparent degradation rate at the conditions of 60 and 80 %RH follow the first order kinetic model for short duration time of 0–30 min under visible light irradiation. In the case of 30 %RH, the apparent degradation rate follows the first order kinetic model in the longer duration time of 0 to 120 min resulting in the higher degradation efficiency.

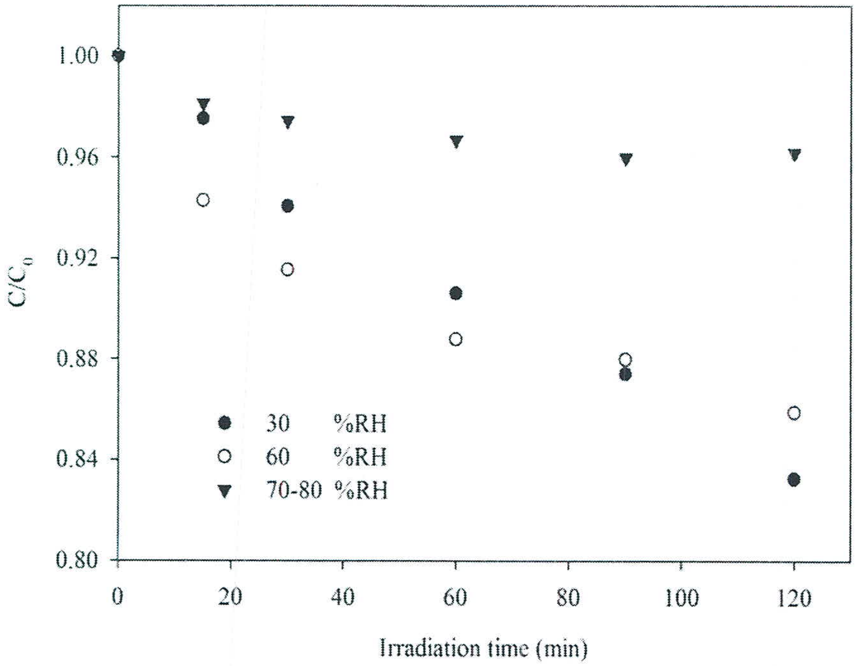

Figure 7.3 Effect of relative humidity (%RH) on photocatalytic activity.

Table 7.3 Degradation efficiency (%) and apparent rate constant (k_{app}) at various %RH conditions.

%RH	Degradation efficiency (%)	k_{app} (min^{-1})	r^2
30	16.8	1.6×10^{-3}	0.988
60	14.1	3.1×10^{-3}	0.958
80	3.8	0.9×10^{-3}	0.921

Hence, the effect of RH on HCHO degradation can be explained as follows: Humidity is an important factor for photocatalytic activity. It has been reported that the formation of $^{\bullet}OH$ and $^{\bullet}O_2^-$ plays an important role for PCD process. For low–medium humidified air (30–60 %RH), the adsorbed water molecules react with electron–hole pairs that are generated by the photoexcitation process. This reaction not only produces high oxidizing agents but also reduces electron–hole recombination. In the case of high humidified air (80 %RH), the excessive adsorbed water molecules on the surface of photocatalyst may suppress the HCHO adsorption resulting in the decrease of HCHO diffusion to the surface of photocatalyst owing to the competitive adsorption between HCHO and water (Lin et al., 2013).

7.2.4 Effect of visible light intensity

The effect of visible light intensity on the photocatalytic degradation of HCHO was investigated as shown in Figure 7.4. It is obvious that under the light intensity of 1.24–1.27 W m^{-2}, the rate of HCHO degradation was more rapid than the conditions of 0.23–0.25 and 0.60–0.62 W m^{-2} visible light irradiation. Table 7.4 shows the degradation efficiency and apparent rate constants of HCHO degradation at various visible light intensities. As the results, it can be concluded that the degradation efficiency including apparent rate of HCHO degradation increase with increasing visible light intensity. However, the degradation efficiency by means of increasing the visible light intensity from 0.23–0.25 to 0.60–0.62 W m^{-2} and from 0.60–0.62 to 1.24–1.27 W m^{-2} can be enhanced with the short range of 7.05 ± 0.75 %.

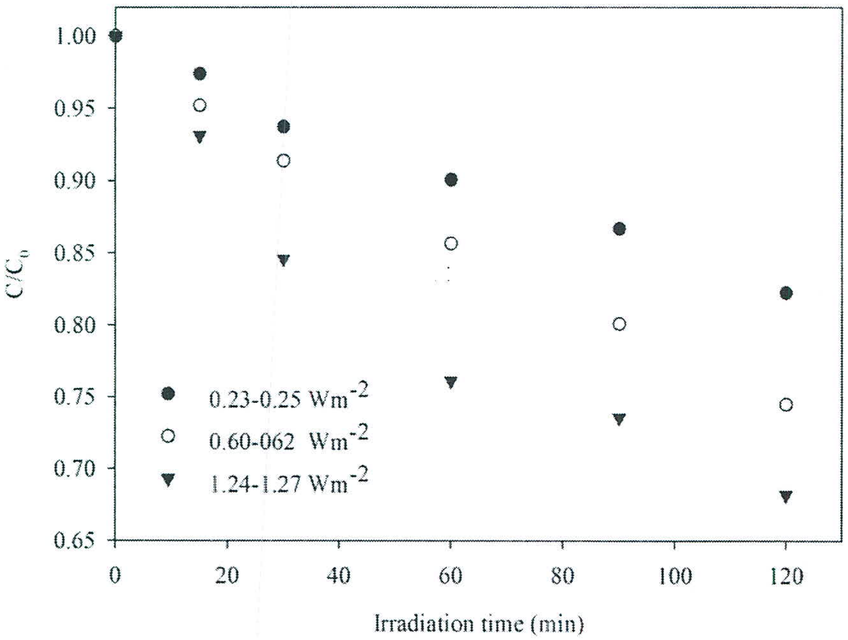

Figure 7.4 Effect of visible light intensity on photocatalytic activity.

Table 7.4 Degradation efficiency (%) and apparent rate constant (k_{app}) at various visible light intensity

Visible light intensity ($W\ m^{-2}$)	Degradation efficiency (%)	k_{app} (min^{-1})	r^2
0.23–0.25	17.7	1.7×10^{-3}	0.988
0.60–0.62	25.5	2.5×10^{-3}	0.993
1.24–1.27	31.8	3.3×10^{-3}	0.992

It may be considered that the degradation efficiency is also limited by other effects such as diffusion and mass transfer (Yu et al., 2007). The estimated band gap of GR/Fe^{3+}–TiO_2 for the photoexcitation process is 2.97 eV. The extendable photo-response under visible light region can be attributed to the synergic effect of graphene and Fe^{3+} dopants (Low and Boonamnuayvitaya, 2013a). Therefore, the intensity of visible light irradiation is an important parameter for the formation of electron-hole pairs from photoexcitation process. Increases in light intensity provide a lot of photons hit on the surface of photocatalyst leading to photoexcitation process. The increase in electron–hole pairs generation lead to the formation of more highly oxidative reactants on the surface of photocatalyst resulting in an enhanced photocatalytic degradation of HCHO as presented in Equations (7.1) – (7.6) (Ao et al., 2004 and Kaewtip et al., 2012b).

$$TiO_2 + hv \longrightarrow e^- + h+ \tag{7.1}$$

$$O_2 + e^- \longrightarrow {}^{\bullet}O_2^- \tag{7.2}$$

$$2O_2^- + 2H_2O \longrightarrow 2H_2O_2 + O_2 \tag{7.3}$$

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^- \tag{7.4}$$

$$h^+ + OH^- \longrightarrow {}^{\bullet}OH \tag{7.5}$$

$$HCHO + {}^{\bullet}OH \text{ or } {}^{\bullet}O_2^- \longrightarrow CO_2 + H_2O \tag{7.6}$$

Therefore, the photo-degradation of GR/Fe^{3+}–TiO_2 photocatalyst film for HCHO removal can be enhanced by increasing the visible light intensity.

7.2.5 The experimental results of the practical use of GR/Fe^{3+}–TiO_2 photocatalyst film

In this section, the practical use of GR/Fe^{3+}–TiO_2 film for car interior HCHO removal was tested using the glass reactor as shown in Figure 3.2. The photocatalytic degradation of HCHO was examined in a real environment with an average HCHO initial concentration of around 670 ± 90 ppmV. The glass reactor was covered with black fabric in order to shut out visible light for 60–90 min until adsorption-desorption equilibrium conditions is reached. Then, the black fabric was removed to start the photocatalytic reaction. The chambers were placed outdoor sunshade exposures. Adsorption and photocatalytic degradation behavior of the practical used of GR/Fe^{3+}–TiO_2 photocatalyst for HCHO removal was shown in Figure 7.5. The decrease in HCHO concentration in dark condition is attributed to the adsorption process and it is also observed that the adsorption–desorption equilibrium is approximately reached around 45–60 min. Under outdoor sunshade irradiation, the decrease in HCHO concentration is attributed to the photocatalytic activity. The photocatalytic degradation of HCHO under outdoor sunshade irradiation was shown in Figures 7.5 and 7.6.

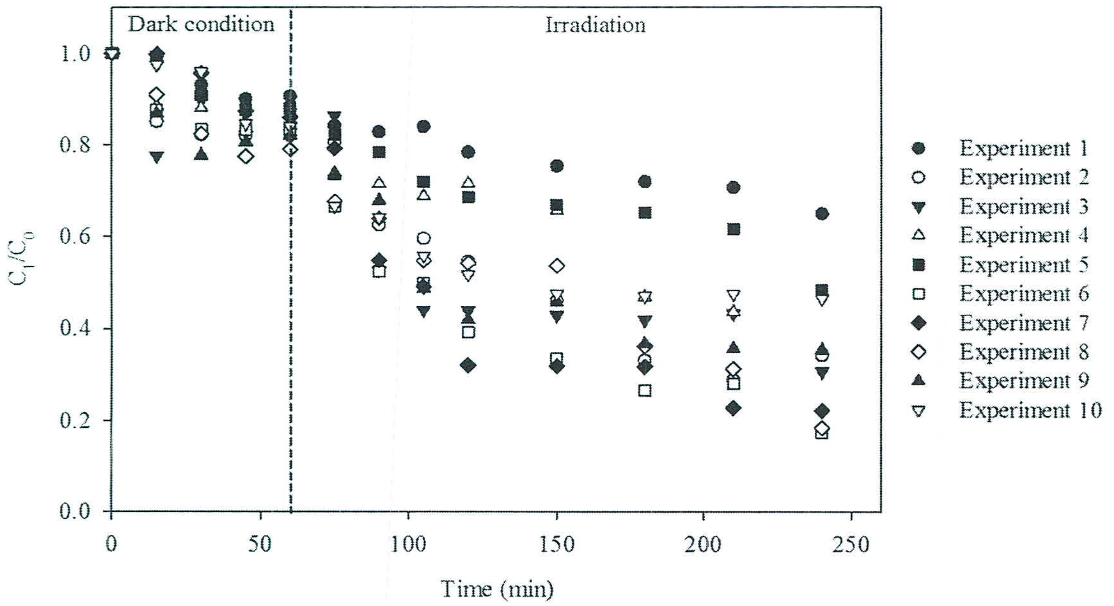

Figure 7.5 Adsorption and photocatalytic degradation behavior of the practical use of GR/Fe^{3+}–TiO_2 photocatalyst for HCHO removal.

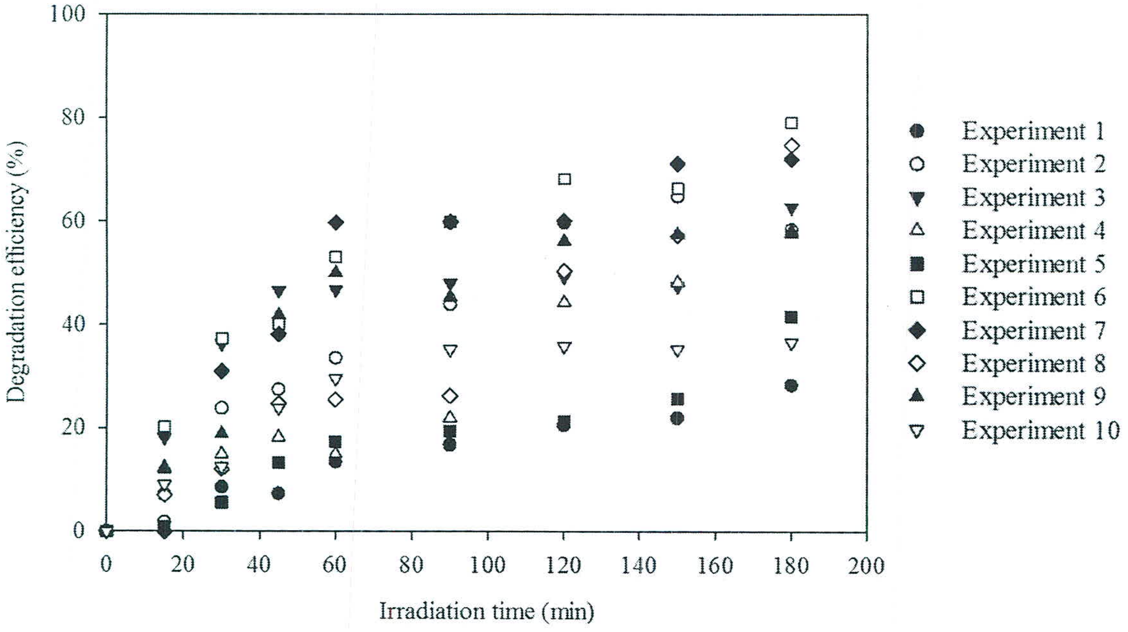

Figure 7.6 Degradation efficiency (%) of GR/Fe^{3+}–TiO_2 photocatalyst.

*The information and the average value of environmental conditions under the outdoor sunshade of experiment 1–10 are shown in Appendix E (Table E4–14) and Table 7.5, respectively.

7.2.6 The experimental results of the practical use of GR/Fe^{3+}–TiO_2 photocatalyst film

In this section, the practical use of GR/Fe^{3+}–TiO_2 film for car interior HCHO removal was tested using the glass reactor as shown in Figure 3.2. The photocatalytic degradation of HCHO was examined in a real environment with an average HCHO initial concentration around of 670 ± 90 ppmV. The glass reactor was covered with black fabric in order to shut out visible light for 60–90 min until adsorption-desorption equilibrium conditions is reached. Then, the black fabric was removed to start the photocatalytic reaction. The chambers were placed outdoor sunshade exposures. Adsorption and photocatalytic degradation behavior of the practical used of GR/Fe^{3+}–TiO_2 photocatalyst for HCHO removal was shown in Figure 7.5. The decrease in HCHO concentration in dark condition is attributed to the adsorption process and it is also observed that the adsorption–desorption equilibrium is approximately reached around 45–60 min. Under outdoor sunshade irradiation, the decrease in HCHO concentration is attributed to the photocatalytic activity. The photocatalytic degradation of HCHO under outdoor sunshade irradiation was shown in Figure 7.6. It was noted that the degradation efficiency (180 min) is generally various from 28 to 80% depending on the environmental condition. The summary environmental condition of temperature, relative humidity the intensity of visible light and UV was measured as shown in Table 7.5.

As the result, the range of the temperature of 28–33 °C had not affected the degradation efficiency as much as that of relative humidity, intensity of visible light and UV. The degradation efficiencies of HCHO removal under real environmental condition can be separated into three groups as shown in Table 7.5. The effect of UV and visible light intensity can be observed on experimental group A and B. The difference of average relative humidity between experimental group A and B is about 1.66 %RH but the photocatalytic activity of group A is lower than that of group B. The intensity of visible light and UV of experimental group B is about 2 times larger than that of group A. Therefore, the increase in the photocatalytic activity of the experimental group B is attributed to the effect of intensity of visible light and UV. A little difference in the quantity of the average intensity of visible light and UV between group B and group C is 0.14 W m^{-2} and 0.18 μW cm^{-2} for visible light and UV, respectively, but the photocatalytic degradation of experimental group C is large in comparison with that of group B. Ii can be clearly observed form Table 7.5 that the relative humidity of group C (35.09 %RH (avg)) is not as much as that of group B (43.66%RH (avg)). Thus, this phenomenon is attributed to the effect of relative humidity. The increase in relative humidity leads to the decrease in photocatalytic activity as reported in Section 7.2.3.

Table 7.5 Summary of the measured environmental conditions (outdoor sunshade).

Group A (40%<)	Temperature (°C)	Visible light intensity (W m^{-2})	Intensity of UV (μW cm^{-2})	Relative humidity (%RH)
Experiment 1	29.38 ± 0.86	1.37 ± 0.28	20.98 ± 4.15	41.92 ± 2.56
Experiment 5	29.96 ± 0.82	1.77 ± 0.11	21.05 ± 3.28	44.31 ± 0.48
Experiment 10	30.81 ± 0.77	1.93 ± 0.73	14.63 ± 2.19	39.77 ± 1.19
Group B (40%<%<70%)	Temperature (°C)	Visible light intensity (W m^{-2})	Intensity of UV (μW cm^{-2})	Relative humidity (%RH)
Experiment 2	30.69 ± 0.31	2.34 ± 0.28	34.53 ± 7.34	44.46 ± 1.22
Experiment 3	29.91 ± 0.37	2.48 ± 0.28	39.41 ± 6.04	45.43 ± 0.97
Experiment 4	30.15 ± 0.36	2.75 ± 0.24	35.85 ± 5.81	45.08 ± 0.27
Experiment 9	30.90 ± 0.93	2.75 ± 0.19	30.93 ± 3.36	39.67 ± 1.22
Group C (>70%)	Temperature (°C)	Visible light intensity (W m^{-2})	Intensity of UV (μW cm^{-2})	Relative humidity (%RH)
Experiment 6	33.00 ± 0.00	3.43 ± 0.20	44.00 ± 2.36	34.15 ± 0.89
Experiment 7	30.00 ± 0.00	2.63 ± 0.46	37.78 ± 4.96	36.62 ± 0.84
Experiment 8	31.23 ± 0.42	2.93 ± 0.43	32.30 ± 4.64	34.50 ± 0.92

This experimental result indicated that the GR/Fe^{3+}–TiO_2 photocatalyst was stable and could be repeatedly applied for car interior HCHO removal under real environmental conditions.

7.3 Conclusions

This study evaluated the effect of initial concentration of HCHO, %RH and visible light intensity on GR/Fe^{3+}–TiO_2 photocatalyst film for HCHO removal. The experimental results show that the degradation efficiency and apparent degradation rate constant increase with increasing HCHO concentration and visible light intensity because of the increase in the collision frequency of HCHO and more striking of photons to the surface of photocatalyst, respectively. In addition, the experimental results showed that high relative humidity level leads to the decrease in photocatalytic activity owing to the competitive adsorption between HCHO and water molecules on the surface of photocatalyst.