PHOTODEGRADATION FOR FORMALDEHYDE REMOVAL BY ADDING TITANIUM DIOXIDE IN ACRYLIC PAINT: A STUDY IN STATIC AIR CHAMBERS

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ABSTRACT

The objective of this research was to determine the effects of influencing factors: the percentage of titanium dioxide added in acrylic paint (2, 5, 10 and 15%), initial formaldehyde concentration (50, 100 and 150 mg/m^3) and irradiation time (90, 180, 270 and 360 min), and their interaction effect on formaldehyde photodegradation process. This research was a 3x4x4 factorial design and it was conducted in static air chambers.

The result showed that influencing factors affected formaldehyde removal (%). It showed that the formaldehyde removal (%) increased when the percentage of titanium dioxide increased and slightly decreased at 15% of titanium dioxide, the formaldehyde removal (%) decreased when the initial formaldehyde concentration increased and the formaldehyde removal (%) slightly increased with the increasing of irradiation times but slightly decreased at 360 min. The formaldehyde removal (%) did not always increase when the percentage of titanium dioxide increased; it depended on the initial concentration of formaldehyde. The irradiation time also depended on the initial concentration of formaldehyde as well; at higher initial formaldehyde concentration, the photodegradation proceeded to mass transfer limit earlier than at lower initial formaldehyde concentration. The results showed that 10% of titanium dioxide at 50 mg/m^3 of initial formaldehyde concentration and 360 min of irradiation time was the condition of highest formaldehyde removal efficiency (60.08%). This research can be applied to the treatment of formaldehyde and also to guidelines regarding the suitable amount of titanium dioxide that should be added into acrylic paint for formaldehyde removal.

KEY WORDS: TITANIUM DIOXIDE / PHOTODEGRADATION /
FORMALDEHYDE REMOVAL / ACRYLIC PAINT /
STATIC AIR CHAMBER

98 pp.

การสลายด้วยแสงของฟอร์มัลดีไฮด์โดยใช้ไททาเนี่ยมไดออกไซด์ที่ผสมลงในสีอะครีลิก: ศึกษาในตู้อากาศแบบสถิตย์
(PHOTODEGRADATION FOR FORMALDEHYDE REMOVAL BY ADDING TITANIUM DIOXIDE IN ACRYLIC PAINT: A STUDY IN STATIC AIR CHAMBERS)

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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลการสลายด้วยแสงของฟอร์มัลดีไฮด์โดยใช้ไททาเนี่ยมไดออกไซด์ที่เติมลงในสีอะครีลิก โดยศึกษาปัจจัยต่างๆที่มีผลต่อการสลายด้วยแสงได้แก่ ความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์ (50, 100 และ 150 ม.ก./ ลบ.ม.), ปริมาณไททาเนี่ยมไดออกไซด์ที่เติมลงไปในสี (2%, 5%, 10% และ 15%), ระยะเวลาฉายแสง (90, 180, 270 และ 360 นาที) และยังศึกษาผลของปัจจัยร่วมทั้ง 3 ที่มีต่อการสลายด้วยแสงของฟอร์มัลดีไฮด์ด้วย โดยเป็นการวิจัยแบบ 3x4x4 แฟคทอเรียล 3 ปัจจัยและทดลองในตู้อากาศแบบสถิตย์

ผลการวิจัยในครั้งนี้แสดงให้เห็นว่า ทั้ง 3 ปัจจัย มีผลต่อการสลายด้วยแสงของฟอร์มัลดีไฮด์ โดยการสลายจะเพิ่มขึ้น หากเพิ่มเปอร์เซ็นต์ไททาเนี่ยมไดออกไซด์ที่เติมลงในสี แต่การสลายด้วยแสงจะลดลงหากเติมไททาเนี่ยมไดออกไซด์ลงในสีอะครีลิกที่ 15%, การสลายจะลดลงหากความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์สูงขึ้น และการสลายด้วยแสงจะเพิ่มขึ้นหากใช้ระยะเวลาฉายแสงที่นานขึ้น แต่จะลดลงเล็กน้อยที่ 360 นาที จากการศึกษาผลของปัจจัยร่วมทั้ง 3 ปัจจัย พบว่า การสลายด้วยแสงของฟอร์มัลดีไฮด์จะไม่สูงขึ้นเสมอไป แม้ว่าจะใช้ปริมาณไททาเนี่ยมไดออกไซด์ที่เติมลงในสีอะครีลิกที่สูงขึ้น แต่ขึ้นอยู่กับปริมาณความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์ ซึ่งเช่นเดียวกับระยะเวลาฉายแสง ที่ปริมาณความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์สูง ปฏิกิริยาจะเข้าสู่ขีดจำกัดการถ่ายเทมวลสารได้เร็วกว่า ทั้งนี้ จากการวิจัยพบว่าการสลายด้วยแสงของฟอร์มัลดีไฮด์ ที่ปริมาณไททาเนี่ยมไดออกไซด์ที่ 10% ที่ความเข้มข้นฟอร์มัลดีไฮด์เริ่มต้นที่ 50 ม.ก/ลบ.ม. และใช้เวลาฉายแสง 360 นาที มีค่าสูงที่สุด คือลดได้ 60.08% ซึ่งงานวิจัยนี้จะเป็นประโยชน์ในการใช้เป็นข้อมูลสำหรับการบำบัดฟอร์มัลดีไฮด์ และเป็นแนวทางในการเลือกใช้ปริมาณไททาเนี่ยมไดออกไซด์ที่ผสมลงในสีอะครีลิกสำหรับการบำบัดฟอร์มัลดีไฮด์อย่างเหมาะสม

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LIST OF ABBREVIATIONS

ABS	Absorbent
ANOVA	Analysis of Variance
C	Concentration
C^o	Degree Celsius
CH_2O, HCHO	Formaldehyde
cm	Centimeter
cm^3	Cubic Centimeter
F^o	Degree Fahrenheit
g	Gram
LSD	Least Significant Difference
mg	Milligram
m^3	Cubic meter
NIOSH	National Occupational Safety and Health
ppm	Part Per Million
Rep.	Replication
S.D.	Standard Deviation
Sig.	Significant
T	Temperature
TiO_2	Titanium Dioxide
UV	Ultraviolet
V	Volume
$\overline{X}$	Mean
%	Percentage

CHAPTER I

INTRODUCTION

1.1 Background

Nowadays, human and other living things on the world have been threatened by air pollution. Pollutants in the air create smog and acid rain, decrease ozone layer in the upper atmosphere, and cause cancer or other effects to human health. Air pollution comes from many different sources: stationary sources such as factories; mobiles sources such as cars, planes, buses and train, all of these are the causes of air pollution. Especially the industries activities create the emission more than any other sources. The emission from industries such as SO_x, NO_x, CO, particulate matter, heavy metals and volatile organic compounds are problems to human environment and ecology (1).

In general, there are many pollutants or emissions in outdoor environment, so many people try to avoid exposing them. Even so, the indoor environment is a risk place from air pollutants and may be higher risk than outdoor because the human use more 16 hours in house or workplace and can expose the indoor pollutant easily. The common indoor air pollutant can be found in house or workplace such as carbon monoxide fumes from adjacent garage, combustion gases and volatile organic based chemical products (2-4).

Volatile organic compounds (VOCs) are common pollutants which are produced by a variety of industries and are environmental concerns. Especially, formaldehyde is a common volatile organic compound and close to the human life because formaldehyde can be found in households such as smoke of cigarettes and tobacco products, furniture containing formaldehyde-based resins, building materials containing urea-formaldehyde resins (5). Furthermore, the increasing temperature from climate change problem may cause increasing formaldehyde evaporation rate from formaldehyde based material and be harmful to human.

Formaldehyde can cause headaches; irritation of eyes, nose and the formaldehyde is classified as a probable human carcinogen by the U.S. Environmental Protection Agency and as having sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans by the International Agency for Research on Cancer (6). Formaldehyde is pollutant in environmental legislations in many countries. In Thailand, Formaldehyde in workplace must be less than 5 ppm or 6.15 mg/m^3 and less than 3 ppm or 3.69 mg/m^3 for 8-hour time weight average (7).

From this problem, many researchers try to develop the advance technologies to remove pollutants by using absorption or adsorption technologies. But these theories are only transfer pollutants from the gaseous phase to solid or liquid phase which eventually cause the disposal problem (8).

In recent years, the new method for removing the volatile organic compound was discovered. That method is photooxidation which can degrade organic pollutants to CO_2 and H_2O by a catalyst and light (3, 9-11). The catalyst used mostly in many studies is titanium dioxide (TiO_2) because it's inexpensive, high efficiency and low toxic. This catalyst will oxidize and degrade the pollutant in 20 – 210 min (10-17). Nevertheless, the use of TiO_2 in many studies was the coating on column for treating the pollution; this design is suitable for treatment at the end of pipe and not compatible for use in indoor environment (8).

One of traditional methods for using TiO_2 to depollute the indoor air environment is adding TiO_2 into acrylic paint and coated on the walls (16, 18). In this method, it easier and compatible for use in workplace or household but this method is necessary to study the suitable volume of TiO_2 added in acrylic paint for high removal efficiency of volatile organic compounds and study the possible factors that affect the photodegradation of the volatile organic compounds by using TiO_2 added into acrylic paint.

In this research, the experiment was performed in the static air chamber that contaminated with formaldehyde as a common indoor air pollutant in order to determine the percentages of TiO_2 in acrylic paint for the removal efficiency of formaldehyde. The related factors affecting photodegradation of formaldehyde at different initial concentrations of formaldehyde and irradiation times were also studied.

Eventually, the benefit of this research was the information of TiO_2 application for treating formaldehyde. The result was the guideline of TiO_2 amount (percentage) added into acrylic paint for the highest efficiency and the pollutant concentration level that can be treated by TiO_2 adding acrylic paint.

1.2 Objectives of the Study

1.2.1 General objective

To study the influencing factors: percentage of titanium dioxide added in acrylic paint; initial formaldehyde concentration; irradiation time, on formaldehyde removal by TiO_2 photodegradation in the static air chamber.

1.2.2 Specific objectives

1. To determine the formaldehyde removal (%) in the static air chamber at different percentages of TiO_2 added in acrylic paint.
2. To determine the formaldehyde removal (%) by using TiO_2 added in acrylic paint at different initial formaldehyde concentrations in the static air chamber.
3. To determine the formaldehyde removal (%) in the static air chamber by using TiO_2 added in acrylic paint at various irradiation times.
4. To determine the formaldehyde removal (%) in the static air chamber at different percentages of TiO_2 added in acrylic paint, initial formaldehyde concentrations and various irradiation times.

1.3 Hypotheses of the Study

1. The formaldehyde removal (%) increases when the percentage of TiO_2 added in acrylic paint increases.
2. The formaldehyde removal (%) at low initial formaldehyde concentration is higher than at high initial formaldehyde concentration.
3. The formaldehyde removal (%) is positively related to the irradiation times.
4. The formaldehyde removals (%) at different percentages of TiO_2 added in acrylic paint, initial formaldehyde concentrations and various irradiation times are different.

1.4 Variables of the Study

1.4.1 Independent Variable

- Percentages of TiO_2 added in acrylic paint.
- Initial formaldehyde concentrations in the static air chamber.
- Irradiation times.

1.4.2 Dependent Variable

- Formaldehyde removal (%) in the static air chamber.

1.4.3 Control Variable

- Light sources.
- Size of the static air chamber.
- Volume of acrylic paint.

1.5 Definition of Terms

1. **Formaldehyde removal (%)**: the percentage of formaldehyde in air between before and after the treatment by TiO_2 added in acrylic paint. The calculation of formaldehyde removal (%) was follows:

$$\textbf{Formaldehyde removal (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

Where; C_i is the initial concentration of Formaldehyde.

C_f is the final concentration of Formaldehyde.

2. **Acrylic paint**: the fast-drying paint containing pigment suspended in an acrylic polymer emulsions that is used for painting interior building.
3. **Photodegradation**: the process of photocatalysis oxidation which uses TiO_2 and light to degrade formaldehyde.
4. **Titanium dioxide (TiO_2)**: the semiconductor as catalyst in degradation process. It was added in acrylic paint at the level of 2, 5, 10, and 15 % (weight by weight) and coated on media and put in a static air chamber. In this study used Degussa TiO_2 P25.
5. **Static Air chamber**: the close-system chamber for Photodegradation experiment and made from glass with a sampling port and mixing fan inside.
6. **Media**: use 40 x 40 cm cerocrete and was coated by TiO_2 added acrylic paint and measured the TiO_2-loading by digital balance.
7. **Irradiation Time**: a time of photodegradation reaction period at 90, 180, 270 and 360 min.
8. **Light source**: the 18W fluorescence lamp.

1.6 Scope of the Study

1. This study was conducted in the laboratory and using the synthetic polluted air by adding formaldehyde in static air chamber.

2. The irradiation times were studied at 0, 90, 180, 270 and 360 min.

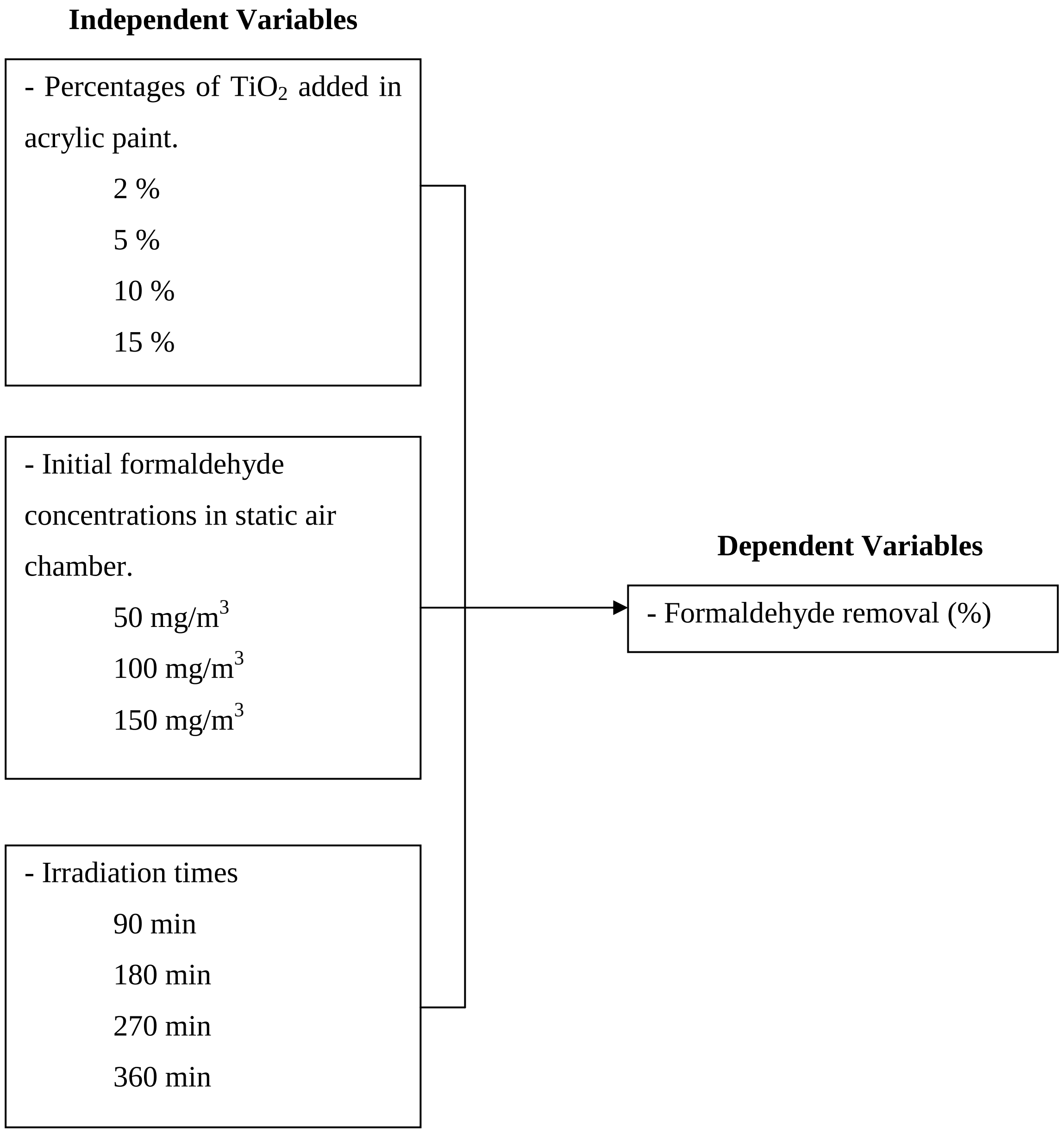
1.7 Limitation of the Study

1. This experiment used impinger for collecting air sample to analyze concentration of formaldehyde by chromotropic acid method. Therefore, the formaldehyde removal (%) in this experiment was plotted graph for each time.

2. The intensive wavelength from 18W fluorescence lamp in this experiment assumed as stable.

3. The initial formaldehyde concentrations in this experiment were slightly more or less. From the controlling, the error of initial formaldehyde concentration was not more than 5% of accuracy.

1.8 Conceptual Framework



CHAPTER II
LITERATURE REVIEW

2.1 Titanium dioxide (TiO_2)

Titanium dioxide, also known as titanium (IV) oxide or Titania, is the naturally occurring oxide of titanium, chemical formula TiO_2 (19). The physical appearance of TiO_2 is white powder as shown in figure 2.1(a), and the structure of TiO_2 as shown in figure 2.1(b).

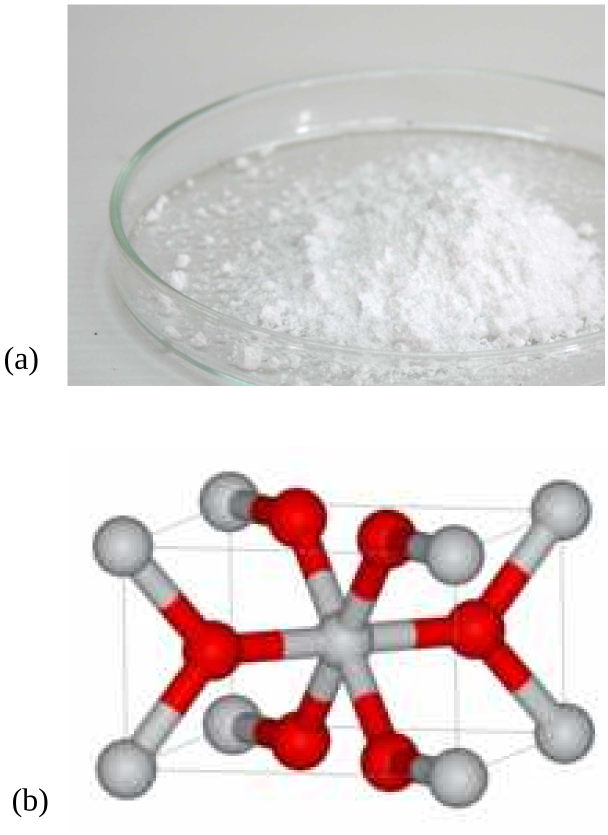


Figure2.1 (a) Titanium dioxide (b) and the structure

The physical-chemical properties of TiO_2 as shown in table 2.1

Table 2.1 Physical-chemical properties for TiO_2

Descriptions	Value
Molecular mass	79.87 g/mol
Appearance	White solid
Odor	Odorless
Taste	Tasteless
Density	4.23 g/cm^3
Melting point	1855 ^{o}C (3371 ^{o}F)
Boiling point	2750 ^{o}C (4982 ^{o}F)
Solubility	Insoluble in cold water
Stability	Stable

Source: Pollution Control Department (20)

The most industrial use titanium dioxide which is widely used as a pigment for paint, coating ink, paper, plastic, cosmatic products, catalyst supports, photoconductors and so on because of its very whiteness, outstanding hiding property and low toxicity that LD_{50} of titanium dioxide is more than 24,000 mg/Kg in rat (21).

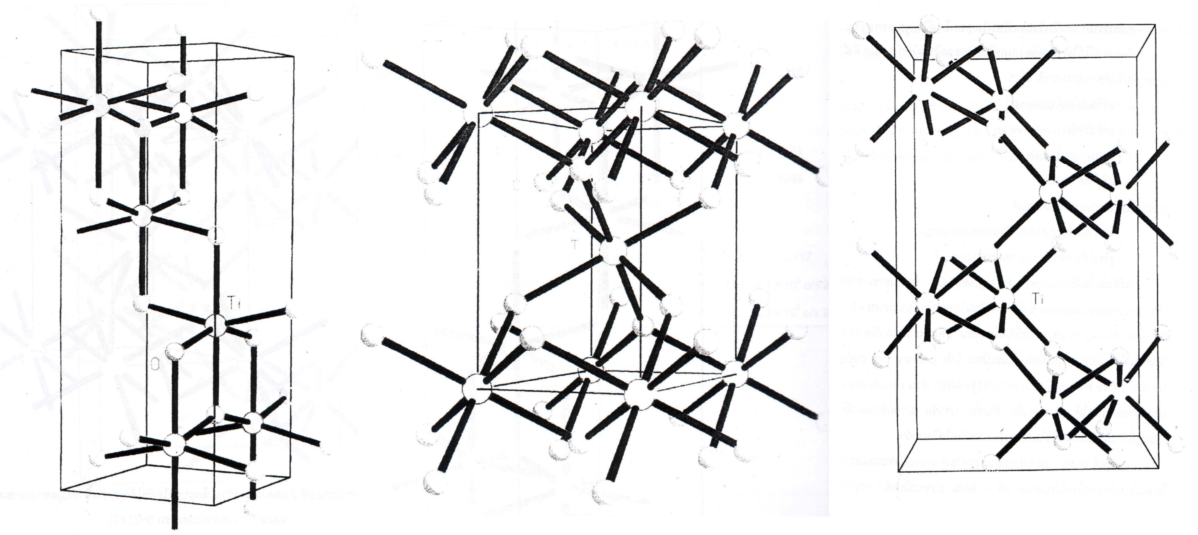
The titanium dioxide occurs in three forms (22-24):

(1) Rutile, a tetragonal mineral usually of prismatic habit, often twinned**;**

(2) Anatase or octahedrite, a tetragonal mineral of dipyramidal habit**;**

(3) Brookite, an orthorhombic mineral. Both anatase and brookite are relatively rare

The structures of three crystal forms anatase, rutile and brookite as shown in figure 2.2



(a) (b) (c)

Figure 2.2 Crystal structures of TiO_2: (a) Anatase, (b) Rutile, (c) Brookite.

The properties of the three crystal forms anatase, brookie and rutile as shown in table 2.2.

Table 2.2 Properties of the three modifications of titanium dioxide

Properties	Anatase	Brookite	Rutile
Density (g/cc)	3.90	4.13	4.27
Hardness (Mohs'scale)	5.5-6.0	5.5-6.0	6.0-6.5
Melting Point (^oC)	Change to rutile	Change to rutile	1840±10
Entropy $S^o_{298.16}$ (cal/deg/m)	11.93	-	12.01
Refractive Index	n_ω 2.5612	n_α 2.5831	n_ω 2.6124
(25 ^oC)	n_ε 2.4880	n_β 2.5843	n_ε 2.8993
(λ = 5893Å)		n_γ 2.7004	
Dielectric Constant	$\varepsilon = 48$	$\varepsilon = 78$	$\varepsilon_{av} \approx 110$
	(powder)		$\varepsilon_{ll} = 180$
			$\varepsilon_{\perp} = 89$

Source: Clark (19)

Titanium dioxide photocatalysis has been studied extensively as a potential technique for treatment of pollutants and microorganisms because titanium dioxid can degrade pollutant in low temperature, less time and low toxic than other method, and highly remove pollutant efficiency. The TiO_2 in the anatase form is a photocatalyst under ultraviolet light. Although recently it has been found that titanium dioxide when spiked with nitrogen ions, will also react as a photocatalyst under lamp light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for sterilizing, deodorizing and anti-fouling properties and is also used as a hydrolysis catalyst. It is also used in the Graetzel cell, a type of chemical solar cell (9).

The photocatalyst used in many studies is TiO_2 P25 (Degussa Company, Frankfurt, Germany) (25) because it’s able to highly photocatalyst when compare the other and easy to used (26-29). The physical-chemical properties for Degussa Titanium dioxides P25 to shown in table 2.3

Table 2.3 Physical -chemical properties for Degussa Titanium dioxides P25

Description	Value
BET surface area	50±15 m^2/g
Average particle size	30 nm
Moisture	<1.5 %
Ignition loss	<1.5 %
pH in 4% aqueous suspension	3 – 4
Structure ratio (Anatase: Rutile)	80:20
Density	3.98 g/cm^3
Titanium dioxide	>99.5 %
Aluminum oxide	<0.3 %
Silica	<0.01 %
Iron oxide	<0.01 %
HCl	<0.3 %

Source: Degussa (25)

2.2 Properties of formaldehyde

Formaldehyde is the chemical compound with the formula CH_2O. The simplest aldehyde, it was first synthesized by the Russian Chemist Aleksandr Butlerov but was conclusively identified by August Wilhelm von Hofmann. The structures of formaldehyde as shown in figure 2.3.

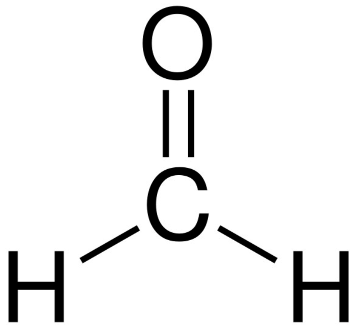


Figure 2.3 The structure of formaldehyde

Generally, formaldehyde has been widely used in many applications; it has medical applications as a sterilant and is used as a preservative in consumer products, such as food, cosmetics and household cleaning agent (5).

There are several indoor environmental sources that can result in human exposure including cigarettes and tobacco products, furniture containing formaldehyde-based resins, building materials containing urea-formaldehyde resins, adhesives containing formaldehyde used for plastic surfaces and parquet, carpets, paints, disinfectants, gas cookers and open fireplaces (4, 5).

Indoor areas of special importance are hospitals and scientific facilities where formaldehyde is used as a sterilizing and preserving agent, and living spaces, such as schools, kindergartens, and mobile homes or apartments where there may be uncontrolled emissions of formaldehyde from tobacco smoking, building materials and furniture (5).

2.2.1 Physical and chemical properties of formaldehyde

The physical and chemical properties of formaldehyde to shown in table 2.4

Table 2.4 The physical and chemical properties of formaldehyde

Properties	Descriptions
Synonym	formic aldehyde; methyl aldehyde; methylanal; methylene oxide; oxomethane; oxymethylene
Boiling point	-19.5 °C (-3.1 °F)
Melting point	-92 °C (-133.6 °F)
Molecular weight	30.03
Vapor pressure	1.33 kPa @ -88 °C
Flash point	50 °C (122 °F) (closed cup aqueous solution with 15% methyl alcohol) appearance: colorless gas; aqueous solutions with methyl alcohol are clear liquid vapor density: 1.08 (air = 1.0)
Molecular formula	CH_2O
Odor	pungent, slightly musty
Explosive limit	7 to 73% by volume
Solubility	very soluble in water, up to 55% soluble in alcohol, ether

Source: NIOSH (6)

2.2.2 Toxicology of formaldehyde

1) Acute exposure

The formaldehyde gases cause the irritation in mucous membranes, nose, eyes and upper respiratory tract. Ingestion of formaldehyde cause severe injury to gastrointestinal tract. The molecules of formaldehyde can interact with human cell membranes and body tissues or fluids (proteins or DNA) and disrupt that functions which the results cause cell death (5).

CNS

The formaldehyde can cause the malaise, headache, sleeping disturbances, irritability, and impairment of dexterity, memory and equilibrium of body (5, 6).

Respiratory

At the low concentrations of formaldehyde can produce rapid onset of nose and throat irritation, causing cough, chest pain, shortness of breath, and wheezing. The higher concentration can cause the inflammation of the lower respiratory tract, swelling of the throat, inflammation of the windpipe and bronchi, narrowing of the bronchi, inflammation of the lungs, and accumulation of fluid in the lungs. The exposure more than 12 hours may cause pulmonary injury (6).

Metabolic

The accumulation of formic acid (product of formaldehyde) can cause an anion-gap acid-base imbalance. If formaldehyde be ingested, the absorption of the methanol may contribute to the imbalance of anion in body (6).

Immunologic

The inhalation and skin contact of formaldehyde may cause skin disorders, asthma-like symptoms, anaphylactic reactions and hemolysis (6).

Gastrointestinal

Ingestion of aqueous solutions of formaldehyde can cause corrosive injury to the esophagus and stomach. Nausea, vomiting, diarrhea, abdominal pain, inflammation of the stomach and ulceration and perforation of the oropharynx, epiglottis, esophagus and stomach may occur. Both of formaldehyde and the methanol stabilizer are easily absorbed and can contribute to systemic toxicity.

Ocular

The exposure of low formaldehyde concentrations vapor can cause eye irritation which abates within fewer minutes after exposure. The splashed of formaldehyde to the eyes can cause corneal ulceration or cloudiness of the eye surface, death of eye surface cells, perforation, and permanent loss of vision.

Dermal

The exposure to formaldehyde vapor or formaldehyde solutions can cause skin irritation and burns. In sensitized persons, contact dermatitis may develop at very low exposure levels.

2) Chronic exposure

The major concerns of repeated formaldehyde exposure are sensitization and cancer. In sensitized persons, formaldehyde can cause asthma and contact dermatitis, prolonged inhalation of formaldehyde at low levels is cause chronic pulmonary injury (6). Adverse effects on the central nervous system such as increased prevalence of headache, depression, mood changes, insomnia, irritability, attention deficit, and the long-term exposure can cause impairment of dexterity, memory and equilibrium. Chronic exposure may be more serious for children because of their potential longer latency period.

Carcinogenicity

The formaldehyde is carcinogen agent (5). In humans, formaldehyde exposure has been weakly associated with increased risk of nasal cancer and nasal tumors were observed in rats chronically inhaling formaldehyde.

Reproductive and developmental effects

The formaldehyde causes adverse reproductive effects. The TERIS database states that the risk of developmental defects to the exposed fetus ranges from none to minimal. Formaldehyde is not included in *Reproductive and Developmental Toxicants*, a 1991 report published by the U.S. General Accounting Office (GAO) that lists 30 chemicals widely acknowledged having reproductive and developmental consequences (5).

There have been reports of menstrual disorders in women occupationally exposed to formaldehyde, but they are controversial. Studies in experimental animals have reported some effects on spermatogenesis. Formaldehyde has not been proven to be teratogenic in animals and is probably not a human teratogen at occupationally permissible levels. Formaldehyde has been shown to have genotoxic properties in human and laboratory animal studies producing sister chromatid exchange and chromosomal aberrations (5).

2.2.3 Routes of exposure

Inhalation

Formaldehyde vapor be absorbed in the lungs. In cases of acute exposure, formaldehyde will be detected by smell; however, persons who are sensitized to formaldehyde may experience headaches and minor eye and airway irritation at levels below the odor threshold (odor threshold is 0.5 to 1.0 ppm; OSHA PEL is 0.75 ppm) (6). For sensitized persons, odor is not an adequate indicator of formaldehyde's presence and may not provide reliable warning of hazardous concentrations. Odor adaptation can occur. Low-dose acute exposure can result in headache, rhinitis, and dyspnea; higher doses may cause severe mucous membrane irritation, burning, and lacrimation, and lower respiratory effects such as bronchitis, pulmonary edema, or pneumonia. Sensitive individuals may experience asthma and dermatitis, even at very low doses. Formaldehyde vapors are slightly heavier than air and can result in asphyxiation in poorly ventilated, enclosed, or low-lying areas.

Skin/Eye contact

Formaldehyde can absorbed through intact skin and may cause irritation or allergic dermatitis and formaldehyde vapors can cause the eye irritation and lacrimation. Formaldehyde solutions may cause transient discomfort and irritation or more severe effects which depend on the formaldehyde concentration.

Ingestion

The ingestion of 30 ml of 37% formaldehyde solution can cause an adult to death (6). Ingestion may cause corrosive injury to the gastrointestinal mucosa, with nausea, vomiting, pain, bleeding, and perforation. Corrosive injuries are usually most pronounced in the pharyngeal mucosa, epiglottis and esophagus. Systemic effects include metabolic acidosis, CNS depression and coma, respiratory distress, and renal failure.

2.3 Principle of photocatalysis reaction

The word “photocatalysis” is composed of two parts**;** the prefix photo, defined as "light”, “catalysis” is the acceleration of the chemical reaction by the substance that known as “catalyst” when it received the activation energy. Therefore, the photocatalysis is mean the reaction which uses light to activate a substance (catalyst) which modifies the rate of a chemical reaction without being involved itself (9).

The principle of photocatalysis can be described as follow. A semiconductor is characterized by an electronic band structure that are occupied valence band and unoccupied conductance band. These two bands are separated by the energy gap called the “band gap” (E_{bg}). When the semiconductor is illuminated with light that has energy equal or higher the band gab, an electron from valence band is promoted to the conductance band, the semiconductor can be exchange electron with other substance (30).

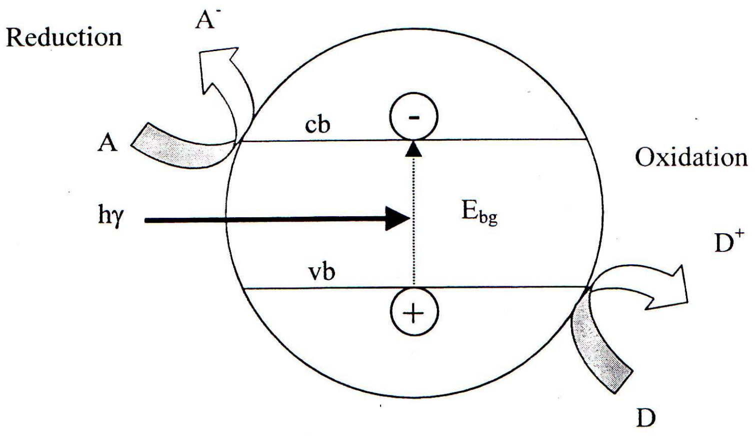


Figure 2.4 The reaction of photocatalysis when the semiconductor was illuminated

The semiconductor used as a photocatalyst should be an oxide or sulfide of metals such as TiO_2, CdS and ZnO. The energy band gap of the photocatalyst should match the energy gained from light source (31) and the band positions of some semiconductor as shown in table 2.6.

Table 2.5 The band positions of some semiconductor

Semiconductor	Valence band (eV)	Conductance Band (eV)	Band gap (eV)	Band gap wavelength (nm)
TiO_2	+3.1	+0.1	3.1	380
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO_3	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887
GaP	+1.3	-1.0	2.3	540

Source: Rungnuch (31)

TiO_2 is a popular semiconductor because the band gap is 3.1 eV. It can be activated in the near ultraviolet light (~380 nm). Irradiation of TiO_2 with light of least the energy of the semiconductor bandgap results in charge separation within the particle, with an electron getting promoted from valence band to the conduction band. The resulting electron (e_{cb}^-) and hole (h_{vb}^+) rapidly migrate to trap sites within the particle, but can also simply recombine with release of heat on the nanosecond timescale.

$$TiO_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+ \quad \text{(Light absorption)}$$

$$e_{cb}^- + h_{vb}^+ \longrightarrow \text{heat} \quad \text{(Recombination)}$$

If an electron donor (D) is adsorbed on semiconductor surface, it will the hole and oxidation reaction occurs.

$$D + h_{vb}^+ \longrightarrow D^+ \quad \text{(Oxidation)}$$

On the other hand, if an electron acceptor (A) is absorbed on the surface, it will receive an electron and the reduction reaction occurs.

$$A + e_{cb}^- \longrightarrow A^- \quad \text{(Reduction)}$$

The oxidation reaction is important in photocatalysis degradation process by semiconductor such as TiO_2. The toxic organic pollutants can undergo mineralization process and transform to CO_2 and water by oxidation reaction.

$$h_{vb}^+ + H_2O \longrightarrow OH^- + H^+$$

$$h_{vb}^+ + OH^- \longrightarrow OH\cdot$$

$$OH\cdot + \text{organic pollutants} + O_2 \longrightarrow CO_2 + H_2O$$

In equation, it shown that the hydroxyl radical react an organic pollutant and transform to CO_2 and water because the hydroxyl radical are extremely reactive and one of strongest oxidants. It can oxidize organic and inorganic substrates (M, R-H …) by electron transfer reaction, hydrogen abstraction and eletrophilic addition (9-12, 15, 24).

2.4.1 Factors influencing the photocatalysis rate of degradation

The Photocatalysis rate can be affected by variable such pH, initial concentration of pollutant, light source, humidity, amount of catalyst and temperature. Therefore, the study for photocatalysis must control all factors affecting of the photocatalysis reaction to organic compounds. These factors are reported as follow (24, 28):

Catalyst

An amount of catalyst is one of affected factors in photocatalysis process. Generally, the available for degradation increase with catalyst loading due to higher surface area of catalyst. An optimum value is present, while above a certain concentration, the solution opacity increases (due to increased light scattering of the catalyst particles) causing a reduction of light penetration in the solution and a consequent rate decrease. Additionally, at high-TiO_2 concentrations, terminal reactions could also contribute to the diminution of Photodegradation rate. The formed Hydroperoxyl radical is less reactive than the $HO^\bullet$ one:

$$H^\bullet + HO^\bullet \longrightarrow H_2O_2$$

$$H_2O_2 + HO^\bullet \longrightarrow H_2O + HO^\bullet_2$$

In slurry photoreactors, the optimal catalyst dosage reported lies in a wide range (from 0.15 to 8 g/l) for different Photocatalyted systems and photo reactors, increasing with increasing light intensity. The optimal catalyst dosage or effective optical penetration length, under given conditions, is very important in designing a slurry reactor for effective use of the reactor space and catalyst. If the solution layer thickness exceeds the optical penetration length at any given illumination intensity and catalyst concentration, the photoreactor will be under-utilized. For TiO_2 immobilized systems, there is also an optimal thickness of the catalyst film. The interfacial area is proportional to the thickness of catalyst, as the film is porous. Thus, thick films favour catalytic oxidation. On the other hand, the internal mass transfer resistance for both organic species and photogenerated electrons/holes will increase with increasing thickness. This increases the recombination possibility of the electron/hole pair and, as a consequence, the degradation performance is reduced (28).

Light source

For the photocatalysis process, light source is one of the important factors because the photocatalysis process need energy for breaking electron, and this energy come from the suitable UV wavelength. In table 2.6, it shown each catalyst need a different wavelength for example, a suitable wavelength for SnO_2 is 318 nm but TiO_2 is 380 nm (30).

The effect of light intensity can be divided into 3 regions. The degradation rate is first order with respect to low intensity. At intermediate, the reaction rate to begin and increase the reaction rate until the reaction is mass transfer limited. The Increasing intensity increases the recombination process faster than the normal oxidation (32-33).

Concentration of pollutant

In the photocatalysis process occurs on the surface of the solid photocatalyst. Therefore, a high adsorption capacity is associated with reaction favoring because the most of the reactions follow an adsorption isotherm (Langmuir-Hinsherwood equation) (11, 28).

$$\frac{-d[X]}{dt} = \frac{kK[X]}{1+K[X]}$$

Where: $\frac{-d[X]}{dt}$ = the degradation rate of substance

k = the reaction rate constant

K = the adsorption coefficient of substance

[X] = the concentration of substance

For high concentration of the pollutant, where saturation coverage of adsorbent surface is achieved (K[X] >> 1), the LH isotherm equation simplifies to a zero-order rate equation.

$$\frac{-d[X]}{dt} = k$$

For very low concentration of substance (K[X] << 1), the LH isotherm equation changes into a pseudo first-order kinetic law.

$$\frac{-d[X]}{dt} = k'[X]$$

With k’= kK being the pseudo first order rate constant. Therefore, at a high initial concentration, the degradation of substance obeys the zero order kinetic while the degradation kinetic at low concentration can be interpreted as an example of the first order kinetics.

Temperature

The photocatalytical oxidation rate is not much affected by minor changes in temperature. This dependence of the degradation rate on temperature is reflected by the low activation energy (a few kJ/mol) compared to ordinary thermal reactions. This is caused by the low thermal energy (kT = 0:026 eV at room temperature), that has almost no contribution to the activation energy of (the wide band gap) TiO_2. In the other hand, these activation energies are quite close to that of hydroxyl radical formation, suggesting that the Photodegradation of these organics is governed by hydroxyl radical reactions (24, 28).

The effect of temperature on the rate of oxidation may be dominated by the rate of interfacial electron transfer to oxygen. Alternatively, the more rapid desorption of both substrates and intermediates from the catalyst at higher temperatures are probably an additional factor, leading to a larger effective surface area for the reaction. At lower temperatures, desorption becomes the rate-limiting step of the process. Changes in relative positions of the Fermi level of TiO_2 powders at temperatures between 21 and 75 ^{o}C have been reported as relatively small (0.04 eV), but still improved interfacial electron-transfer kinetics are observed when the temperature is increased (24, 28).

Irradiation time

The Photodegradation efficiency and irradiation time have be relationship, the Photodegradation rate increase when increases the illumination time because the photocatalytic degradation reaction of organic pollutants occurs on the surface of TiO_2. Under UV illumination, electron–hole pairs are created on the TiO_2 surface. Oxygen adsorbed on the TiO2 surface prevents the recombination of electron–hole pairs by trapping electrons, the OH· radicals are formed from holes reacting with either H_2O or OH^- adsorbed on the TiO_2 surface (12, 34).

$$TiO_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+$$

$$h_{vb}^+ + H_2O \longrightarrow OH^- + H^+$$

$$h_{vb}^+ + OH^- \longrightarrow OH\cdot$$

In result, the process give the ·OH radicals which strong enough to completely oxidize organic pollutant.

$$OH\cdot + \text{organic pollutants} + O_2 \longrightarrow CO_2 + H_2O$$

However, the long illumination time no always increases the Photodegradation rate. Each organic pollutant needs time for treated in different such as 25 hours for remove dimethyl sulfide or 30 min for remove methyl butanol. The time for suitable depend on the any factor such as organic pollutant, temperature, flow rate (in case of pack column) and initial pollutant concentration.

2.6 Related research about photodegradation by TiO_2

Alberici R.M. (10) studied the gas-phase photocatalytic destruction of 17 VOCs over illuminated titanium dioxide (Degussa P-25). The study was investigated by using a plug flow reactor with the following experimental conditions: 200 ml mm -I flow rate, 23% relative humidity, 21% oxygen and an organic compound concentration range of 400-600 ppm. At steady state, high conversion yields were obtained for trichloroethylene (99.9%), isooctane (98.9%), acetone (98.5%), methanol (97.9%), methyl ethyl ketone (97.1%), t-butyl methyl ether (96.1%), dimethoxymethane (93.9%), methylene chloride (90.4%), methyl isopropyl ketone (88.5%), isopropanol (79.7%), chloroform (69.5%) and tetrachloroethylene (66.6%).

Zhao J. and Yang X. (3) concluded about the TiO_2 in their studies-photocatalytic oxidation for indoor air purification: the literature indicated that the TiO_2 was widely used as a photocatalyst due to its superior characteristics because it was inexpensive, safe and very stable showing high photocatalytic efficiency, it promoted ambient temperature oxidation of the major classes of indoor air pollutants, complete degradation of a broad range of pollutants could be achieved under certain operating conditions and no chemical additives were required. So the TiO_2 was the choice of heterogeneous support materials for Photo-oxidation air pollutants.

Poon C.S. et al (14) studied the affected factors of NO removal by TiO_2 adding into waste concrete paving block. The factors were porosity of block, the type of waste material used and percentage of TiO_2. The results showed that the photodegradation of NO positive was related to the porosity of block and percentage of TiO_2, and it was also found that the crushed recycled glass used to a part of concrete block was benefit to NO photodegradation rate.

Maggos Th. et al. (16) studied photocatalytic degradation of NO_x gases using TiO_2-containing paint: a real scale study. The researcher covered the surface of car park with 10% TiO_2-containing white acrylic paint and studied the removal of NO_x gases in there under UV lamps irradiation for 5 hours. The result showed a significant photocatalytic oxidation of NO_x gases. The photocatalytic removal of NO and NO_2 was calculated as 19% and 20%, respectively, while the photocatalytic rate ranged between 0.05 and 0.13 $\mu g\ m^{-2}s^{-1}$ for NO and between 0.09 and 0.16 $\mu g\ m^{-2}s^{-1}$ for NO_2.

Carp O. (28) explained the TiO_2 photodegradation mechanism. The photoinduced process, operational parameter which affected the photodegradation rate and the application of TiO_2 was also discussed in detail in this review, but the main theme was focused on the photocatalytic activity to degrade the organic and inorganic compounds which were found in wastewater or in air.

Jeong JY. et al (32) studied the TiO_2 photodegradation of toluene efficiency by comparing the effect of short-wave length light source (254+128 nm) and other light sources: black light (365 nm) and germicidal light (265 nm). The result showed that the photodegradation by using short-wave length light source was high conversion.

Jeong JY. Et al (33) studied the decomposition characteristic and identified the by-product of toluene and benzene photodegradation by TiO_2 with short-wave length light source (254+128 nm). The result was found that the by-products from the photodegradation of toluene and benzene with the short-wave length light source (254+128 nm) were CO_2, CO and some water-soluble organics were also formed under the reaction condition.

Hong Q. et al. (34) studied the formaldehyde degradation by $UV/TiO_2/O_3$ process by using continuous flow reactor. It was found that the O_3 combination affected to the formaldehyde photodegradation increased from 39% to 94.1% when O_3 content increased from 0 to 144 mg/m^3. Nevertheless, the result showed the formaldehyde degradation increased with prolonging residence time.

Juliana C.G. and Kaito T. (35) studied the photodegradation of imazaquin by using aqueous suspension of TiO_2. The factors of the sonication effect: time, catalyst loading, initial concentration of imazaquin, hydrogen peroxide and pH, temperature and radiation source, were also examined. The result was found that the photodegradation at pH 3–11 range were highly, the photocatalytic effect was more efficient in a suspension containing 2.0 g/l TiO_2 with 1 hour sonication time in the dark rather than with 20 min sonication before irradiation at temperature 20-40^oC.

Nogushi T. et al. (36) studied the Langmuir-Hinshelwood model to analyze the decomposition rate of gaseous formaldehyde on TiO_2 thin film. The studied decomposition rate of formaldehyde was also compared with the decomposition rate of acetaldehyde (standard test reactor). The result was found that the constant rate adsorption constant K_{app} of formaldehyde onto TiO_2 was larger than acetaldehyde.

Thus in the low concentration, the reaction of formaldehyde was greater than the acetaldehyde. Finally, this study concluded that the TiO_2 was the good adsorbent and a photocatalyst for the elimination of gaseous formaldehyde.

Ching W.H. et al. (37) studied solar photocatalytic degradation of gaseous formaldehyde by sol–gel TiO_2 thin film for enhancement of indoor air quality. The tested photoreactors were made of a borosilicate glass tube with the inner surface coated with a sol–gel TiO_2 thin film because that could be applied for coating on windows or glass building for indoor air purification. The researcher found that reactant respected with the solar UVA irradiance and exposure time. When comparing the apparent photonic efficiency between the sol–gel TiO_2 thin film and Degussa P25 TiO_2 coating, it was found the sol–gel TiO_2 thin film had a lower apparent photonic efficiency of solar photocatalysis than a Degussa P25 TiO_2 coating and the maximum reaction rate constant of sol-gel thin film was 0.148 min^{-1} under an exposure to sunlight. However, the findings of this study could be designed to apply the indoor air purification by TiO_2-coating.

Norman S.A. et al. (38) studied the degradation and stabilization of polymers and coatings: nano versus pigmentary Titania particle. The researcher showed the experiment to analyze the stabilization of TiO_2 nanosize (30-50 nm) and microsize (0.24-0.29µm) containing with acrylic paint films under the artificial weathering (irradiation using a number of light sources, test the films in hot air oven at 90 and 110^{o}C, hydroperoxide analysis). It was found that the TiO_2 nanosize films was more photoactive and could play a major role for the photocatalyst more than microsize. Under the artificial weathering, the nanosize was more stable than microsize because the microsize had Van der Waals force lower than nanosize.

Ao C.H. (39) studied the photodegradation of formaldehyde by photocatalyst TiO_2- effects on the presences of NO, SO_2 and VOCs. The researcher used 5% of TiO_2 (Degussa P25) suspended with water that coated on a glass fiber filter (Whatman). The catalyst was fixed horizontally with a vertical distance of 5 cm between the UV lamp in a continuous flow reactor with a volume of 18.6 liters and flowed the vapor of formaldehyde, NO_2, SO_2 and other VOCs (BTEX) for studying the effect of NO, SO_2 and VOCs to the formaldehyde degradation. It was found that NO was achieved by the OH radicals generated from the Photodegradation of NO that promoted the conversion of formaldehyde, Under the presence of SO_2, the formation of sulfate ion was observed and competed with formaldehyde for adsorption sites on the TiO_2 surface so the presence of SO_2 was inhibited the formaldehyde conversion and other VOCs also decreased the conversion of formaldehyde because Benzaldehyde and benzyl alcohol were generated from the Photodegradation of BTEX. These intermediates block the active sites of TiO_2 and inhibited the conversion of formaldehyde.

CHAPTER III

MATERIALS AND METHODS

3.1 Research Design

This study was a 3x4x4 factorial design with 3 replications, which consisted of 3 factors: initial formaldehyde concentrations in the static chamber (50, 100 and 150 mg/m^3); percentages of TiO_2 in acrylic paint (2, 5, 10 and 15%); irradiation times (90, 180, 270 and 360 min). It was designed: (a) to determine the effect of percent TiO_2 added to acrylic paint; (b) to study the effect of initial formaldehyde concentration for treating the formaldehyde; (c) to study the formaldehyde removal (%) in the static air chamber by used TiO_2 added in acrylic paint at various irradiation times.

3.2 Place of the Study

The experiment was performed at the laboratory of the department of Environmental Health Sciences, Faculty of Public Health, Mahidol University, Bangkok, Thailand.

3.3 Equipment used

The equipment was used in this study as follow:

1. Static air chamber (self construction by apply from previous researches (13, 15))
2. 18W fluorescent lamp (Sylvania F18WT8/154 Daylight)
3. Impinger (Duran)
4. Personal sampling pump (Escort, MSA)
5. Spectrometer (Thermo electron corporation)
6. Cuvettes

7. Thermometer, Hygrometer and Barometer
8. Digital balance (Oertling RB153)
9. Micropipette (Eppendorf)
10. Power supply and 7 cm-diameter fan

3.4 Chemical used

The chemical reagent was used in this studied follow as:

1. Titanium dioxide (TiO_2), Degussa P25- TiO_2.
2. Formaldehyde (HCHO) 40% (analytical grade), Carlo erba.
3. Chromotropic acid disodium salt dehydrate ($C_{10}H_6Na_2O_8S_2\cdot 2H_2O$) (analytical grade), Merck.
4. Sulfuric acid (H_2SO_4) 95 – 97% (analytical grade), Merck.
5. Distilled, Deionized water

3.5 Experiment Methods

3.5.1 Catalyst Preparation

The catalyst used in this studied was TiO_2 (Aeroxide P25 TiO_2, Degussa Germany). It was added into white acrylic paint for 0 (for control), 2, 5, 10, and 15% weight by weight. After added TiO_2, the paint was coated on 40 x 40 cm cerocrete at the room temperature and then the paint film was dried and repeated coating for 2 times. The weight of acrylic paint will be measured by digital balance.

3.5.2 Preparation of the static air chamber

The air chambers in this study were made of glass. The chamber volume was 216 liters (60 cm x 60 cm x 60 cm) and had a sampling port in front of the chamber. A 7 cm-diameter fan was installed inside the chamber for mixing air and put a cerocrete with TiO_2 added acrylic paint inside. The chamber was irradiated with an 18W fluorescence lamp that was installed outside at a 60 cm distance from a catalyst and the chamber was covered by future board and black plastic bag to protect any light source unless 18W fluorescent lamp.

In this study, 4 chambers were used: 1 chamber for control (no TiO_2 added in acrylic paint) and 3 chambers (3 replications) for experiment. The experiment set up is shown in figure 3.1

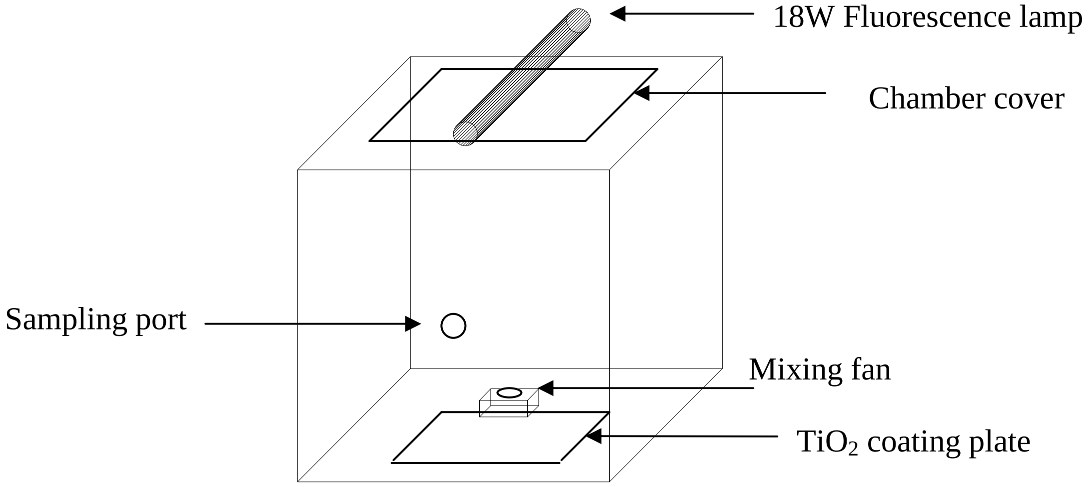


Figure 3.1 The air chamber used in this study

After the static air chambers were used, the inside of chambers would be cleaned by tap water and then the chamber cover was opened for one night to remove the formaldehyde gas that still remained in the chambers. Before implementing the experiment, the chambers would be cleaned again with sponge; then covered and sealed the chambers with glue tape for preventing the air leak.

3.5.3 Experimental conditions

Studying the degradation of formaldehyde in the static air chamber, the temperature, atmospheric pressure and humidity inside chamber were measured by thermometer, barometer and hygrometer respectively for calculating the reference condition (temperature at 25 ^oC and Atmospheric pressure 760 mmHg). In this study, it was investigated TiO_2 percentage added in acrylic paint and the effect of initial formaldehyde concentration on formaldehyde removal (%).

The initial formaldehyde concentrations at 0 (for control), 5, 100 and 150 mg/m^3 were developed by adding formalin by micropipette into the chamber. The volume of formaldehyde (ml) would be calculated by using the perfect gas law (40):

$$\overline{V} = 24.47\left(\frac{760}{p}\right)\left(\frac{t+273.2}{298.2}\right)$$

$$ppm = \frac{10^6 w / M.W.}{V / \overline{V}}$$

$$mg/m^3 = \frac{ppm \times M.W.}{22.4}$$

Where: ppm = the concentration of formaldehyde in chamber (ppm)

w = weight of formaldehyde (g)

M.W. = molecular weight of formaldehyde

V = volume of air (l)

$\overline{V}$ = molar volume of mixture at temperature and atmospheric pressure (l/mole)

p = atmospheric pressure (mmHg)

t = Temperature (^{o}C)

3.6 Formaldehyde Sampling and Analysis

3.6.1 Formaldehyde sampling method

The method of formaldehyde sampling in this study followed the analytical method of NIOSH. The method of laboratory sampling by 2 impingers (each impinger with 20 ml distilled water (41)) was set the flow rate at 1 l/min for 5 min. The samples were taken to analyze at 0 (for calculated percent removal), 90, 180, 270 and 360 min of irradiation times. The sample was analyzed by the visible absorption spectrometer that would be used chromotropic acid and sulfuric acid for developing the color which the accuracy of this method is ±18% (41) whereas the accuracy of HPLC (High performant liquid chromatography) is ±19% (42).

3.6.2 Sample preparation

1) Transferred of each impinger solution to a clean, dry 25 ml graduated cylinder. Recorded the volume of solution from front impinger, Mf (ml) and backup impinger, Mb (ml).
2) Pipetted 4 ml aliquots from each sample solution into 25 ml glass-stoppered flasks.
3) Added 0.1 ml 1% chromotropic acid to the flask and mix.
4) Added 6 ml conc. H_2SO_4 slowly to the flask. Replaced the stopper gently. Gently swirl the solution to mix.
5) Allowed the solution to cool at room temperature for 2 to 3 hours.

3.6.3 Standard curve of formaldehyde

1) Formaldehyde standard solution A**:** dilute 2.7 ml of 37% formalin solution to 1 liter with distilled water.
2) Formaldehyde standard solution B: Dilute 1 ml of formaldehyde standard solution A to 100 ml with distilled water.
3) Pipetted 0, 0.1, 0.3, 0.5, 0.7, 1 and 2 ml of standard solution B**.**
4) Diluted to 25 ml with distilled water
5) Analyzed together with samples and blank by 580nm spectrometer.
6) Prepared calibration graph (absorbance vs. µg formaldehyde/ml)

3.6.4 Analytical method

1. Set spectrophotometer according to manufacturer's recommendations and fill 1-cm cuvette with sample
2. Read sample absorbance at 580 nm.
3. Calculated the mass, µg of formaldehyde in each front impinger (M_f), back impinger (M_b) and average reagent blank (M_B).
4. Calculated the concentration, C, of formaldehyde in the air volume sampled, V(l):

$$C = \frac{M_f + M_b - 2M_B}{V}, mg/m^3$$

3.6.5 The calculation of formaldehyde concentration at reference condition

The actual condition of experiment was adjusted to the reference condition (temperature at 25 ^{o}C and atmospheric pressure 760 mmHg) by gas law theory (19). The equation was illustrated below:

$$\frac{C_1 \cdot V_1}{T_1} = \frac{C_2 \cdot V_2}{T_2}$$

Where: C_1 = Concentration of pollutant
V_1 = Atmospheric pressure
T_1 = Temperature
C_2 = Concentration of pollutant at reference condition
V_2 = Atmospheric pressure at reference condition (25 ^{o}C)
T_2 = Temperature at reference condition (760 mmHg)

3.7 Statistical Analysis

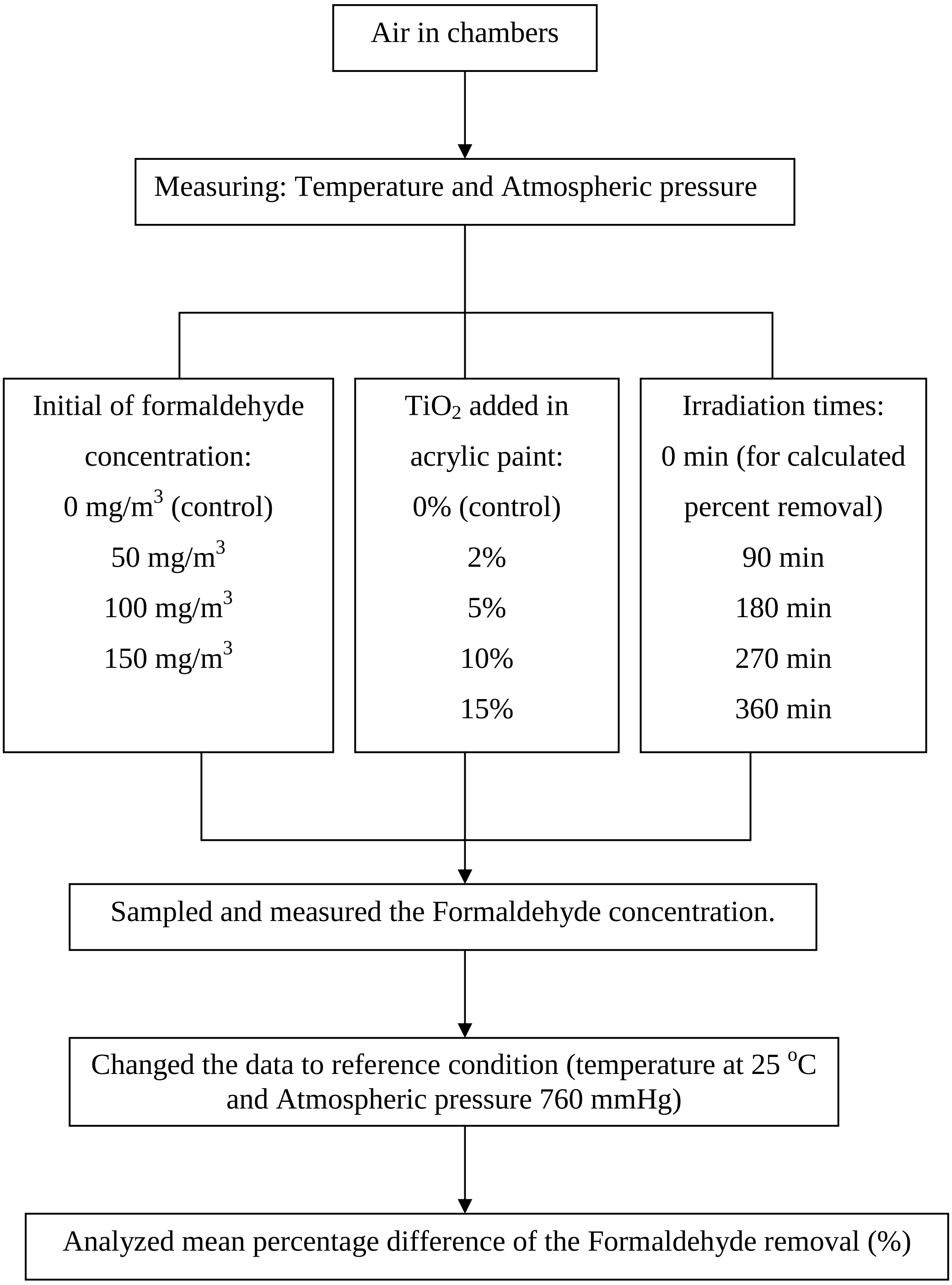
3.7.1 Descriptive Statistics

The data of the formaldehyde removal (%) for each condition: percentages of TiO_2 added in acrylic paint (2, 5, 10 and 15%); initial concentrations of formaldehyde in the static air chamber (50, 100 and 150 mg/m^3) and irradiation times (90, 180, 270 and 360 min) were analyzed and illustrated as the mean percentage and standard deviation.

3.7.2 Inferential Statistics

A research design of this experiment was a 3x4x4 factorial design. The mean percentage differences of the formaldehyde removal (%) for each conditions (percentage of TiO_2 added in acrylic paint and initial concentration of formaldehyde) in the air - depended on irradiation times- were analyzed by using the Analysis of Variance (43) and nonparametric kruskal-wallis test (44). The significant difference was compared by multiple comparisons for testing the different pair by using least significant difference method (LSD). The significant level would be determined at α level of 0.05.

3.8 Flow Diagram



3.9 Research Diagram

Initial formaldehyde concentration	TiO_2 added in acrylic paint	Time (min)			
		90	180	270	360
50 mg/m^3	2%	-	-	-	-
	5%	-	-	-	-
	10%	-	-	-	-
	15%	-	-	-	-
100 mg/m^3	2%	-	-	-	-
	5%	-	-	-	-
	10%	-	-	-	-
	15%	-	-	-	-
150 mg/m^3	2%	-	-	-	-
	5%	-	-	-	-
	10%	-	-	-	-
	15%	-	-	-	-

CHAPTER IV
RESULTS

In this research, the experiment was set up for studying the influencing factors: percentage of titanium dioxide (TiO_2) added in acrylic paint at the levels of 2, 5, 10, and 15 % (weight by weight); initial formaldehyde concentrations at 50, 100 and 150 mg/m^3; irradiation times at 90, 180, 270 and 360 min, on formaldehyde removal (%) by TiO_2 photodegradation in the static air chamber.

The static air chamber in this study used 4 chambers; one for control and 3 chambers as replications of treatment. Each formaldehyde concentration value of 3 replications was subtracted by control value for the actual percent removal of formaldehyde that degraded by TiO_2.

4.1 Descriptive statistics results

The formaldehyde removal (%) was determined by calculating the formaldehyde concentration in air chamber between before and after the treatment by TiO_2 added in acrylic paint. The summary results of raw data of formaldehyde concentration in the static air chamber at different percentages of TiO_2 added in acrylic paint, initial formaldehyde concentrations and irradiation times are shown in Appendix C.

The results showed that the formaldehyde in the static air chamber was degraded by TiO_2 added in acrylic paint between 2.11 – 60.08%, which depended on the influencing factors (percentage of TiO_2 used, initial formaldehyde concentration and various irradiation times) and the grand mean of formaldehyde removal (%) by using TiO_2 added in acrylic paint was 28.81%.

The total means of formaldehyde removal was 16.13% when used 2% TiO_2; which the mean formaldehyde removals were 13.94%, 15.59%, 17.88% and 17.08% when using 90, 180, 270 and 360 min of irradiation times respectively. The mean formaldehyde removals when used 2% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 24.55%, 17.09% and 5.93% respectively.

The total means of formaldehyde removal was 26.60% when used 5% TiO_2; which the mean formaldehyde removals were 26.17%, 27.62%, 25.91% and 26.59% when using 90, 180, 270 and 360 min of irradiation times respectively. The mean formaldehyde removals when used 5% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 37.70%, 27.97% and 14.12% respectively.

The total means of formaldehyde removal was 36.61% when used 10% TiO_2; which the mean formaldehyde removals were 28.69%, 38.22%, 40.17% and 39.37% when using 90, 180, 270 and 360 min of irradiation times respectively. The mean formaldehyde removals when used 10% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 54.25%, 35.14% and 22.04% respectively.

The total means of formaldehyde removal was 35.94% when used 15% TiO_2 which the mean formaldehyde removals were 31.59%, 36.67%, 38.00% and 37.50% when using 90, 180, 270 and 360 min of irradiation times respectively. The mean formaldehyde removals when used 15% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 48.02%, 36.57% and 23.23% respectively.

As can be seen from table 4.1, it showed that the formaldehyde removal (%) by using 10% TiO_2 at 50 mg/m^3 of initial formaldehyde concentration was highest and the formaldehyde removal (%) by using 2% at 150 mg/m^3 of initial formaldehyde concentration was lowest. The results are also shown in figure 4.1.

Table 4.1 The formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint, initial formaldehyde concentration in the static air chamber and irradiation time

	Percentage of TiO_2 added	2%				5%				10%				15%				Overall			
	Initial formaldehyde concentration (mg/m^3)	50	100	150	$\overline{X}_{2\%}$ (SD)	50	100	150	$\overline{X}_{5\%}$ (SD)	50	100	150	$\overline{X}_{10\%}$ (SD)	50	100	150	$\overline{X}_{15\%}$ (SD)	50	100	150	$\overline{X}_{overall}$ (SD)
Irradiation time (min)	90	29.38	10.34	2.11	13.94 (12.18)	35.85	26.33	16.32	26.17 (8.64)	45.79	30.35	9.93	28.69 (15.63)	38.63	33.66	22.49	31.59 (7.25)	37.42	25.18	12.71	25.10 (12.86)
	180	21.94	21.90	2.91	15.59 (9.62)	36.72	32.73	13.64	27.62 (10.68)	53.47	35.85	25.35	38.22 (12.33)	46.73	37.28	26.00	36.67 (9.03)	39.66	31.94	16.98	29.53 (13.57)
	270	23.62	20.68	9.35	17.88 (6.84)	38.37	26.15	13.25	25.91 (11.02)	57.66	34.83	28.02	40.17 (13.49)	52.89	37.20	23.92	38.00 (12.61)	43.14	29.71	18.63	30.49 (14.19)
	360	23.20	18.70	9.34	17.08 (6.29)	39.83	26.67	13.29	26.59 (11.68)	60.08	33.15	24.86	39.37 (15.96)	53.84	38.13	20.53	37.50 (14.49)	44.25	29.16	17.00	30.13 (15.14)
$\overline{X}$ total (SD)		24.55 (3.32)	17.09 (5.05)	5.93 (3.83)	16.13 (8.78)	37.70 (1.93)	27.97 (3.74)	14.12 (1.97)	26.60 (10.13)	54.25 (5.74)	35.14 (2.29)	22.04 (7.53)	36.61 (14.58)	48.02 (6.56)	36.57 (1.92)	23.23 (2.19)	35.94 (11.03)	41.12 (12.27)	28.99 (7.93)	16.33 (8.25)	28.81 (13.99)

Remark: Grand mean is 28.81

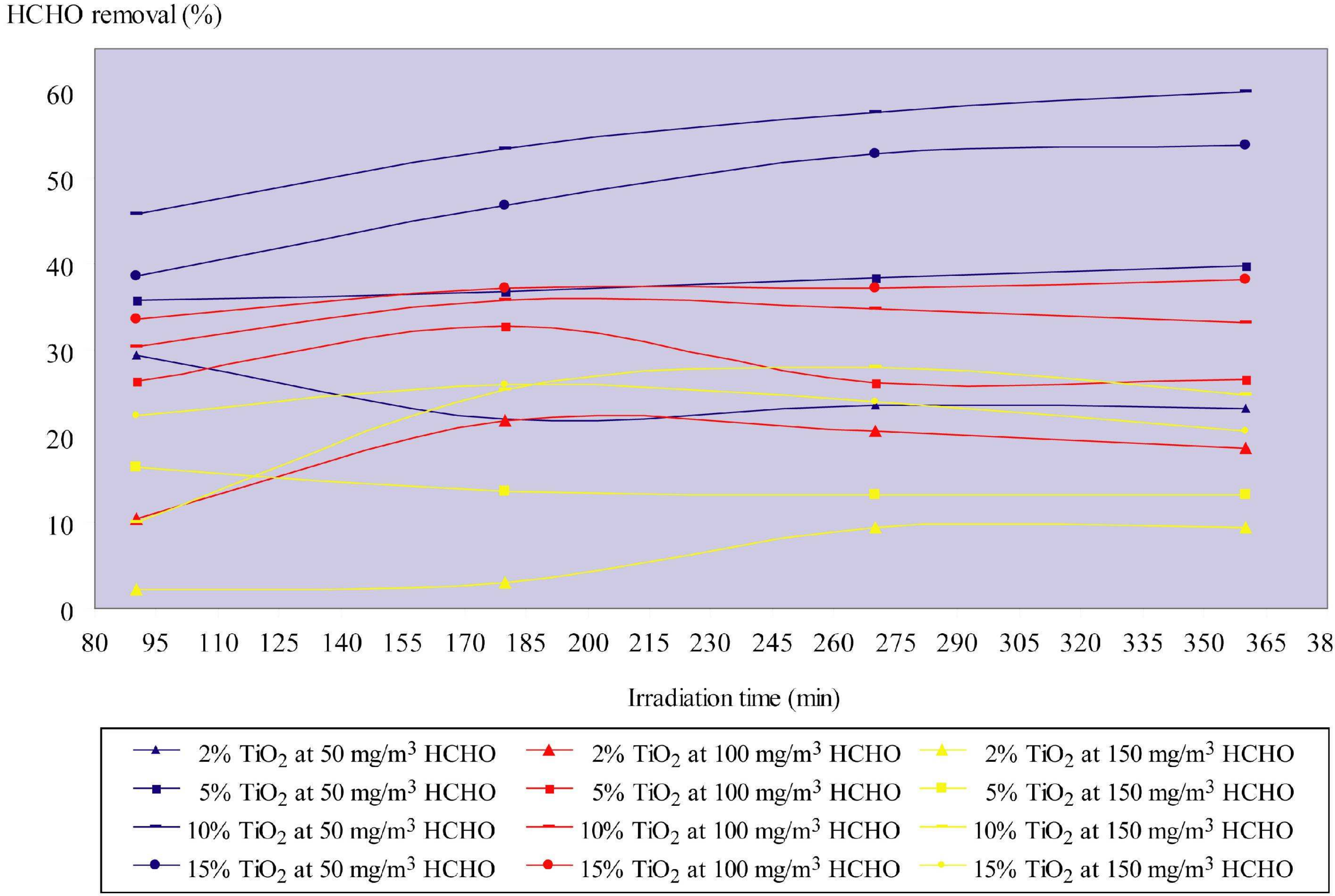


Figure 4.1 The formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint, initial formaldehyde concentrations in the static air chamber and irradiation times

4.1.1 The formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint

As shown in figure 4.2, the total means of formaldehyde removals (%) at 2% 5% 10% and 15% TiO_2 were 16.13, 26.60, 36.61 and 35.94 respectively. The results showed that the trend of formaldehyde removal (%) in the static air chamber at different percentages of TiO_2 added in acrylic paint increased when the TiO_2 added in acrylic paint increased until 10% TiO_2 adding, and after that the formaldehyde removal (%) slightly dropped.

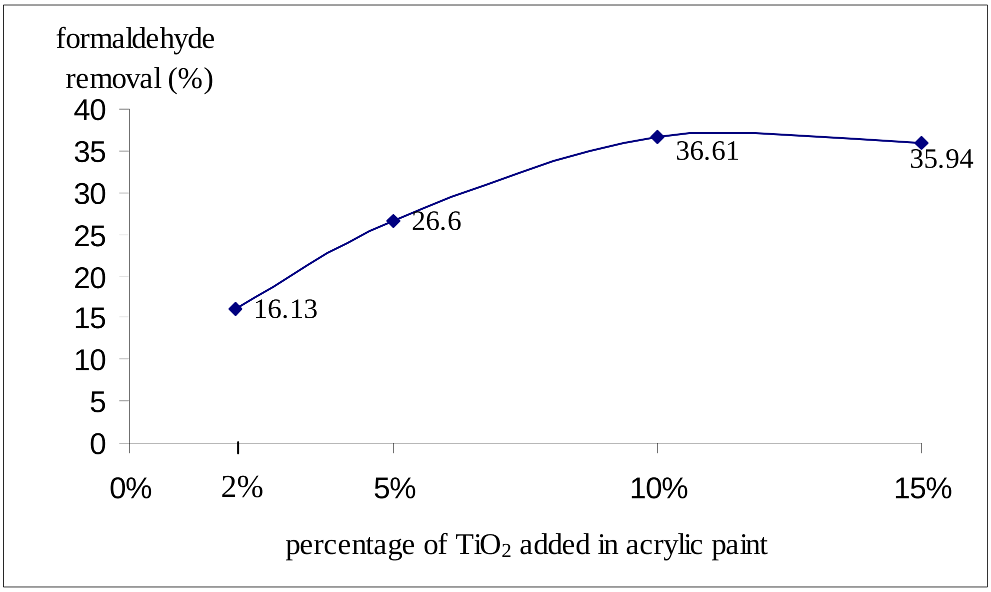


Figure 4.2 The total means of formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint

As shown in table 4.2, when the factor on percentage of TiO_2 added in acrylic paint interacted with the factor on initial formaldehyde concentration, it was found that the formaldehyde removals (%) at 50 mg/m^3 initial formaldehyde concentration by using 2%, 5%, 10% and 15% TiO_2 were 24.55, 37.70, 54.25 and 48.02 respectively.

The formaldehyde removals (%) at 100 mg/m^3 initial formaldehyde concentration by using 2%, 5%, 10% and 15% TiO_2 were 17.09, 27.97, 35.14 and 36.57 respectively. The formaldehyde removals (%) at 150 mg/m^3 initial formaldehyde concentration by using 2%, 5%, 10% and 15% TiO_2 were 5.93, 14.12, 22.04 and 23.23 respectively. The data are shown in table 4.2 and figure 4.3.

Table 4.2 The mean formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and initial formaldehyde concentrations

Initial formaldehyde concentration	Percentage of TiO_2 added in acrylic paint			
	2%	5%	10%	15%
50 mg/m^3	24.55	37.70	54.25	48.02
100 mg/m^3	17.09	27.97	35.14	36.57
150 mg/m^3	5.93	14.12	22.04	23.23

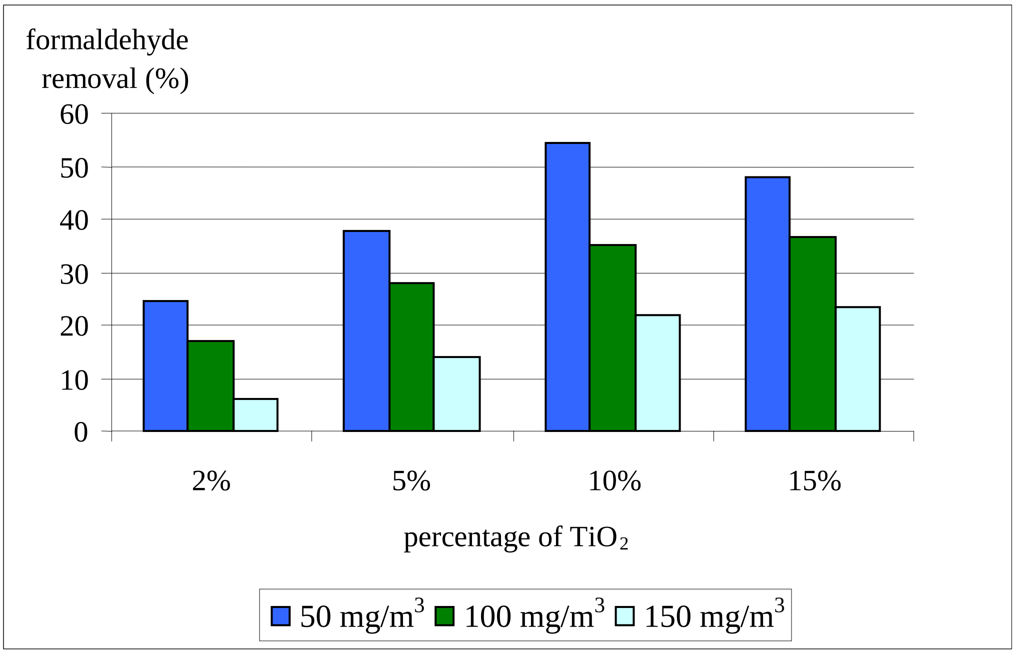


Figure 4.3 The mean formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and initial formaldehyde concentrations

As shown in figure 4.3, it was found that the formaldehyde removal (%) at 2% TiO_2 added in acrylic paint and the initial formaldehyde concentration of 150 mg/m^3 was lowest (5.93%) whereas the formaldehyde removal (%) at 10% TiO_2 added in acrylic paint and the initial formaldehyde concentration of 50 mg/m^3 was highest (54.25%).

Although the formaldehyde removal (%) at 10% and 15% TiO_2 adding slightly increased from 35.14 to 36.57 at the initial formaldehyde concentration of 100 mg/m^3 and from 22.04 to 23.23 at the initial formaldehyde concentration of 150 mg/m^3, the formaldehyde removal (%) slightly decreased from 54.52 to 48.02 at 50 mg/m^3 of the initial formaldehyde concentration.

In addition, from table 4.3 and figure 4.4 when the factor on percentage of TiO_2 added in acrylic paint interacted with the factor on irradiation time, it was found that at 90 min of irradiation time, the mean formaldehyde removals at 2%, 5%, 10% and 15% TiO_2 adding were 13.94%, 26.17%, 28.69% and 31.59% respectively. At 180 min of irradiation time, the mean formaldehyde removals at 2%, 5%, 10% and 15% TiO_2 adding were 15.59%, 27.62%, 38.22% and 36.67% respectively. At 270 min of irradiation time, the mean formaldehyde removals at 2%, 5%, 10% and 15% TiO_2 adding were 17.88%, 25.91%, 40.17% and 38.00% respectively. At 360 min of irradiation time, the mean formaldehyde removals at 2%, 5%, 10% and 15% TiO_2 adding were 17.08%, 26.59%, 39.37% and 37.50% respectively.

Table 4.3 The mean formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and various irradiation times

Irradiation times	Percentage of TiO_2 added in acrylic paint			
	2%	5%	10%	15%
90 min	13.94	26.17	28.69	31.59
180 min	15.59	27.62	38.22	36.67
270 min	17.88	25.91	40.17	38.00
360 min	17.08	26.59	39.37	37.50

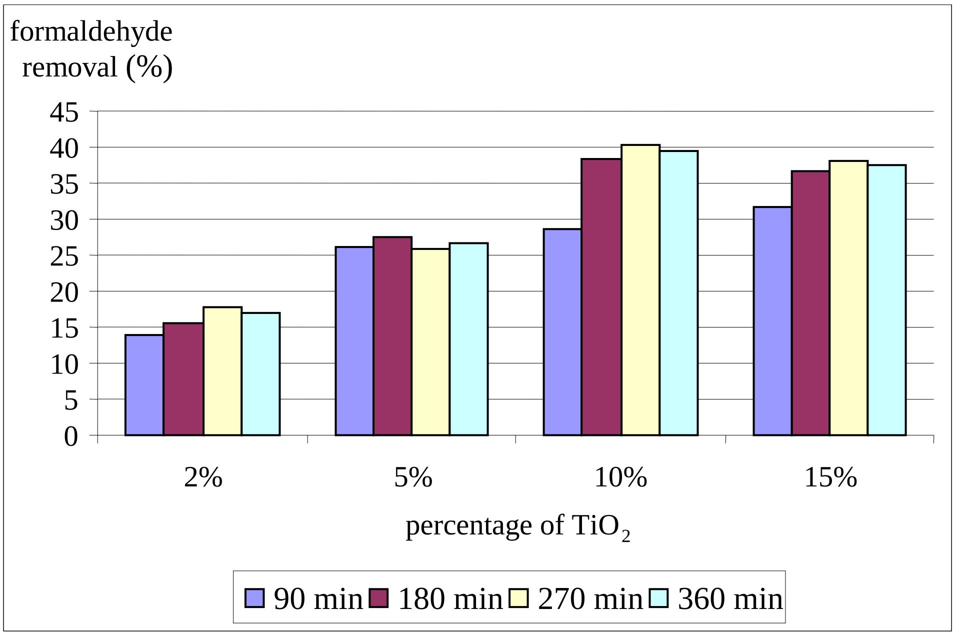


Figure 4.4 The mean formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and various irradiation times

As the results of formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and irradiation times, it was found that the mean formaldehyde removal (%) at 2%, 10% and 15% TiO_2 adding increased with increasing irradiation times but the formaldehyde removal (%) decreased at 360 min. Lastly, at 5% TiO_2 added in acrylic paint the formaldehyde removal (%) was nearly stable although the irradiation times increased.

4.1.2 The formaldehyde removal (%) at different initial formaldehyde concentrations

The results showed that the formaldehyde removal (%) in the static air chamber decreased with initial formaldehyde concentrations increased. The means of formaldehyde removals (%) at 50, 100 and 150 mg/m^3 initial formaldehyde concentrations in the static air chamber were 41.12, 28.99 and 16.33 respectively. The formaldehyde removal trend is shown in figure 4.5.

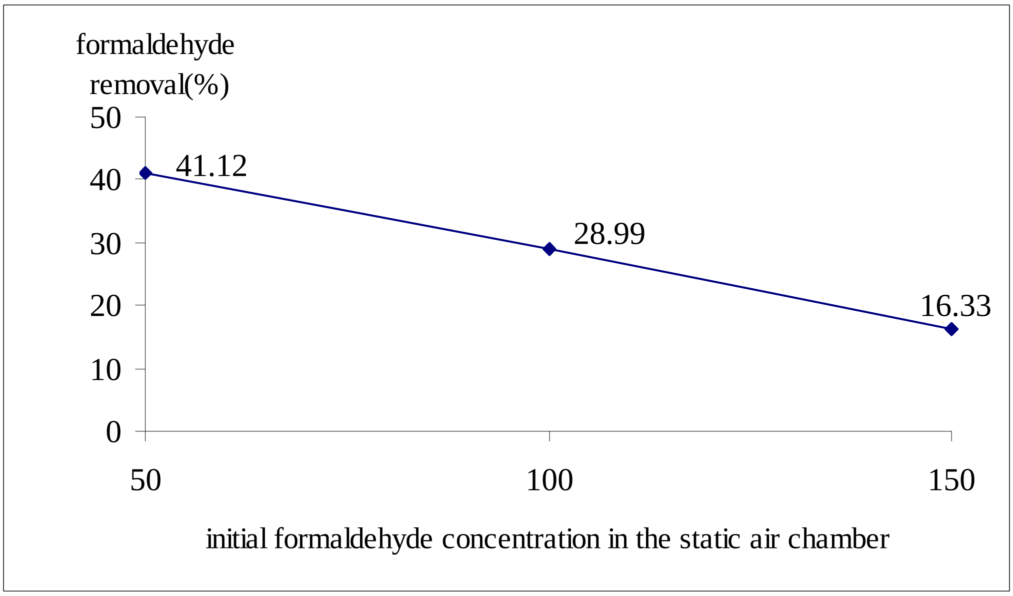


Figure 4.5 The mean formaldehyde removal (%) at different initial formaldehyde concentrations in the static air chamber

As the results of mean formaldehyde removal (%) at different initial formaldehyde concentrations (figure 4.5), when the factor on initial formaldehyde concentration interacted with the factor on percentage of TiO_2 added in acrylic paint, it was found that the formaldehyde removals (%) by using 2% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 24.55, 17.09 and 5.93 respectively. The formaldehyde removal (%) by using 5% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 37.70, 27.97 and 14.12 respectively. The formaldehyde removals (%) by using 10% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 54.25, 35.14 and 22.04 respectively. The formaldehyde removals (%) by using 15% TiO_2 at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 48.02, 36.57 and 23.23 respectively. The results are shown in table 4.4 and figure 4.6.

Table 4.4 The mean formaldehyde removal (%) at different initial formaldehyde concentrations and percentages of TiO_2 added in acrylic paint

Percentage of TiO_2 added in acrylic paint	Initial formaldehyde concentration		
	50 mg/m^3	100 mg/m^3	150 mg/m^3
2%	24.55	17.09	5.93
5%	37.70	27.97	14.12
10%	54.25	35.14	22.04
15%	48.02	36.57	23.23

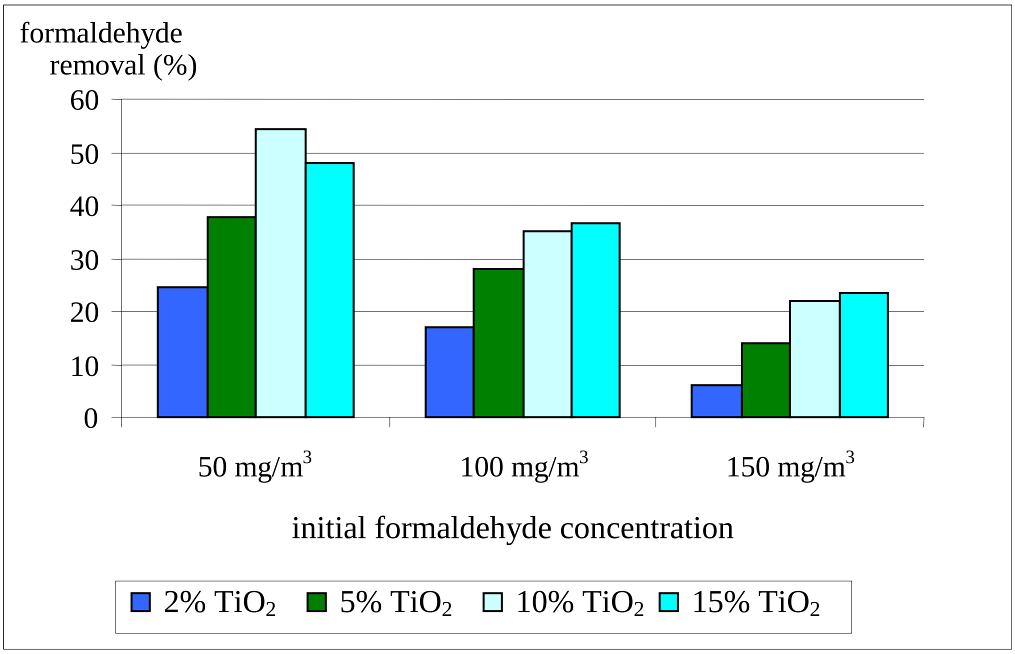


Figure 4.6 The mean formaldehyde removal (%) at different initial formaldehyde concentrations and percentages of TiO_2 added in acrylic paint

As shown in figure 4.6, the total means of formaldehyde removal (%) decreased when initial formaldehyde concentration increased and the mean formaldehyde removal (%) increased when percentage of TiO_2 added in acrylic paint increased. At 50, 100 and 150 mg/m^3 of initial formaldehyde concentrations, the formaldehyde removals (%) between 2%, 5% and 10% TiO_2 were obviously different but the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentrations with 15% TiO_2 using was slightly lower than the removal with 10% TiO_2 using.

When the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration with using different percentages of TiO_2 were compared, the mean formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration and using 10% TiO_2 added in acrylic paint was highest (54.25%).

In addition, when considering the interaction of the initial formaldehyde concentration factor and the irradiation time factor. The formaldehyde removals (%) at 90 min of irradiation time with 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 37.42, 25.18 and 12.71 respectively. The formaldehyde removals (%) at 180 min of irradiation time with 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 39.66, 31.94 and 16.98 respectively. The formaldehyde removals (%) at 270 min of irradiation time with 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 43.14, 29.71 and 18.63 respectively. The formaldehyde removals (%) at 360 min of irradiation time with 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 44.25, 29.16 and 17.00 respectively. The results are shown in table 4.5 and figure 4.7.

Table 4.5 The means formaldehyde removal (%) at different initial formaldehyde concentration and various irradiation times

Irradiation times	Initial formaldehyde concentration		
	50 mg/m^3	100 mg/m^3	150 mg/m^3
90 min	37.42	25.18	12.71
180 min	39.66	31.94	16.98
270 min	43.14	29.71	18.63
360 min	44.25	29.16	17.00

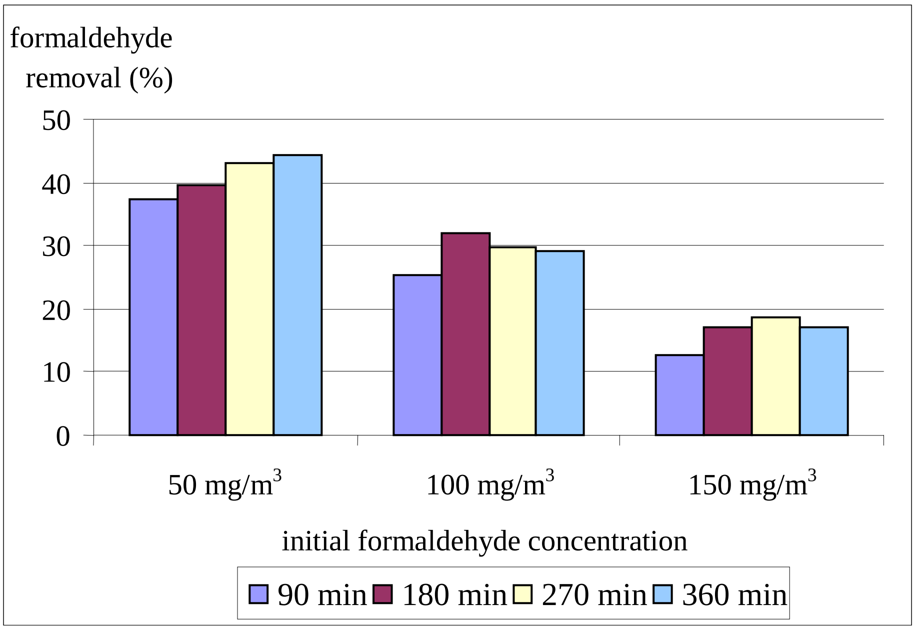


Figure 4.7 The mean formaldehyde removal (%) at different initial formaldehyde concentrations and various irradiation times

As the study results, it was found that the formaldehyde removals (%) by TiO_2 added in acrylic paint under the interaction effect of initial formaldehyde concentration and irradiation time decreased when initial formaldehyde concentration increased.

4.1.3 The formaldehyde removal (%) at various irradiation times

As the results in table 4.1, it showed that the overall means of formaldehyde removal (%) at various irradiation times increased with increasing irradiation times but slightly decreased at 360 min. The formaldehyde removal (%) at 90, 180, 270 and 360 min of irradiation times were 25.1, 29.53, 30.49 and 30.13 respectively. The results are shown in figure 4.8.

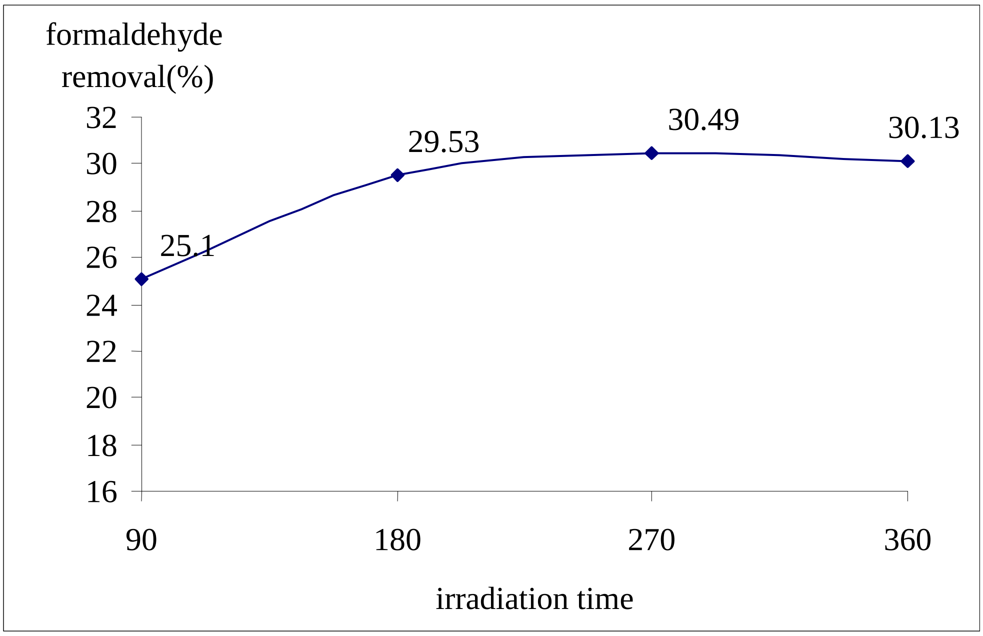


Figure 4.8 The overall mean formaldehyde removal (%) at various irradiation times

When considering the overall means of formaldehyde removal (%) under the interaction effect of the factor on irradiation time and the factor on percentage of TiO_2 added in acrylic paint, it was found that the formaldehyde removals (%) at 2% TiO_2 with 90, 180, 270 and 360 min of irradiation times were 13.94, 15.59, 17.88 and 17.08 respectively. At 5% TiO_2 with 90, 180, 270 and 360 min of irradiation times were 26.17%, 27.62%, 25.91% and 26.59% respectively. At 10% TiO_2 with 90, 180, 270 and 360 min of irradiation times were 28.69%, 38.22%, 40.17% and 39.37% respectively. At 15% TiO_2 with 90, 180, 270 and 360 min of irradiation times were 31.59%, 36.67%, 38.00% and 37.50% respectively. The results are shown in table 4.6 and figure 4.9.

Table 4.6 The mean formaldehyde removal (%) at various irradiation times and percentage of TiO_2 added in acrylic paint

Percentage of TiO_2 added in acrylic paint	Irradiation times			
	90 min	180 min	270 min	360 min
2%	13.94	15.59	17.88	17.08
5%	26.17	27.62	25.91	26.59
10%	28.69	38.22	40.17	39.37
15%	31.59	36.67	38.00	37.50

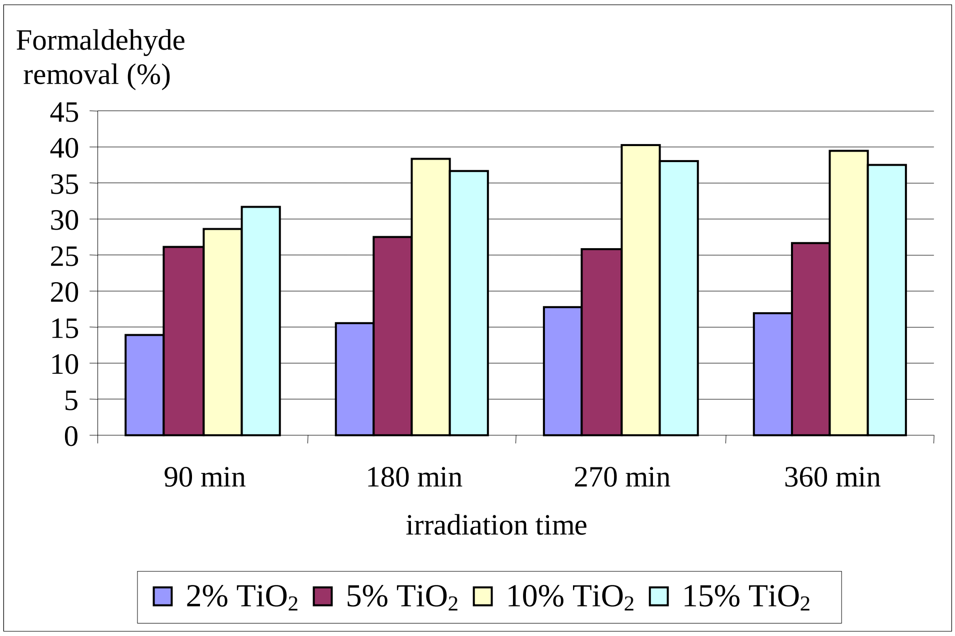


Figure 4.9 The mean formaldehyde removal (%) at various irradiation times and percentages of TiO_2 added in acrylic paint

As the study results, it was found that the formaldehyde removal (%) at 90 min of irradiation times increased with the increased percentages of TiO_2 but the formaldehyde removal (%) at 5%, 10% and 15% TiO_2 were slightly different. The trend of formaldehyde removal (%) at 180, 270 and 360 min of irradiation times were nearly similar; but the formaldehyde removal (%) at 10% TiO_2 was highest whereas at 15% TiO_2, the formaldehyde removal (%) decreased slightly.

When considering the results of formaldehyde removal (%) at the factor on various irradiation times interacted with the factor on initial formaldehyde concentration, it was found that the formaldehyde removals (%) at 50 mg/m^3 initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time were 37.42, 39.66, 43.14 and 44.25 respectively. The formaldehyde removals (%) at 100 mg/m^3 initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time were 25.17, 31.94, 29.71 and 29.16 respectively. The formaldehyde removals (%) at 150 mg/m^3 initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time were 12.71, 16.98, 18.63 and 17.00 respectively. The results are shown in table 4.7 and figure 4.10.

Table 4.7 The means formaldehyde removal (%) at various irradiation times and initial formaldehyde concentration

Initial formaldehyde concentration	Irradiation times			
	90 min	180 min	270 min	360 min
50 mg/m^3	37.42	39.66	43.14	44.25
100 mg/m^3	25.17	31.94	29.71	29.16
150 mg/m^3	12.71	16.98	18.63	17.00

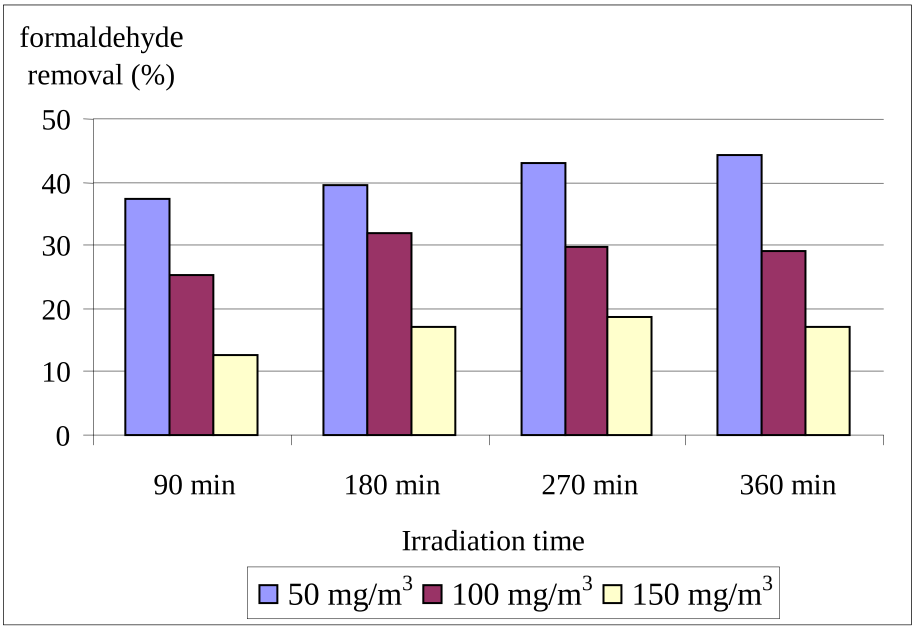


Figure 4.10 The mean formaldehyde removal (%) at various irradiation times and initial formaldehyde concentrations

As figure 4.10, it was shown that the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration increased with increasing irradiation times; except the formaldehyde removal (%) at 100 mg/m^3 of initial formaldehyde concentration increased until 180 min of irradiation time then it decreased, like the formaldehyde removal (%) at 150 mg/m^3 of initial formaldehyde concentration increased until 270 min of irradiation time and after that it decreased.

4.2 Inferential Statistics results

4.2.1 The analysis of variance

This study was a 3x4x4 factorial design. The mean percentage difference of the formaldehyde removal (%) for each experimental condition (percentage of TiO_2 added in acrylic paint, initial formaldehyde concentration and various irradiation times) was analyzed by using the Analysis of Variance (ANOVA). The results of analysis of variance are shown in table 4.8

Table 4.8 The result of analysis of variance

Factors	P-value	Significant
Percentage of TiO_2 added in acrylic paint	<.0001	Sig.
Initial formaldehyde concentration	<.0001	Sig.
Irradiation time	<.0001	Sig.
Percentage of TiO_2 added in acrylic paint* initial formaldehyde concentration	<.0001	Sig.
Percentage of TiO_2 added in acrylic paint* Irradiation time	<.0001	Sig.
Initial formaldehyde concentration* Irradiation time	<.0001	Sig.
Percentage of TiO_2 added in acrylic paint* initial formaldehyde concentration* Irradiation time	<.0001	Sig.

Remarks: Compared using $\alpha = .05$, R Squared = .991 (Adjusted R Squared = .987)
The summary of analysis of variance is shown in appendix D.

The mean formaldehyde removal (%) values at each experimental condition (percentages of TiO_2 added in acrylic paint at the level of 2%, 5%, 10%, and 15%; initial formaldehyde concentration at 50, 100 and 150 mg/m^3; irradiation time at 90, 180, 270 and 360 min) were significantly different. In addition, the results showed that there were the interaction effects among all factors; the percent formaldehyde removals due to both the 2-factor and 3-factor interactions were significantly different.

As the significant results of main effects and interaction effects of the study factors, the multiple comparisons were analyzed for determining the significant difference in pair by using least significant difference method (LSD).

4.2.2 The multiple comparisons of formaldehyde removal (%) at the different percentages of TiO_2 added in acrylic paint

The multiple comparisons at α level of 0.05 of formaldehyde removal (%) at the 2%, 5%, 10% and 15% TiO_2 added in acrylic paint were significantly different except the mean formaldehyde removal (%) at 10% and 15% TiO_2 added in acrylic paint was non-significantly different. The results are shown in table 4.9.

Table 4.9 The multiple comparisons of formaldehyde removal (%) at the different percentages of TiO_2 added in acrylic paint

Pair wise	P-value	Sig
2% and 5%	<.0001	Sig
2% and 10%	<.0001	Sig
2% and 15%	<.0001	Sig
5% and 10%	<.0001	Sig
5% and 15%	<.0001	Sig
10% and 15%	.080	Non-Sig

Remarks: Compared using α = .05

The summary of multiple comparisons is shown in appendix E.

4.2.3 The multiple comparisons of formaldehyde removal (%) at different initial formaldehyde concentrations.

The multiple comparisons of formaldehyde removal (%) by using TiO_2 added in acrylic paint at 50, 100 and 150 mg/m^3 of initial formaldehyde concentrations were significantly different at α level of 0.05, the results are shown in table 4.10.

Table 4.10 The multiple comparisons of formaldehyde removal (%) by used TiO_2 added in acrylic paint at different initial formaldehyde concentration

Pair wise	P-value	Sig
50 and 100 mg/m^3	<.0001	Sig
50 and 150 mg/m^3	<.0001	Sig
100 and 150 mg/m^3	<.0001	Sig

Remarks: Compared using $\alpha = .05$

The summary of multiple comparisons is shown in appendix E.

4.2.4 The multiple comparisons of formaldehyde removal (%) at various irradiation times

The multiple comparisons of formaldehyde removal (%) at various irradiation times showed that the removal of 90 min was significantly different from the one at 180, 270 and 360 min of irradiation times at α level of 0.05. The formaldehyde removal (%) at 180 min was significantly different from the one at 270 min of irradiation time at α level of 0.05, except the formaldehyde removal (%) at 180 min was not significantly different from the one at 360 min as well as the removal at 270 min was not significantly different from the one at 360 min of irradiation time. The results are shown in table 4.11.

Table 4.11 The multiple comparisons of formaldehyde removal (%) by using TiO_2 added in acrylic paint at various irradiation times

Pair wise	P-value	Sig
90 and 180 min	<.0001	Sig
90 and 270 min	<.0001	Sig
90 and 360 min	<.0001	Sig
180 and 270 min	.012	Sig
180 and 360 min	.111	Non-Sig
270 and 360 min	.350	Non-Sig

Remarks: Compared using $\alpha = .05$

The summary of multiple comparisons is shown in appendix E.

4.2.5 The multiple comparisons of formaldehyde removals (%) under the interaction effect between the different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations

The multiple comparisons at α level of 0.05 of formaldehyde removal (%) under the interaction effect between the different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations showed the significantly different pairs except the following pairs: the formaldehyde removal (%) by using 2% TiO_2 at 50 mg/m^3 of initial formaldehyde concentration was non-significantly different from the removal by using 5% TiO_2 at 100 mg/m^3, 10% TiO_2 at 150 mg/m^3 and 15% TiO_2 at 150 mg/m^3 of initial formaldehyde concentrations.

The formaldehyde removal (%) by using 5% TiO_2 at 50 mg/m^3 of initial formaldehyde concentration was non-significantly different from the removal by using 15% TiO_2 at 100 mg/m^3. The removal by using 10% TiO_2 at 100 mg/m^3 of initial formaldehyde concentration was non-significantly different from the removal by using 15% TiO_2 at 100 mg/m^3 of initial formaldehyde concentrations.

The formaldehyde removal (%) by using 10% TiO_2 at 150 mg/m^3 of initial formaldehyde concentration was non-significantly different from the removal by using 15% TiO_2 at 150 mg/m^3 of initial formaldehyde concentration.

As the study results, it showed that most of the formaldehyde removal (%) under the interaction effect between the percentages of TiO_2 added in acrylic paint and initial formaldehyde concentrations were significantly different at α level of 0.05. The results are shown in table 4.12.

Table 4.12 The multiple comparisons of formaldehyde removals (%) at the different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations

Percentage of TiO_2 added in acrylic paint and initial formaldehyde concentration	2% TiO_2, 50 mg/m^3	2% TiO_2, 100 mg/m^3	2% TiO_2, 150 mg/m^3	5% TiO_2, 50 mg/m^3	5% TiO_2, 100 mg/m^3	5% TiO_2, 150 mg/m^3	10% TiO_2, 50 mg/m^3	10% TiO_2, 100 mg/m^3	10% TiO_2, 150 mg/m^3	15% TiO_2, 50 mg/m^3	15% TiO_2, 100 mg/m^3	15% TiO_2, 150 mg/m^3
2% TiO_2, 50 mg/m^3												
2% TiO_2, 100 mg/m^3	+											
2% TiO_2, 150 mg/m^3	+	+										
5% TiO_2, 50 mg/m^3	+	+	+									
5% TiO_2, 100 mg/m^3	**o**	+	+	+								
5% TiO_2, 150 mg/m^3	+	+	+	+	+							
10% TiO_2, 50 mg/m^3	+	+	+	+	+	+						
10% TiO_2, 100 mg/m^3	+	+	+	+	+	+	+					
10% TiO_2, 150 mg/m^3	**o**	+	+	+	+	+	+	+				
15% TiO_2, 50 mg/m^3	+	+	+	+	+	+	+	+	+			
15% TiO_2, 100 mg/m^3	+	+	+	**o**	+	+	+	**o**	+	+		
15% TiO_2, 150 mg/m^3	**o**	+	+	+	+	+	+	+	**o**	+	+	

+ = significantly different at α level of .05

o = non- significantly different at α level of .05

However, as the multiple-comparison results, it was found that the total mean formaldehyde removal (%) by using 10% TiO_2 adding at 50 mg/m^3 of initial formaldehyde concentration was highest (54.25%).

4.2.6 The multiple comparisons of formaldehyde removals (%) at the different percentages of TiO_2 added in acrylic paint and various irradiation times

The multiple comparisons at α level of 0.05 of formaldehyde removal (%) under the interaction effect between the different percentages of TiO_2 added in acrylic paint and various irradiation times showed the significantly different pairs as follows: the formaldehyde removals (%) by using 2% TiO_2 at 90 min of irradiation time was significantly different from 5% TiO_2 at 90, 180, 270 and 360 min, different from using 10% TiO_2 at 90, 180, 270 and 360 min, and different from using 15% TiO_2 at 90, 180, 270 and 360 min of irradiation times. The formaldehyde removal (%) by using 2% TiO_2 at 180 min of irradiation time was significantly different from the formaldehyde removals (%) by using 5% TiO_2 at 180 and 360 min, different from using 10% TiO_2 at 90, 180, 270 and 360 min, and different from using 15% TiO_2 at 90, 180, 270 and 360 min of irradiation time. The formaldehyde removals (%) by using 2% TiO_2 at 270 and 360 min were significantly different from the formaldehyde removals (%) by using 10% TiO_2 at 90, 180, 270 and 360 min, and different from using 15% TiO_2 at 90, 180, 270 and 360 min of irradiation time.

The formaldehyde removal (%) by using 5% TiO_2 at 90 min was significantly different from the formaldehyde removals (%) by using 10% TiO_2 at 180, 270 and 360 min, and different from using 15% TiO_2 at 270 and 360 min of irradiation time. The formaldehyde removal (%) by using 5% TiO_2 at 180 min was significantly different from the formaldehyde removals (%) by using 10% TiO_2 at 270 and 360 min of irradiation time. The formaldehyde removal (%) by using 5% TiO_2 at 270 min was significantly different from the formaldehyde removals (%) by using 10% TiO_2 at 180, 270 and 360 min, and different from using 15% TiO_2 at 180, 270 and 360 min of irradiation time. The formaldehyde removal (%) by using 5% TiO_2 at 360 min was significantly different from the formaldehyde removal (%) by using 10% at 180, 270 and 360 min, and different from using 15% TiO_2 at 270 and 360 min of irradiation time. The formaldehyde removal (%) by using 10% TiO_2 at 90 min of irradiation time was significantly different from the formaldehyde removals (%) by using 10% TiO_2 at 270 min of irradiation time.

As the study results, it showed that the formaldehyde removals (%) under the interaction effect between the different percentages of TiO_2 added factor and various irradiation times were significantly different at α level of 0.05. But at the same percentage level of TiO_2 added, the formaldehyde removals (%) at various irradiation times were non-significantly different at α level of 0.05. Furthermore, the formaldehyde removal (%) at using 10% TiO_2 was non-significantly different at α level of 0.05 from using 15% TiO_2 added although considering their interactions with various irradiation time factor. The results are shown in table 4.13.

Table 4.13 The multiple comparisons of formaldehyde removals (%) at the different percentages of TiO_2 added in acrylic paint and various irradiation time

Percentage of TiO_2 added in acrylic paint and irradiation time	2% TiO_2, 90 min	2% TiO_2, 180 min	2% TiO_2, 270 min	2% TiO_2, 360 min	5% TiO_2, 90 min	5% TiO_2,180 min	5% TiO_2, 270 min	5% TiO_2, 360 min	10% TiO_2, 90 min	10% TiO_2, 180 min	10% TiO_2, 270 min	10% TiO_2, 360 min	15% TiO_2, 90 min	15% TiO_2, 180 min	15% TiO_2, 270 min	15% TiO_2, 360 min
2% TiO_2, 90 min																
2% TiO_2, 180 min	**o**															
2% TiO_2, 270 min	**o**	**o**														
2% TiO_2, 360 min	**o**	**o**	**o**													
5% TiO_2, 90 min	+	**o**	**o**	**o**												
5% TiO_2, 180 min	+	+	**o**	**o**	**o**											
5% TiO_2, 270 min	+	**o**	**o**	**o**	**o**	**o**										
5% TiO_2, 360 min	+	+	**o**	**o**	**o**	**o**	**o**									
10% TiO_2, 90 min	+	+	+	+	**o**	**o**	**o**	**o**								
10% TiO_2, 180 min	+	+	+	+	+	**o**	+	+	**o**							
10% TiO_2, 270 min	+	+	+	+	+	+	+	+	+	**o**						
10% TiO_2, 360 min	+	+	+	+	+	+	+	+	**o**	**o**	**o**					
15% TiO_2, 90 min	+	+	+	+	**o**	**o**	**o**	**o**	**o**	**o**	**o**	**o**				
15% TiO_2, 180 min	+	+	+	+	**o**	**o**	+	**o**	**o**	**o**	**o**	**o**	**o**			
15% TiO_2, 270 min	+	+	+	+	+	**o**	+	+	**o**	**o**	**o**	**o**	**o**	**o**		
15% TiO_2, 360 min	+	+	+	+	+	**o**	+	+	**o**	**o**	**o**	**o**	**o**	**o**	**o**	

+ = significantly different at α level of .05

o = non- significantly different at α level of .05

In addition, as the multiple comparison results, it was found that the formaldehyde removal (%) by using 10% TiO_2 adding at 270 min of irradiation time was highest (30.49%).

4.2.7 The multiple comparisons of formaldehyde removals (%) at the different initial formaldehyde concentrations and various irradiation times

The multiple comparisons at α level of 0.05 of formaldehyde removal (%) under the interaction effect between the different initial formaldehyde concentrations and various irradiation times showed the significantly different pair as follows: the formaldehyde removal (%) by using TiO_2 added in acrylic paint at 50 mg/m^3 of initial formaldehyde concentration with 90 min of irradiation time was significantly different from the formaldehyde removals (%) at 100 mg/m^3 of initial formaldehyde concentration with 90 and 360 min of irradiation time, and different from 150 mg/m^3 with 90, 180, 270 and 360 min of irradiation time. The formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration with 180 min of irradiation time was significantly different from the formaldehyde removals (%) at 100 mg/m^3 of initial formaldehyde concentration with 90, 270 and 360 min of irradiation time and different from 150 mg/m^3 with 90, 180, 270 and 360 min of irradiation time. The formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration with 270 min of irradiation time was significantly different from the formaldehyde removals (%) at 100 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time and different from 150 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time. The formaldehyde removals (%) at 50 mg/m^3 of initial formaldehyde concentration with 360 min of irradiation time was significantly different from the formaldehyde removals (%) at 100 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min and different from 150 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time.

The formaldehyde removal (%) by using TiO_2 added in acrylic paint at 100 mg/m^3 of initial formaldehyde concentration with 90 min of irradiation time was significantly different from the formaldehyde removals (%) at 150 mg/m^3 of initial formaldehyde concentration with 90, 180 and 360 min of irradiation time. The formaldehyde removal (%) at 100 mg/m^3 of initial formaldehyde concentration with 180 min of irradiation time was significantly different from the formaldehyde removals (%) at 150 mg/m^3 with 90, 180, 270 and 360 min of irradiation time. The formaldehyde removal (%) at 100 mg/m^3 of initial formaldehyde concentration with 270 min of irradiation time was significantly different from the formaldehyde removals (%) at 150 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time. The formaldehyde removal (%) at 100 mg/m^3 of initial formaldehyde concentration with 360 min was significantly different from the formaldehyde removals (%) at 150 mg/m^3 of initial formaldehyde concentration with 90, 180, 270 and 360 min of irradiation time. The results are shown in table 4.14.

As the study results, the multiple comparisons of the formaldehyde removals (%) under the interaction effect between initial formaldehyde concentration and various irradiation times were the same as the multiple comparison results of the formaldehyde removals (%) under the interaction effect between the percentages of TiO_2 added and various irradiation times, it showed that the formaldehyde removals (%) at various irradiation times with similar initial formaldehyde concentration level were non-significantly different at α level of 0.05.

Table 4.14 the multiple comparisons of formaldehyde removals (%) at the different initial formaldehyde concentrations and variance irradiation times

Initial formaldehyde concentration and irradiation time	50 mg/m^3, 90 min	50 mg/m^3, 180 min	50 mg/m^3, 270 min	50 mg/m^3, 360 min	100 mg/m^3, 90 min	100 mg/m^3, 180 min	100 mg/m^3, 270 min	100 mg/m^3, 360 min	150 mg/m^3, 90 min	150 mg/m^3, 180 min	150 mg/m^3, 270 min	150 mg/m^3, 360 min
50 mg/m^3, 90 min												
50 mg/m^3, 180 min	**o**											
50 mg/m^3, 270 min	**o**	**o**										
50 mg/m^3, 360 min	**o**	**o**	**o**									
100 mg/m^3, 90 min	+	+	+	+								
100 mg/m^3, 180 min	**o**	**o**	+	+	**o**							
100 mg/m^3, 270 min	**o**	+	+	+	**o**	**o**						
100 mg/m^3, 360 min	+	+	+	+	**o**	**o**	**o**					
150 mg/m^3, 90 min	+	+	+	+	+	+	+	+				
150 mg/m^3, 180 min	+	+	+	+	+	+	+	+	**o**			
150 mg/m^3, 270 min	+	+	+	+	**o**	+	+	+	**o**	**o**		
150 mg/m^3, 360 min	+	+	+	+	+	+	+	+	**o**	**o**	**o**	

+ = significantly different at α level of .05

o = non- significantly different at α level of .05

In addition, as the multiple-comparison results, it was found that the formaldehyde removal (%) by using TiO_2 adding at 50 mg/m^3 of initial formaldehyde concentration and 360 min of irradiation time was highest (44.25%).

4.2.8 The multiple comparisons of formaldehyde removals (%) at the different percentages of TiO_2 added in acrylic paint, different initial formaldehyde concentrations and various irradiation times

As the results, it was found that the formaldehyde removal (%) by using low amount of TiO_2 adding and high initial formaldehyde concentrations were almost non-significantly different from the formaldehyde removal (%) by using high amount of TiO_2 adding and low initial formaldehyde concentrations. The formaldehyde removal (%) by using 2% TiO_2 adding and 50 mg/m^3 of initial formaldehyde concentration was the same as the formaldehyde removals (%) by using 15% TiO_2 adding and 150 mg/m^3 of initial formaldehyde concentration. When increasing the percentage of TiO_2 to 5% and at 50 mg/m^3 of initial formaldehyde concentration, the formaldehyde removal (%) was non-significantly different from the formaldehyde removals (%) by using 15% TiO_2 adding and 100 mg/m^3 of initial formaldehyde concentration.

As the multiple comparison results, it was found that the formaldehyde removal (%) by using 10% TiO_2 adding at 50 mg/m^3 of initial formaldehyde concentration and 360 min of irradiation time was highest (60.08%) and significantly different from others. However, the formaldehyde removal (%) by using 10% TiO_2 adding at 50 mg/m^3 of initial formaldehyde concentration and 270 min of irradiation time was non-significantly different from the formaldehyde removals (%) by using 10% TiO_2 adding and 150 mg/m^3 of initial formaldehyde concentration and 360 min of irradiation time, and the formaldehyde removal (%) by using 10% TiO_2 adding at 100 mg/m^3 of initial formaldehyde concentration and 90 min of irradiation time was non-significantly different from the formaldehyde removals (%) by using 2% TiO_2 and 50 mg/m^3 of initial formaldehyde concentration and 90 min and 10% TiO_2 and 150 mg/m^3 of initial formaldehyde concentration and 270 min of irradiation time. The results are shown table 4.15.

Table 4.15 the multiple comparisons of formaldehyde removals (%) at the different percentages of TiO_2, different initial formaldehyde concentrations and various irradiation times

			2%												5%												10%												15%											
			50				100				150				50				100				150				50				100				150				50				100				150			
			90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360	90	180	270	360
2%	50	90																																														
		180	+																																													
		270	+	o																																												
		360	+	o	o																																											
	100	90	+	+	+	+																																										
		180	+	o	o	o	+																																									
		270	+	+	+	o	+	o																																								
		360	+	+	+	+	+	+	o																																							
	150	90	+	+	+	+	+	+	+	+																																						
		180	+	+	+	+	+	+	+	+	o																																					
		270	+	+	+	+	o	+	+	+	+	+																																				
		360	+	+	+	+	o	+	+	+	+	+	o																																			
5%	50	90	+	+	+	+	+	+	+	+	+	+	+	+																																		
		180	+	+	+	+	+	+	+	+	+	+	+	+	o																																	
		270	+	+	+	+	+	+	+	+	+	+	+	+	o	o																																
		360	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o																															
	100	90	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																														
		180	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																													
		270	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+																												
		360	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	o																											
	150	90	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+																										
		180	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																									
		270	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o																								
		360	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o																							
10%	50	90	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																						
		180	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																					
		270	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																				
		360	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																			
	100	90	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																		
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15%	50	90	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+										
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		360	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+	o							
	100	90	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+						
		180	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	+	+	+	+	+	o	+	+	+	+					
		270	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	+	+	+	+	+	o	+	+	+	+	o				
		360	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+	+	+	+	o	+	+	+	+	o	o			
	150	90	+	o	o	o	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+		
		180	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+	
		270	+	o	o	o	+	o	+	+	+	+	+	+	+	+	+	+	o	+	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	o	+	+	+	+	+	+	+	+	o	o
		360	+	o	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	+

+ = significantly different at α level of .05

o = non- significantly different at α level of .05

However, the mean formaldehyde-removal (%) values by using the different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations in this study were not homogeneity. So, the statistical analysis by ANOVA may be less than 95% of confidence. To confirm the statistical analysis results, the means of formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations were also analyzed by the nonparametric Kruskal-Wallis test of significant level at 0.05.

From the nonparametric statistical results, it confirmed the result of analysis of variance (ANOVA) that determined means of formaldehyde removal (%) at different percentages of TiO_2 added in acrylic paint and different initial formaldehyde concentrations was significantly different at a significant level of 0.05. These results are presented in the appendix F.

CHAPTER V
DISCUSSION

This study intended to determine the formaldehyde removals (%) in the static air chambers at different percentages of TiO_2 added in acrylic paint, different initial formaldehyde concentrations and at various irradiation times.

The comparisons were done by using the analysis of variance (ANOVA) and least significant difference method (LSD) at the significance level of 0.05 (α) for determining the multiple comparisons. The mean formaldehyde removals (%) were compared to determine the TiO_2 photodegradation efficiency in different conditions.

In overall results, the grand mean of formaldehyde removal (%) in this study was 28.81% and maximum was 60.08%. That result was less than the removal efficiency of related studies that the formaldehyde removals were up to 80% (3, 10, 34 and 45). The removal rate in this study was less than others may cause from the reason that the experiment in this study was set up in large 216 liters static air chamber which the removal rate depends on nature of reaction geometry (45). In dynamic chamber or air flow column experiments that most studies used, the organic pollutant can contact with TiO_2 catalyst more than the static air chamber experiment, so the removal rate in static process always was less than in dynamic chamber (32, 34).

Furthermore, the TiO_2 catalyst in this study was immobilized by the acrylic paint which was different from other studies that used pure TiO_2. It was possible that the removal rate in this study was less because the photodegradation depends on surface area, particle size of catalyst and thin film characteristic (14). In this study, the removal efficiency of catalytic photodegradation by using acrylic paint film immobilized may drop because the paint film may cover the surface layers of TiO_2. However, the overall means of formaldehyde removal in this study was 28.81% and nearly equal with the percent removal of NOx gases by using TiO_2-containing paint which Maggos Th. studied (16), his study was found that the TiO_2-containing paint can treated NOx gases for 20% approximately.

5.1 The effect of different percentages of TiO_2 added in acrylic paint on formaldehyde removal

From the results, the total means of formaldehyde removals (%) at 2%, 5%, 10% and 15% TiO_2 were 16.13, 26.60, 36.61 and 35.94 respectively. It showed that the formaldehyde removal (%) increased when the TiO_2 added in acrylic paint increased and slightly dropped at 15% TiO_2.

The increasing of formaldehyde removal (%) when TiO_2 increased was in agreement with the first hypothesis that the formaldehyde removal (%) increases when the percentage of TiO_2 added in acrylic paint increases. This phenomenon was explained by Poon C.S. study (14) who reported that the reaction rate for formaldehyde removal increased when the dosage of TiO_2 increased because the increasing TiO_2 is implied the increasing surface area and the photodegradation rate was positively related to surface area.

However, this study was found that the formaldehyde removal (%) at 15% TiO_2 was slightly lower than the formaldehyde removal (%) at 10% TiO_2. From this result, it showed that the formaldehyde removal rate did not always increase when increasing the amount of TiO_2 to highly, because of the reaction rate of photodegradation has the limit. From Juliana’s study (35), the oxidation process on the surface site of TiO_2 increased with increasing TiO_2 concentration until reached the saturated point. After that, the photodegradation rate was stable or decreased with increasing TiO_2 dosage.

According to the statistical analysis of variance, it was found that the result was in agreement with the first hypothesis, which the formaldehyde removal (%) increased when the percentage of TiO_2 added in acrylic paint increased at the significance level of 0.05 (α). However, the result of multiple comparisons for the significant pair between the different percentages of TiO_2 added in acrylic paint was found that the mean formaldehyde removals (%) of 10% and 15% TiO_2 added in acrylic paint was not different at α level 0.05 of significance. The multiple comparisons confirmed that the 10% TiO_2 was the optimal dosage for formaldehyde photodegradation in this study and 15% TiO_2 was the over dosage for photodegradation efficiency.

When considering the effect of the percentage of TiO_2 added in acrylic paint interacted with the initial formaldehyde concentration on the formaldehyde removal, it was found that the formaldehyde removals (%) by using 2% TiO_2 added in acrylic paint at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were lowest (24.55, 17.09 and 5.93% respectively) and the formaldehyde removals (%) increased when increasing the percentage of TiO_2 respectively. Except the formaldehyde removal (%) by using 15% TiO_2 at 50 mg/m^3 of initial formaldehyde concentration which dropped to 48.02% from 54.25% (at 10% TiO_2 using) whereas the formaldehyde removals (%) by using 15% TiO_2 at 100 and 150 mg/m^3 were slightly increased to 36.57 from 35.14 (at 10% TiO_2) and up to 23.23% from 22.04 (at 10% TiO_2) respectively.

Although the increasing of catalyst amount is the increasing of the surface area for organic oxidation, the proper limit of catalyst amount will decrease the photooxidation rate. From Carp’s study (28), his report showed the mass transfer resistance for both organic species and photogenerated electrons/holes would increase when increasing of catalyst amount. Therefore, it was possible that the formaldehyde removal (%) by using 15% TiO_2 was nearly stable because has more resistance for the mass transfer, the photodegradation rate would be inhibited. In case of the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration, it dropped whereas 100 and 150 mg/m^3 slightly increased, it possible that the photodegradation at the low formaldehyde concentration (50 mg/m^3) was proceeded to the transfer limit early than high initial formaldehyde concentration (100 and 150 mg/m^3) which the limit of this study was not over 360 min of irradiation time.

From the statistical analysis of variance, it was found that the interaction of the percentage of TiO_2 added and the initial formaldehyde concentration affected the formaldehyde removal (%) at the significance level of 0.05 (α). However, the multiple comparisons was found that the formaldehyde removal (%) by using 10% TiO_2 at 50 mg/m^3 greater than the formaldehyde removal (%) by using 15% TiO_2 at 50 mg/m^3 and both of percent removal were different at α level 0.05 of significance, whereas the formaldehyde removal (%) by using 15% TiO_2 at 100 and 150 mg/m^3 were not different with the formaldehyde removal (%) by using 10% TiO_2 at 100 and 150 mg/m^3 respectively. From this phenomenon, it showed that the photodegradation rate did not always increasing although the percentage of TiO_2 increased but it was depend on the concentration of initial formaldehyde. In case of highly pollutant concentration, the increasing percentage of TiO_2 was not useful. Therefore, this study was concluded that the optimum is the using of 10% TiO_2 at 50 mg/m^3 of initial formaldehyde concentration because of the formaldehyde removal at this point is the highest (54.25%).

When considering the effect of the percentage of TiO_2 added in acrylic paint interacted with the irradiation time to the formaldehyde removal, it was found that the formaldehyde removal (%) at 90 min of irradiation time increased when increasing the percentage of TiO_2, whereas the irradiation time at 180, 270 and 360 min, the formaldehyde removals (%) increased when increasing the percentage of TiO_2 added but decreased at 15% TiO_2. From this result, it agrees with the previous observation that the trend of formaldehyde removal (%) at 15% TiO_2 was stable or decreased because 15% TiO_2 might be over the optimum dosage. In Addition, this result was in agreement with Yang’s study (46), his study showed that the reaction rate of photodegradation did not depend on the catalyst amount that coated on media only but it concern with the irradiation light too. At the high catalyst amount and low irradiation light, the formaldehyde could not be degraded efficaciously.

From the statistical analysis of variance, it was found that the interaction of the percentage of TiO_2 added and the factor on irradiation time affected the formaldehyde removal (%) at the significance level of 0.05 (α). However, the multiple comparison of the interaction of the percentage of TiO_2 and the irradiation time to the formaldehyde removal (%) result confirmed the possibility of 15% TiO_2 was over the optimum dosage. Due to the multiple comparison results, the formaldehyde removal (%) by using 15% TiO_2 was non-significantly different when the irradiation finished. In addition, the formaldehyde removal (%) by using 15% TiO_2 at 90-360 min of irradiation times was non-significantly different with the formaldehyde removal (%) by using 10% TiO_2 at 90-360 min of irradiation times also. It was showed that the increasing irradiation time did not affect the increasing of formaldehyde removal only, but it also depended on the optimum dosage of TiO_2. Therefore, this study indicated that the optimum dosage is the using of 10% TiO_2 at 270 min of irradiation time, because the formaldehyde removal (%) at this dosage was highest (40.17%).

5.2 The effect of different initial formaldehyde concentrations on formaldehyde removal by using TiO_2 added in acrylic paint

From the study result, it was found that the overall means of formaldehyde removal (%) decreased when increasing the initial formaldehyde concentration which the formaldehyde removals (%) at 50, 100 and 150 mg/m^3 of initial formaldehyde concentration were 41.12, 28.99 and 16.33 respectively. This result was in agreement with the Jeong's study (32, 33) which found the effect of initial concentration on the degradation rate of organic pollutant in TiO_2 photodegradation process-the degradation rate decreased when the pollutant concentration rises. From Hong's (34) study, it was reported that the photodegradation of formaldehyde by used the combination of UV, TiO_2 and O_3 were decreased when the concentration of formaldehyde increased. Juliana's study (35) also reported that the TiO_2 photodegradation rate decreased significantly with the increase of initial organic pollutant concentration.

In the kinetic of the formaldehyde photocatalysis, the rate of formaldehyde decomposition is relatively high in the low formaldehyde concentration and quickly slows down in high formaldehyde concentration because the formaldehyde molecule reaches to the catalyst surface and the photooxidation can occur on it. At the low concentration, TiO_2 molecule is able to adsorb most of formaldehyde molecule. On the other hand, the process is inverted at higher concentration, formaldehyde molecule compete for the adsorption site. As a consequence, there is a decrease in the rate of photodegradation because the number of available active site is diminished for the reaction. It is difficult for high concentration to be adsorbed on photocatalytic surface, resulting photooxidation of high concentration was long time. From the reason is agreement with the research of Nogushi T. et al. (36), their explanation that the degradation rate depends on catalyst surface. The kinetic of TiO_2 surface has the mass transfer limited.

The analysis of variance showed the results for determining the effect of different initial formaldehyde concentration on formaldehyde removal (%) by using TiO_2 added in acrylic paint. It was found that the results were in agreement with the second hypothesis, which stated that the formaldehyde removal (%) at low initial formaldehyde concentration is higher than at high initial formaldehyde concentration at the significance level of 0.05 (α). From the multiple comparison of formaldehyde removal (%) at different initial formaldehyde concentration, it confirmed that the decreasing initial formaldehyde concentration affected the increasing of formaldehyde removal (%) because each pair was significant at 95% confidence. Therefore, this study indicated that the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration was highest (41.12%)

Considering the effect of the initial formaldehyde concentration interacted with the irradiation time on the formaldehyde removal, it was found that the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration increased when increasing the irradiation time whereas the formaldehyde removal (%) at 100 mg/m^3 increased until 180 min and decreased after that, and the formaldehyde removal (%) at 150 mg/m^3 increased until 270 min and decreased at 360 min of irradiation time. It was that because the formaldehyde photodegradation at higher concentration would proceed to the mass transfer limit early than at low initial formaldehyde concentration

(35). Thus, the formaldehyde removal (%) at 50 mg/m^3 of initial formaldehyde concentration continuously increased when increasing the irradiation time.

. The analysis of variance showed the results of interaction of the initial formaldehyde concentration and the irradiation time affected the formaldehyde removal at α level 0.05 of significance. However, from the multiple-comparison results, it was found that at the same percentage level of TiO_2 added, the formaldehyde removals (%) at various irradiation times were non-significantly different at the significance level of 0.05 (α). This result showed that the various irradiation times almost did not affect the formaldehyde removals (%) at the same percentage level of TiO_2 added but the role of the irradiation time would be raised when changing the initial formaldehyde concentration factor.

Therefore, this studied could be concluded that the optimum of initial formaldehyde concentration and irradiation time is 50 mg/m^3 of initial formaldehyde concentration and 270 min of irradiation time because the formaldehyde removal rate at this condition was higher and used shorter time than 360 min. Although the formaldehyde removal at 360 min was highest, the statistical result of the formaldehyde removals at 270 and 360 min of irradiation time were non-significantly difference.

5.3 The effect of various irradiation times on formaldehyde removal (%) by using TiO_2 added in acrylic paint.

From the study result, it was found that the overall means of the formaldehyde removal (%) slightly increased with increasing of irradiation times but slightly decreased at 360 min. The formaldehyde removal (%) increased when increasing of irradiation times was in agreement with Hong's research (34) which studied the effect of residence time on formaldehyde degradation by using TiO_2, UV and O_3 combination with flow reactor. The result showed that the degradation of formaldehyde increased along with prolonged residence time for both UV and TiO_2 processes. When short residence time (40 min), the degradation of formaldehyde was 33.33% and when longer residence time to 300 min, the formaldehyde degradation was achieved to 96.2%.

However, the trend of formaldehyde removals (%) at 180, 270 and 360 min of irradiation time was nearly stable (29.53, 30.49 and 30.13 respectively). It was possible that the formaldehyde photodegradation proceeded to mass transfer limit at 180 min of irradiation time. Nevertheless, from Alberici and Jardim's study (10), they explained about the photodegradation theory that the TiO_2 catalyst used many times for processing the oxidation reaction. At the beginning time, the photodegradation was in progress and pollutant molecules were not yet adsorbed on TiO_2 surface. So the pollutant removal in first stage would be low. When the irradiation time finished, the pollutant adsorbed on TiO_2 surface increase. Thus, the pollutant removal in the middle stage is high. When the last time, the pollutant was adsorbed till not available surface for adsorb. So, the pollutant removal in last stage was stable. Thus, the result of formaldehyde removal (%) in this study was in agreement with this theory because the formaldehyde removal (%) was lower at the first stage of irradiation (90 min), then the removal rate (mg of pollutant removal/min) was higher at the middle stage (180-270 min) and at the last stage (360 min), the formaldehyde removal (%) dropped.

The analysis of variance showed the results for determining the effect of various irradiation times on formaldehyde removal (%) by using TiO_2 added in acrylic paint. It was found that the formaldehyde removal (%) at various irradiation times were significantly different at 95% confidence. Therefore, the results of multiple comparisons were found that formaldehyde removal (%) at 90 min of irradiation time was significantly different with 180, 270 and 360 min of irradiation time, and the formaldehyde removal (%) at 180 min was significantly different with 270 min whereas the formaldehyde removal (%) at 180 and 270 min was not significantly different with 360 min. Thus, the result showed that it did not exactly agree with the third hypothesis which stated that trend of formaldehyde removal (%) was positive relation for the irradiation times, but the formaldehyde removal (%) increased until 270 min and dropped at 360 min of irradiation time. However, from the multiple-comparison result that they confirmed to the possibility of the photodegradation theory, that the 90 min was the first stage, 180-270 min was the middle stage and at 360 min of irradiation time was the last stage. Therefore, this studied could be concluded that the greatest irradiation time was 180 min because this time was the shortest time for formaldehyde removal efficiency.

5.4 The interaction effect of the percentage of TiO_2 added, initial formaldehyde concentration and irradiation time on the formaldehyde removal (%)

The analysis of variance showed the results for determining the interaction effect of the percentage of TiO_2 added in acrylic paint, initial formaldehyde concentration and irradiation time on the formaldehyde removals (%), that were significantly different at 95% confidence. It was concluded that among percentages of TiO_2 added, initial formaldehyde concentrations and irradiation times were interaction affect the formaldehyde removal (%). This result agreed with the fourth hypothesis and the catalyst photodegradation theory that the amount of catalysts, pollutant concentration and irradiation time were the operation parameter aspect for the pollutant oxidation, which was in agreement with Carp's research (28) who concluded the photoinduced reactivity of TiO_2.

From the result of multiple comparisons showed that the formaldehyde removals (%) at various irradiation times was almost non-significant different when the same percentage of TiO_2 added and initial formaldehyde concentration level, except at using of 10% TiO_2 added with 50 mg/m^3 of initial concentration. The reason may be that the amount of TiO_2 at 2% and 5% were not enough surface size for achieving formaldehyde degradation, so the photodegradation reaction proceeded to mass transfer limit early than 90 min. In addition, the formaldehyde removals (%) by using 15% TiO_2 added at 100 and 150 mg/m^3 initial formaldehyde concentration were the same as using 2% and 5% TiO_2 adding also. Although the surface size of TiO_2 at 15% is more enough for achieving the formaldehyde degradation, it was possible that 15% TiO_2 was over optimal dosage, which was the reason of increasing the mass transfer resistance.

In this study, it may be concluded that the initial formaldehyde concentration is the first considered factor that affected the formaldehyde degradation because the TiO_2 added in acrylic paint could not degrade the formaldehyde in high initial concentrations although more using amount of TiO_2. The next is the factor on percentage of TiO_2 added in acrylic paint because the amount of TiO_2 relates to the surface size for photooxidation process. The last affecting factor is the irradiation time, in this study, the irradiation time factor slightly affected the removal rate when it interacted with the percentage of TiO_2 adding and initial formaldehyde concentration because the removal rate were almost stable at various irradiation times. But it was possible that the photooxidation process may proceed to mass transfer limit earlier than 90-180 min of irradiation time. Thus, when the irradiation time finished, the formaldehyde removals (%) would not significantly increase. Therefore, the result of this study recommended the using of 10% TiO_2 adding in acrylic paint at 50 mg/m^3 of initial concentration and 360 min of irradiation time because the formaldehyde removal (%) in this condition was highest (60.08%).

CHAPTER VI

CONCLUSION AND RECOMMENDATION

This research studied the effect of three influencing factors in formaldehyde photodegradation by using TiO_2 added in acrylic paint. Those factors were the percentage of TiO_2 added in acrylic paint, initial formaldehyde concentration and irradiation time. The conclusions and recommendations of this research were described as follows.

6.1 Conclusion

In this research, it was found that the TiO_2 added in acrylic paint treated the formaldehyde in air chamber for 2.11-60.08% which the removal efficiency depended on the levels of influencing factors.

6.1.1 The effect of different percentages of TiO_2 added in acrylic paint on formaldehyde removal

In this research, the percentage of TiO_2 added in acrylic paint had the effect on the formaldehyde removal (%). Similar to other researches, it was found the percentage of catalyst (TiO_2) was an influencing factor of photodegradation rate. However, this research indicated that the formaldehyde removals (%) of 10% and 15% TiO_2 added in acrylic paint were not different. Moreover, the formaldehyde removal (%) of 10% TiO_2 was highest (36.61%).

6.1.2 The effect of different initial formaldehyde concentrations on formaldehyde removal by using TiO_2 added in acrylic paint

In this research, the initial formaldehyde concentrations had the effect on formaldehyde removal (%). The photodegradation rate (formaldehyde removal) decreased when increasing the initial formaldehyde concentration. Similar to other researches, it was found the initial formaldehyde concentration was an influencing factor of photodegradation rate.

6.1.3 The effect of various irradiation times on formaldehyde removal (%) by using TiO_2 added in acrylic paint

In this research, the irradiation times had the effect on formaldehyde removal (%). The formaldehyde removal (%) increased when increasing of irradiation times, which was in agreement with the other researches that the irradiation time was an influencing factor of photodegradation rate. However, this research was found that the formaldehyde removals (%) ran to the middle stage after 180 min of irradiation time. Thus, the formaldehyde removals (%) at 180, 270 and 360 min was nearly stable.

6.1.4 The interaction effect of the percentage of TiO_2 added, initial formaldehyde concentration and irradiation time on the formaldehyde removal (%)

In this research, it was found that the percentage of TiO_2 added, initial formaldehyde concentration and irradiation time had the effect on the formaldehyde removal (%), which was in agreement with the catalyst photodegradation theory.

This research indicated that the photodegradation rate did not always increase although the percentage of TiO_2 increased but it depend on the initial formaldehyde concentration. At high formaldehyde concentration, the increasing percentage of TiO_2 overmuch was not useful. Thus, considering of initial pollutant concentration was necessary when using of TiO_2 photodegradation. In addition, the irradiation time was an influencing factor concerned. At the same of irradiation time level, higher percentage of TiO_2 or lower initial formaldehyde concentration level had greater formaldehyde removal (%). However, at higher initial formaldehyde concentration, the formaldehyde removal (%) decreased early than at lower initial formaldehyde concentration. Therefore, the research recommended the using of 10% TiO_2 adding in acrylic paint at 50 mg/m^3 of initial concentration and 360 min of irradiation time because the formaldehyde removal (%) in this condition was highest.

6.2 Recommendation

6.2.1 Recommendation of research methodology

The analysis of formaldehyde concentration in this research used the chromotropic acid method which has some restrictions such as uncomfortable sampling and analysis when comparing with the gas chromatography analysis, as well as slightly lower accuracy.

6.2.2 Recommendations for the further study

For further study about the photodegradation by using TiO_2 added in acrylic paint, the following aspects were recommended for further investigation:

1. The formaldehyde removal (%) by using TiO_2 added in acrylic paint should be applied to real situation. It can be studied in closed room or air controllable room.
2. In this study, the TiO_2 catalyst was immobilized by the acrylic paint, which was different from using the pure TiO_2. Thus, the mechanism or structure of TiO_2-acrylic paint thin film should be studied for comparing with pure TiO_2 structure.
3. The light intensity is also a significant influencing factor of photodegradation process which was not studied in this research. Thus, the further study should be studied the effect of different light intensity on the pollutant photodegradation rate.

6.2.3 Recommendation for research application

This research aimed to study the application of TiO_2 to treat formaldehyde for easier and compatible use in indoor air or workplace. So this research result is the guidance for treating formaldehyde, which the result showed the adding 10% TiO_2 into acrylic paint is the highest efficiency. Furthermore, the initial formaldehyde concentration is the important influencing factor for using TiO_2 added in acrylic paint. Thus, the initial formaldehyde concentration would be estimated before the using of TiO_2 added in acrylic paint and initial formaldehyde concentration was not more than the limit of TiO_2 percentage (at 50 mg/m^3 of initial formaldehyde concentration, 10% TiO_2 can remove the formaldehyde up to 60% in 360 min).

REFERENCES

1. Wang S, Ang H.M., Moses O. T. Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. Environment International. 2007; 33(5): 694-705.

2. Roberts J, Nelson W.C. National Human Activity Pattern Survey Data Base. USEPA. Research Triangle Park. 1995.

3. Zhao J, Yang X. Photocatalytic oxidation for indoor air purification: a literature review. Building and Environment. 2003; 38(5): 645-654.

4. Zou L, Luo Y, Hooper M, Eric H. Removal of VOCs by Photocatalysis process using adsorption enchanced TiO_2-SiO_2 catalyst. Chemical Engineering and processing. 2006; 45(11): 959-964.

5. World Health Organization. Formaldehyde, Environmental health criteria 89. 1989.

6. NIOSH. Pocket Guild to Chemical Hazards, Formaldehyde [Online]. Available from www.cdc.gov/niosh/npg/npgd0293.html [Accessed 2007 July 28].

7. ประกาศกระทรวงมหาดไทย, เรื่องความปลอดภัยในการทำงานเกี่ยวกับภาวะแวดล้อม (สารเคมี), ตารางหมายเลข 3, 2520

8. Jiao Z, Luo P, Wu Y, Ding S, Zhang Z. Absorption of lean formaldehyde from air with Na_2SO_3 solution. Journal of Hazardous Materials. 2006; 134(1-3): 176-182.

9. Vicki H.G. Environmental catalysis. Boca Raton (USA): Taylor & Francis. 2005.

10. Alberici R.M, Jardim W.F. Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide. Applied Catalysis. 1997; 14(1-2): 55-68.

11. Huili Y, Zhang K, Rossi C. Theoretical study on photocatalytic oxidation of VOCs using nano-TiO_2 photocatalyst. Journal of Photochemistry and Photobiology. 2007; 188(1, 30): 65-73

12. Luo Y, Ollis D.F. Heterogenous Photocatalytic Oxidation of Trichloroethylene and Toluene Mixtures in Air: Kinetic Promotion and Inhibition. Time-Dependent Catalyst Activity. Journal of catalyst; 1996.
13. Maggos Th, Kotzias D. et al. Investigations of TiO_2-containing construction meterials for decomposition of NOx in environmental chamber; 2005.
14. Poon C.S, Cheung E. NO removal efficiency of photocatalytic paving blocks prepared with recycled materials. Construction and Building Materials. 2007; 22(8): 1746-1753.
15. Guo M.Z, Zhen X.C, Chen H, Guo W.L, Miao T. Study on photocatalytic degradation of several volatile organic compounds. Journal of hazardous materials. 2006; 128(1-3): 158-163.
16. Maggos Th., Bartzis J.G., Liakou M, Gobin C. Photocatalytic degradation of NOx gases using TiO_2-containing paint: A real study. Journal of hazardous materials. 2007; 146(3): 668-673.
17. Ratchata Titayanurak. Degradation of Formaldehyde by UV/TiO_2 Process. Chulalongkorn University; 2003.
18. Guarino M, Costa A, Porro M. Photocatalytic TiO_2 coating-to reduce ammonia and greenhouse gases concentration and emission from animal husbandries. Bioresource Technology. 2007.
19. Clark R.J.H. The Chemistry of Titanium and Vanadium. Elsevier; 1968.
20. Pollution Control Department. Material Safety Data Sheet (MSDS). Titanium dioxide [Online]. Available from msds.pcd.go.th/searchName.asp?vID=1421 [Accessed 2007 July 28].
21. Imperial supplies LLC. Material Safety Data Sheet (MSDS 7611) [Online]. Available from http://www.imperialinc.com/msds0076160.shtml [Accessed 2008 Oct 29].
22. Chamnan Randorn. Study of the Chemical Properties of Titanium Dioxide. Prince of Songkla University; 2001.
23. Wissanu Choychangtong. Synthesis and Characterization of Titanium Dioxide. Prince of Songkla University; 2004.
24. Ulrike D. The surface science of titanium dioxide. Surface Science Reports. 2003; 48(5-8): 53-229.

25. Degussa Technical Bulletin No 56. Aluminum oxide, Titanium dioxide P25 Two highly dispersed metallic oxide from Dugussa Produced by the AEROSIL Process; 1982.

26. Sudarat Jitrapattarasakul. TiO_2 Thin Film Preparation Using Diethanolamine in Sol-Gel Process for Chromium (VI) Removal from wastewater; 2004.

27. Ávila P, Sánchez B, Cardona A.I, Rebollar M, Candal R. Influence of the method of TiO_2 incorporation in monolithic catalysts for photocatalytic destruction of chlorinated hydrocarbons in gas phase. Catalyst Today. 2002; 76(2-4): 271-278.

28. Carp O, Huisman G.L, Reller A. Photoinduced reactivity of titanium dioxide. Progress in Solid State Chemistry. 2004; 32(1-2): 33-177.

29. Ao C.H, Lee S.C, Mak C.L, Zou S.C. Inhibition effect of SO_2 on NOx and VOCs during the Photodegradation of synchronous indoor air pollutants at part per billion (ppb) level by TiO_2. Applied Catalysis. 2004; 49(3): 187-193.

30. Kulas J, Rousar I, Krysa J. Photocatalytic degradation rate of oxalic acid on the semiconductive layer of n-TiO_2 particles in the batch mode plate reactor Part1: Mass transfer limits. Journal of applied electrochemistry; 1998.

31. Rungnuch Tharathonpisutthikul. Photocatalytic degradation of 4-chlorophenol using Pt/TiO_2-SiO_2 prepared by the sol-gel method; 2520.

32. Jeong J.Y, Kazuhiko S.G, Kazuhiko S. Photochemical and photocatalytic degradation of gaseous toluene using short-wavelength UV irradiation with TiO_2 catalyst: comparison of three UV sources. Chemosphere. 2004; 57(7): 663-671.

33. Jeong J., Sekiguchi K., Lee W., Sakamoto K. Photodegradation of gaseous volatile organic compounds (VOC_S) using TiO_2 photoirradiated by an ozone-producting UV lamp: decomposition characteristics, identification of by-products and water-soluble organic intermediates. Journal of Photochemistry and Photobiology. 2004; 169: 279-287.

34. Hong Q, Zhi S.D., Qing C.G. Formaldehyde degradation by UV/TiO_2/O_3 process Using continuous flow mode. Journal of Environmental Sciences. 2007; 19:1136-1140.

35. Juliana C.G., Keiko T. Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide. Journal of Photochemistry and Photobiology. 2002; 155: 215-222.

36. Nogushi T, Fujishima A, Sawunytama P, Hashimoto K, Phocatalytic degradation of gaseous formaldehyde using TiO_2 film. Environmental Science and Technology. 1998; 32: 3831-3833.

37. Ching W.H., Leung M, Leung D. Solar photocatalytic degradation of gaseous formaldehyde by sol–gel TiO_2 thin film for enhancement of indoor air quality. Solar Energy. 2004; 77(2): 129-135.

38. Norman S.A, Edge M, Ortega A et al. Degradation and stabilization of polymers and coatings: nano versus pigmentary Titania particle. Polymer Degradation and Stability. 2004; 85(3): 927-946.

39. Ao C.H., Lee S.C, Yu J.Z, Xu J.H. Photodegradation of formaldehyde by Photocatalyst TiO_2: effects on the presences of NO, SO_2 and VOCs. Applied Catalysis. 2004; 54(1): 41-50.

40. Sukhothai Thammathirat Open University. Fundamentals of industrial hygiene**;** 1990.

41. NIOSH. Manual of Analytical Methods for formaldehyde by VIS. 4th ed; 1994.

42. NIOSH. Manual of Analytical Methods for formaldehyde by HPLC. 2nd ed; 2003.

43. Kanlaya V. The using SPSS for windows in data analysis. Chulalongkorn University. 2003.

44. Robert H. Handbook of univariate and multivariate data analysis and interpretation with SPSS. Chapman & Hall/CRC. 2006.

45. Liu T.X., Li F.B., Li X.Z. TiO_2 hydrosols with high activity for photocatalytlc Degradation of formaldehyde in gaseous phase. Journal of Hazardous Materials. 2007; 152: 347-355.

46. Yang L.P., Liu Z., Shi J., Hu H., Shanggurn W. Design consideration of photocatalytic oxidation reactor using TiO_2-coated from nickels for degrading indoor gaseous formaldehyde. Catalyst Today. 2007; 126: 359-368.

47. Strini A, Cassese S, Schiavi L. Measurement of benzene, toluene, ethylbenzene and o-xylene gas phase Photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor. Applied Catalysis. 2005; 61(1-2): 90-97.
48. Ao C.H., Lee S.C., Mak C.L., Chan L.Y.. Photodegradation of volatile organic compounds (VOCs) and NO for indoor air purification using TiO_2: Promotion versus inhibition effect of NO. Applied Catalysis. 2003; 42(2): 119-129.
49. Jo W.K, Park K.H. Heterogeneous photocatalysis of aromatic and chlorinate volatile organic compounds (VOCs) for non-occupational indoor air application. Chemosphere. 2004; 57(7): 555-565.
50. Suchart Sriplienchun. Study of the efficiency of a formaldehyde gas sampler modified by using available domestic materials. [M.S. thesis in Occupational Health] Bangkok: Faculty of Graduate Studies, Mahidol university; 1989.
51. Kandavelu V., Kastien H., Thampi K.R. Photocatalytic degradation of isothiazolin-3-ones in water and emulsion paints containing nanocrystalline TiO_2 and ZnO catalysts. Applied Catalysis. 2003; 48: 101-111.

APPENDIX

APPENDIX A

Example of calculating the formaldehyde concentration in the static air chamber

Prepare 50 mg/m^3 formaldehyde concentration in the 216 L static air chamber (determines temperature 28^{o}C, at atmosphere 756 mm/Hg, molecular weight of formaldehyde is 30.03 g/mol and density of formaldehyde is 0.8153 g/cm^3)

From $$\overline{V} = 24.47\left(\frac{760}{p}\right)\left(\frac{t+273.2}{298.2}\right)$$

$$\overline{V} = 24.47\left(\frac{760}{756}\right)\left(\frac{28+273.2}{298.2}\right)$$

$$\overline{V} = 24.84$$

From $$mg/m^3 = \frac{ppm \times M.W.}{22.4}$$

$$50 = \frac{ppm \times 30.03}{22.4}$$

$$ppm = 37.3$$

From $$ppm = \frac{10^6 w / M.W.}{V/\overline{V}}$$

$$w = \frac{37.3 \times 216 \times 30.03}{24.84 \times 10^6}\ \mathrm{g}$$

$$w = \frac{241945.7}{24.84 \times 10^6} = \frac{9740.16}{10^6} = 0.00974g$$

$$= \frac{0.00974}{0.8153}\ \mathrm{g}$$

$$= 0.0119\ \mathrm{ml} \ \approx 12\ \mu\mathrm{l}$$

Then add 12 µl formaldehyde by micropipette into the static air chamber for prepare 50 mg/m^3 initial formaldehyde concentration.

APPENDIX B

Example of changing the formaldehyde concentration data to the reference condition (temperature at 25 ^{O}C and atmospheric pressure 760 mmHg)

Change formaldehyde concentration from 100 mg/m^3 at 29 ^{o}C and atmospheric pressure 759 mmHg to concentration at reference condition (temperature at 25 ^{o}C and atmospheric pressure 760 mmHg)

From
$$\frac{C_1 \cdot V_1}{T_1} = \frac{C_2 \cdot V_2}{T_2}$$

$$\frac{100 \times 759}{29} = \frac{C_2 \times 760}{25}$$

So
$$C_2 = \frac{100 \times 759 \times 25}{29 \times 760}$$

$$C_2 = 86.09$$

Then formaldehyde concentration at reference condition is 86.09 mg/m^3

APPENDIX C

The data of experiment

Table A The formaldehyde concentration at different percentage of TiO_2 added in acrylic paint, initial formaldehyde concentration and irradiation time

Percentage of TiO_2 added in acrylic paint			2 %			5 %		
Initial formaldehyde concentration (mg/m^3)			50	100	150	50	100	150
Irradiation times	0 min	Control	49.55	96.25	147.96	49.01	98.47	149.38
		Rep. 1	48.68	98.62	153.38	51.37	103.46	146.11
		Rep. 2	48.18	101.79	146.59	52.19	101.39	147.04
		Rep. 3	50.92	97.57	147.54	48.50	97.29	146.29
		$\overline{X}$	49.26	99.33	149.17	50.69	100.71	146.48
	90 min	Control	44.09	82.43	107.20	41.89	93.00	118.69
		Rep. 1	30.24	74.79	106.03	25.10	68.48	94.22
		Rep. 2	28.36	76.37	105.08	26.76	67.47	92.35
		Rep. 3	29.56	73.21	103.60	23.63	69.66	90.86
		$\overline{X}$	29.39	74.79	104.90	25.16	68.54	92.48
	180 min	Control	38.28	77.82	96.15	39.40	85.56	105.90
		Rep. 1	27.85	60.99	95.83	21.82	54.54	85.82
		Rep. 2	26.31	58.50	91.19	23.45	54.28	82.74
		Rep. 3	27.67	56.13	90.77	21.15	54.70	83.02
		$\overline{X}$	27.28	58.54	92.60	22.14	54.51	83.86
	270 min	Control	37.02	69.29	78.37	37.97	76.24	96.93
		Rep. 1	25.93	53.41	71.09	19.90	50.83	78.35
		Rep. 2	24.39	51.18	64.02	20.97	51.00	73.12
		Rep. 3	25.25	48.29	60.22	18.62	52.93	75.45
		$\overline{X}$	25.19	50.96	65.11	19.83	51.59	75.64
	360 min	Control	33.59	63.54	69.08	36.85	73.00	91.51
		Rep. 1	24.52	49.10	58.11	17.60	49.53	73.51
		Rep. 2	23.16	47.69	55.05	19.24	44.57	67.89
		Rep. 3	24.30	44.28	54.00	16.94	49.20	69.38
		$\overline{X}$	23.99	47.02	55.72	17.93	47.77	70.26

Table A (continued) The formaldehyde concentration at different percentage of TiO_2 added in acrylic paint, initial formaldehyde concentration and irradiation time

Percentage of TiO_2 added in acrylic paint			10 %			15 %		
Initial formaldehyde concentration (mg/m^3)			50	100	150	50	100	150
Irradiation times	0 min	Control	50.81	99.62	146.43	49.33	98.88	151.33
		Rep. 1	51.89	101.76	147.95	49.69	98.62	148.67
		Rep. 2	47.75	101.25	144.23	49.07	99.65	147.16
		Rep. 3	48.48	99.19	149.20	49.23	97.85	145.92
		$\overline{X}$	49.37	100.73	147.13	49.33	98.71	147.25
	90 min	Control	46.18	92.50	108.10	41.74	94.44	116.34
		Rep. 1	22.90	63.44	90.41	23.59	60.20	80.31
		Rep. 2	21.59	62.92	94.91	21.56	61.82	82.01
		Rep. 3	22.27	62.50	96.63	22.91	61.14	77.94
		$\overline{X}$	22.25	62.95	93.98	22.69	61.05	80.09
	180 min	Control	43.88	36.21	99.33	40.63	87.87	106.69
		Rep. 1	17.36	52.46	64.69	18.43	50.21	67.58
		Rep. 2	15.43	51.44	59.25	16.72	51.49	65.03
		Rep. 3	15.95	49.30	63.64	17.60	51.06	63.99
		$\overline{X}$	16.25	51.07	62.53	17.58	50.92	65.53
	270 min	Control	42.49	79.42	89.60	39.15	81.12	98.35
		Rep. 1	14.46	46.74	50.57	14.24	43.63	60.57
		Rep. 2	12.32	45.29	47.17	12.01	44.31	60.76
		Rep. 3	11.74	43.67	48.66	12.94	44.83	60.10
		$\overline{X}$	12.84	45.23	48.80	13.06	44.26	60.48
	360 min	Control	41.30	73.79	84.30	38.23	74.68	91.66
		Rep. 1	10.78	42.56	49.25	12.91	36.99	59.63
		Rep. 2	10.20	41.45	48.01	10.54	36.31	59.24
		Rep. 3	10.41	39.66	47.05	11.57	37.42	58.02
		$\overline{X}$	10.46	41.22	48.10	11.67	36.91	58.96

APPENDIX D

The statistical analysis of variance (ANOVA)

Table B The result of analysis of variance.

Dependent variable: the formaldehyde removal (%)

Source	Type III Sum of squares	df	Mean square	F	Sig.
Corrected Model	27732.385(a)	47	590.051	226.971	.000
Intercept	119556.893	1	119556.893	45989.108	.000
TiO_2(b)	9996.450	3	3332.150	1281.755	.000
Initial(c)	14743.206	2	7371.603	2835.583	.000
Time(d)	679.329	3	226.443	87.104	.000
TiO_2 * Initial	834.134	6	139.022	53.477	.000
TiO_2 * Time	422.421	9	46.936	18.054	.000
Initial * Time	194.097	6	32.349	12.444	.000
TiO_2 * Initial * Time	862.748	18	47.930	18.437	.000
Error	249.569	96	2.600		
Total	147538.847	144			
Corrected Total	27981.954	143			

(a) R Squared = .991 (Adjusted R Squared = .987)

(b) TiO_2 is percentage of TiO_2 added in acrylic paint.

(c) Initial is initial formaldehyde concentration.

(d) Time is irradiation time.

APPENDIX E

The statistical analysis of multiple comparisons

Table C The multiple comparison of formaldehyde removal (%) at the difference the percentage of TiO_2 added in acrylic paint.

Dependent variable: the formaldehyde removal (%)

[I]TiO_2	[J]TiO_2	Mean Difference [I-J]	Std. Error	Sig.	95% confidence interval	
					Lower bound	Upper bound
2%	5%	-10.4536*	.38003	.000	-11.2080	-9.6992
	10%	-20.4903*	.38003	.000	-21.2446	-19.7359
	15%	-19.8142*	.38003	.000	-20.5716	-19.0629
5%	2%	10.4536*	.38003	.000	9.6992	11.2080
	10%	-10.0367*	.38003	.000	-10.7910	-9.2823
	15%	-9.3636*	.38003	.000	-10.1180	-8.6092
10%	2%	20.4903*	.38003	.000	19.7359	21.2446
	5%	10.0367*	.38003	.000	9.2823	10.7910
	15%	.6731	.38003	.080	-.0813	1.4274
15%	2%	19.8172*	.38003	.000	19.0629	20.5716
	5%	9.3636*	.38003	.000	8.6092	10.1180
	10%	-.6731	.38003	.080	-1.4274	.0813

*, The mean difference is significant at 0.05 level.

TiO_2, the percentage of TiO_2 added in acrylic paint.

Table D The multiple comparison of formaldehyde removal (%) by used TiO_2 added in acrylic paint at different initial formaldehyde concentration.

Dependent variable: the formaldehyde removal (%)

[I]Initial	[J]Initial	Mean Difference [I-J]	Std. Error	Sig.	95% confidence interval	
					Lower bound	Upper bound
50	100	12.1219*	.32912	.000	11.4686	12.7752
	150	24.7831*	.32912	.000	24.1298	25.4364
100	50	-12.1219*	. 32912	.000	-12.7752	-11.4686
	150	12.6612*	. 32912	.000	12.0080	13.3145
150	50	-24.7831*	. 32912	.000	-25.4364	-24.1298
	100	-12.6612*	. 32912	.000	-13.3145	-12.0080

*, The mean difference is significant at 0.05 level.

Initial, the initial formaldehyde concentration (mg/m^3).

Table E The multiple comparison of formaldehyde removal (%) by used TiO_2 added in acrylic paint at variance irradiation time.

Dependent variable: the formaldehyde removal (%)

[I]Time	[J]Time	Mean Difference [I-J]	Std. Error	Sig.	95% confidence interval	
					Lower bound	Upper bound
90	180	-4.4253*	.38003	.000	-5.1796	-3.6709
	270	-5.3936*	.38003	.000	-6.1480	-4.6392
	360	-5.0367*	.38003	.000	-5.7910	-4.2823
180	90	4.4253*	.38003	.000	3.6709	5.1796
	270	-.9683*	.38003	.012	-1.7227	-.2140
	360	-.6114	.38003	.111	-1.3658	.1430
270	90	5.3936*	.38003	.000	4.6392	6.1480
	180	.9683*	.38003	.012	.2140	1.7227
	360	.3569	.38003	.350	-.3974	1.1113
360	90	5.0367*	.38003	.000	4.2823	5.7910
	180	.6114	.38003	.111	-.1430	1.3658
	270	-.3569	.38003	.350	-1.1113	.3974

*, The mean difference is significant at 0.05 level.

Time, irradiation time (min).

APPENDIX F

The statistical of analysis of non-parametric Kruskal-Wallis

Table F The statistical analysis of the formaldehyde removal (%) for the different percentage of TiO_2 added in acrylic paint

percentage of TiO_2 added in acrylic paint	mean percentage of the formaldehyde removal (%)	S.D.	n.	χ^2	d.f.	P-value
2%	16.13	8.77	36	52.768	3	<0.000
5%	26.6	10.12	36			
10%	36.61	14.57	36			
15%	35.94	11.03	36			

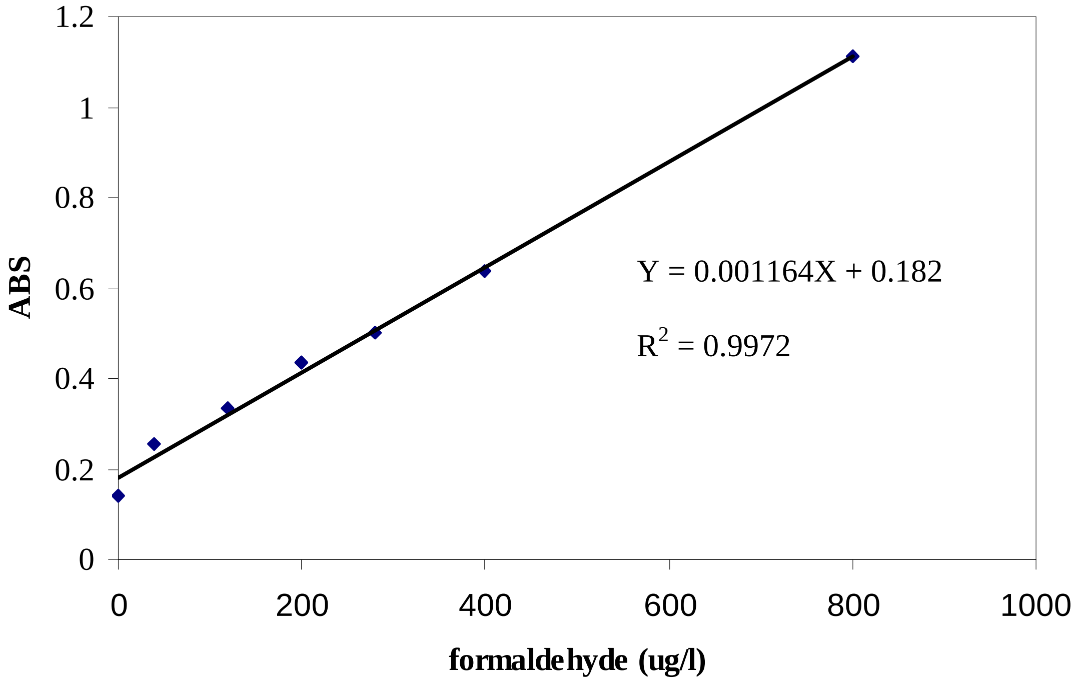
Table G The statistical analysis of the formaldehyde removal (%) for the different initial formaldehyde concentration

initial formaldehyde concentration	mean percentage of the formaldehyde removal (%)	S.D.	n.	χ^2	d.f.	P-value
50 mg/m^3	41.12	12.27	48	74.507	2	<0.000
100 mg/m^3	28.99	7.93	48			
150 mg/m^3	16.33	8.25	48			

APPENDIX G

Standard Curve for the Analysis of Formaldehyde

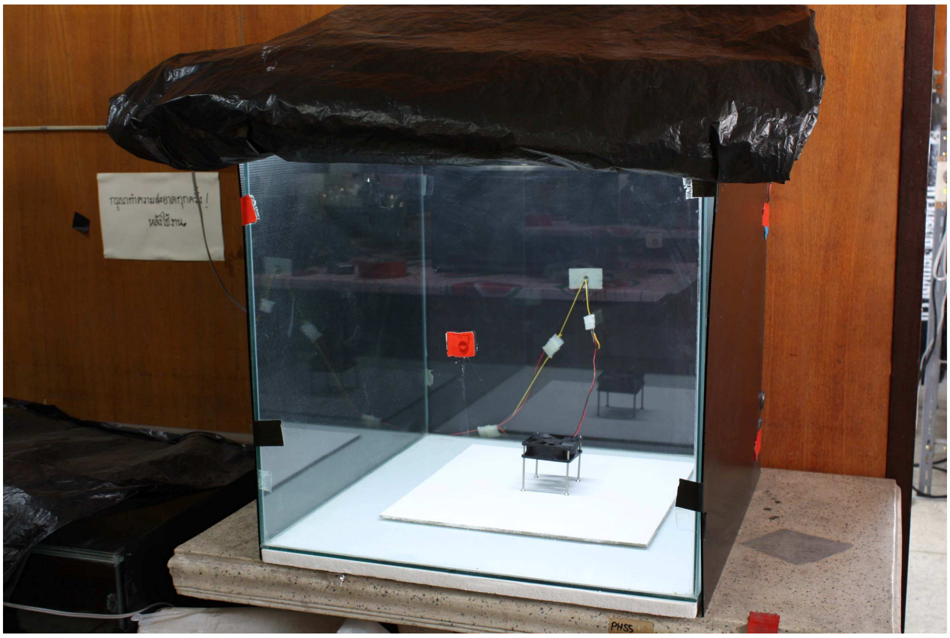
Concentration (microgram)	0	40	120	200	280	400	800
ABS	0.1395	0.2561	0.3335	0.4366	0.5015	0.6354	1.1129



APPENDIX H

RESEARCH EXPERIMENT

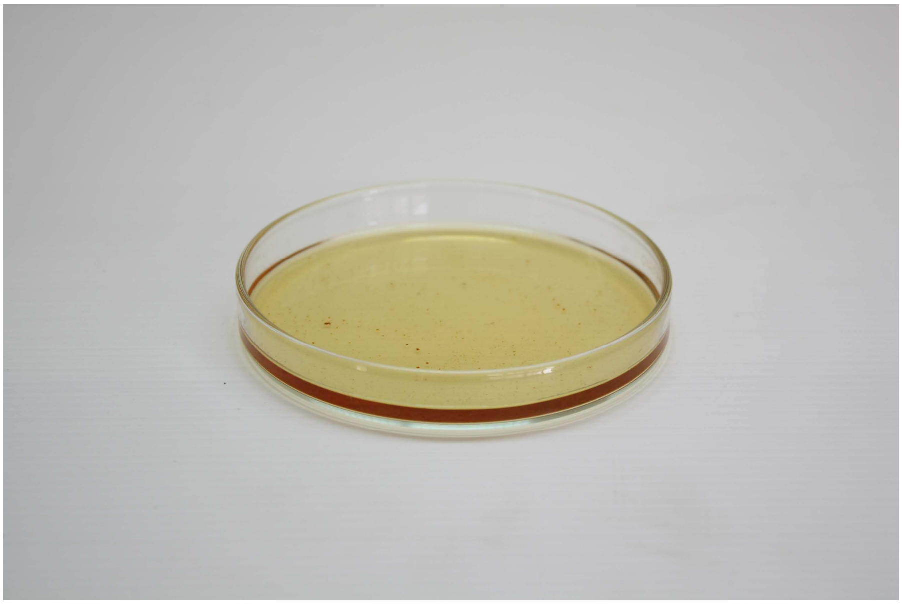
1. Static air chamber



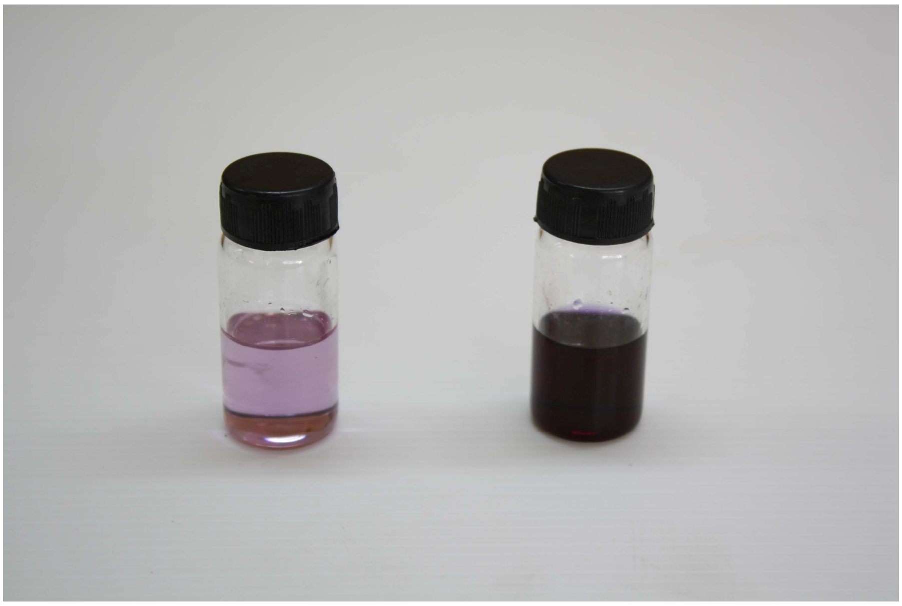
2. Impingers


ESCORT ELF® Pump
LOW
BATT
FLOW
FAULT
RUN
HOLD
SAMPLE
FLOW — TIME
RUN/
HOLD

3. The Developing color of chromotropic acid method



1% chromotropic acid



Developing color when added 6 ml conc. H_2SO_4

- Color in low formaldehyde concentration (left)

- Color in high formaldehyde concentration (right)

BIOGRAPHY

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