การสลายพาราควอทด้วยปฏิกิริยาโฟโตแคทไลติกส์บน TiO_2/RH-SiO_2

นางสาวนวพร กาญจนศิรานนท์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2553

PHOTOCATALYTIC DEGRADATION OF PARAQUAT USING TiO_2/RH-SiO_2

Miss Navaporn Kanjanasiranont

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2010

Thesis Title PHOTOCATALYTIC DEGRADATION OF PARAQUAT USING TiO_2/RH-SiO_2
By Miss Navaporn Kanjanasiranont
Field of Study Environmental Management
Thesis Advisor Associate Professor Nurak Grisdanurak, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………………Dean of the Graduate School
(Associate Professor Pornpote Piumsomboon, Ph.D.)

THESIS COMMITTEE

……………………………………………Chairman
(Assistant Professor Chantra Tongcompou, Ph.D.)

……………………………………………Thesis Advisor
(Associate Professor Nuruk Grisdanuruk, Ph.D.)

……………………………………………Examiner
(Associate Professor Jin Anotai, Ph.D.)

……………………………………………Examiner
(Patiparn Punyapalakul, Ph.D.)

……………………………………………External Examiner
(Pongtanawat Khemthong, Ph.D.)

นวพร กาญจนศิรานนท์ : การสลายพาราควอทด้วยปฏิกิริยาโฟโตแคทไลติกส์บน $TiO_2/RH-SiO_2$. (PHOTOCATALYTIC DEGRADATION OF PARAQUAT USING $TiO_2/RH-SiO_2$.) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร. นุรักษ์ กฤษดานุรักษ์, 59 หน้า.

ตัวเร่งปฏิกิริยาไทเทเนียมไดออกไซด์ซึ่งใช้ซิลิกาที่สกัดได้จากแกลบข้าวเป็นตัวรองรับ ($TiO_2/RH-SiO_2$) ถูกเตรียมด้วยวิธีเอิบชุ่ม จากการคัลไซน์สารที่อุณหภูมิ 500 องศาเซลเซียสเป็นเวลา 5 ชั่วโมงทำให้ได้ตัวเร่งปฏิกิริยาที่ประกอบด้วยไทเทเนียมไดออกไซด์เฟสอนาเทสและซิลิกาอะมอร์ฟัส สำหรับประสิทธิภาพของปฏิกิริยาแสงร่วมบนตัวเร่ง $TiO_2/RH-SiO_2$ ในการย่อยสลายของสารละลายพาราควอทภายใต้แสงยูวี พบว่าซิลิกามีผลช่วยต่อการดูดซับโดยมีพฤติกรรมแบบแลงเมียร์ อย่างไรก็ตามเมื่อทำการขึ้นรูปแบบเคลือบด้วยวิธีทางกลจะให้การดูดซับมากกว่าเมื่อนำไปขึ้นรูปด้วยวิธีการอัดเม็ด สำหรับการศึกษาประสิทธิภาพในการย่อยสลายสารละลายพาราควอทพบว่า ตัวเร่งปฏิกิริยาที่ 10% โดยน้ำหนักของ$TiO_2/RH-SiO_2$ (10% wt $TiO_2/RH-SiO_2$) ให้ค่าการย่อยสลายได้ดีที่สุดโดยมีพฤติกรรมแบบ LHHW แต่เมื่อนำไปขึ้นรูปทั้งสองแบบพบว่าให้ผลที่ไม่สามารถนำไปใช้งานได้เนื่องจากการเสียรูป

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต น.ส. นวพร กาญจนศิรานนท์
ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

5287540520 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : PHOTOCATALYST/ PARAQUAT/ RH-SiO_2/ TiO_2/RH-SiO_2

NAVAPORN KANJANASIRANONT: PHOTOCATALYTIC DEGRADATION OF PARAQUAT USING TiO_2/RH-SiO_2
ADVISOR : ASSOC. PROF. NURAK GRISDANURAK, Ph.D., 59 pp.

TiO_2/RH-SiO_2 photocatalysts were successfully prepared by impregnation of TiO_2 colloid solution on silica, extracted from rice husk. The calcined catalysts at 500°C for 5 hr showed only the anatase phase of TiO_2 along with the amorphous phase of RH-SiO_2. For the photocatalytic performances on the decomposition of paraquat under UV irradiation, silica assisted the performance by the adsorption phenomena fitted with Langmuir behavior. The study on pellet fabrication of catalyst was found that mechanical coating method provided higher paraquat adsorption than pressing method. For the degradation part, 10 wt% TiO_2/RH-SiO_2 catalyst yielded the highest efficiency of paraquat degradation. The reaction was fitted with LHHW model. The catalyst pellet fabrication for both cases, including mechanical coating and pressing, was inapplicable for the use. The deforming of pellet was a main factor.

Field of Study: Environmental Management   Student's Signature...NAVAPORN..KANJANASIRAN
Academic Year: 2010   Advisor's Signature.........................

ACKNOWLEDGEMENTS

This thesis would not have been possible without the kindly support from many people, who always support me from the initial to the final stage.

I am heartily thankful to my advisor, Associate Professor Dr. Nurak Grisdanuruk for his guidance, encouragement, and many grateful suggestions and made this thesis possible.

I sincerely thank to my thesis guides, Mr. Puek Tantriratana, Dr. Pongtanawat Khemthong, Dr. Kitirote Wantala, Dr. Jitladda Chumee for guidance and the value advices and it is a pleasure for me to thank the members of the Environmental Catalysis and Material Laboratory (Thammasat University), who always assist me in everything. Moreover, I would like to thank NCE-EHWM (Chulalongkorn University) to support my thesis.

Lastly, I would like to appreciate my family who constantly comfort, support and warmly encourage me all the time.

CONTENTS

Page

CHAPTER

Chapter **Page**

Chapter **Page**

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

LIST OF ABBREVIATIONS

˚C	degree Celsius
BET	Brunauer-Emmett-Teller
Fig.	figure
g	gram
h	hour
Kg	kilogram
min	minute
RH-SiO_2	Rice husk silica
SEM	Scanning Electron Microscope
SEM-EDS	Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy
SiO_2	Silica, Silicon dioxide
TiO_2	Titanium dioxide, Titania
TiO_2/ RH-SiO_2	Titania supported rice husk silica
UV-Vis DRS	UV-Vis Diffuse Reflectance Spectroscopy
XRD	X-Ray Diffraction
XRF	X-ray Fluorescence Spectrometer

CHAPTER I

INTRODUCTION

1.1 Background

Paraquat (1,1-dimethyl-4,4'-bipyridylium chloride) is generally used to remove weeds in our agricultural country and commonly contaminated in herbicide waste effluent including agricultural wastewater. Paraquat is an active and non-selective contact herbicide, which suppresses the photosynthesis reaction via adsorption to the chloroplasts of green plant tissue that comes in contact (Hsu and Pan, 2007; Cantavenera et al., 2007). Although, the efficiency of this chemical will no longer continue when it is adsorbed on the soil particles (Leyva et al., 1999). Nowadays, the use of paraquat tends to be increased in the future due to its properties and application in order to control weeds effectively. However, paraquat is highly toxic to human via several exposure routes and the toxicity level is depended on the degree of exposure. This commercial herbicide can cause both of chronic and acute effect to human. Moreover, paraquat poisoning may cause fatal multi-organ failure after ingestion of the large quantities. Hence, the removal and degradation of paraquat is extremely significant.

There are several methods of herbicide control such as ion exchange; membrane separation, adsorption onto clays or carbon filters, photocatalytic degradation and microbiological processes (Hsu and Pan, 2007; Danish, 2010). Nevertheless, the main processes for paraquat removal in waste effluent are recuperative and destructive processes (Tsai, 2004). Photocatalytic degradation is one of the processes which can treat low residual paraquat in the water efficiently (Leyva et al., 1999). Recently, the use of TiO_2 as a photocatalyst was investigated to remove paraquat in aqueous solution (Lee, 2003). TiO_2 is widely used in photo-process due to its chemical-physical properties, for example, high effective photoactivity, innocuousness, high stability including its large band gap (Hashimoto et al., 2005; Gao et al., 2006; Enright, 2008). Moctezuma and Leyva [1998] shown that photocatalytic process with the presence of oxygen can gradually degrade paraquat whereas the use TiO_2 as a photocatalyst in the process was increasing the rate of photocatalytic reaction significantly totally oxidizing paraquat in aqueous solution with low level (Leyva et al., 1999).

The applied used of TiO_2 has been introduced to increase the efficiency of its photocatalytic properties by coating with the support or carrier such as silica. Silica is widely used as a support because of its properties like high surface area and high chemical inertness. It was found that TiO_2/RH-SiO_2 always presented in higher surface area, thermally stable and good mechanical properties of TiO_2 (Kim et al., 2003). However, there are a few studies concerning the use of TiO_2/RH-SiO_2 for paraquat removal in aqueous solution. Thus, the aim of this study is to modify TiO_2/RH-SiO_2 catalyst and used for the degradation of paraquat under UV light with both of powder and granular form.

1.2 Objectives

To fabricate modified TiO_2/RH-SiO_2 catalyst and utilize for photocatalytic degradation of paraquat by TiO_2/RH-SiO_2 under UV light.

1.3 Hypothesis

The modified TiO_2/RH-SiO_2 photocatalysts is effective and practical for the photocatalytic degradation of paraquat under UV.

1.4 Scopes of the study

1.4.1 The extraction of RH-SiO_2 using the acid leaching technique.
1.4.2 The preparation of TiO_2/RH-SiO_2 catalyst by wet impregnation method.
1.4.3 The synthesized photocatalysts include
    - TiO_2-RH-SiO_2 with Ti loading of 5, 10, 15% by weight
    - Calcination temperature: 500°C
1.4.4 The preparation of granular sample include
    - The mechanical coating technique

- The extrusion technique

1.4.4 The parameter conditions of paraquat adsorption include

- Reaction temperature: 25°C
- The concentration of paraquat in synthetic waste water: 5, 10, 20, 30 and 40 ppm

1.4.5 The parameter conditions of paraquat degradation include

- Reaction temperature: 25°C
- Irradiation source: 400W UV lamp
- The concentration of paraquat in synthetic waste water: 5 ppm

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Paraquat

Paraquat is an active and non-selective contact herbicide, which suppresses the photosynthesis reaction via adsorption to the chloroplasts of green plant tissue that comes in contact (Hsu and Pan, 2007; Cantavenera et al., 2007). Although, the efficiency of this chemical will no longer continue when it is adsorbed on the soil particles (Moctezuma et al., 1999). Paraquat is a viologen that cause to quick-acting and not affect on the deep root plant or has low capability for the root part of plant. The properties of paraquat are shown in Table 2.1, and the structure is shown in Figure2.1. In neutral and acidic media, this herbicide is stable whereas in alkaline media, it is unstable and tends to be hydrolyzed immediately. Moreover, paraquat can be degraded by photocatalytic process under ultraviolet range in aqueous solution.

Table 2.1 Properties of paraquat

Molecular formular	$C_{12}H_{14}Cl_2N_2$
CAS formula name	1,1-dimethyl-4,4'-dipyridylium dichloride
CAS number	1910-42-5
Physical state	White to yellow powder
Molecular weight	257.2 g
Melting point	175-180^{o}C
Boiling point	ca. 300^{o}C
Vapor pressure	Non-volatile
Density	1.25 g/cm^3
Solubility in water at 20 C	0.7 g/cm^3
pH of liquid formulation	6.5 – 7.5

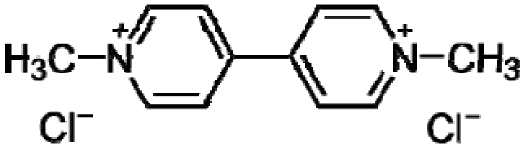


Figure 2.1 Chemical structure of paraquat.

Paraquat is extremely toxic and causes both chronic and acute effects to human. Moreover, this herbicide toxicity may cause the mortality by exposing with large quantities. There are several routes for human to expose paraquat and the effects of this herbicide are depended on the degree, duration time and route of exposure by following:

1. Effect of ingestion route

Target organ is lung and kidney due to its function in order to excrete paraquat from the body. The effect level of symptom is depended on dose of paraquat.

1.1 Gastrointestinal system effects at below 20 mg paraquat ion per kg of body weight.

1.2 Pulmonary fibroplasias which experienced at 20-40 mg paraquat ion per kg of body weight approximately.

1.3 Fatal multi-organ occurs at above 40 mg paraquat ion per kg of body weight.

2. Effect of dermal route

The effect from this route is acute effect. The symptoms will be occurring on the localized area of tissues that expose to the chemical. The extent of poisoning contact will cause to the abrasion and ulceration.

3. Effect of inhalation route

Paraquat may be toxic to the target organ but due to its low vapor pressure therefore it does not affect the lung.

2.2 Paraquat removal using various processes

As a consequence of highly toxicity of paraquat in animal and human, several processes have been applied to remove paraquat effectively. There are various techniques for paraquat removal such as adsorption, photocatalytic degradation and microbiological processes (Moctezuma et al., 1999; Danish et al., 2010). However, the treatment processes of paraquat removal in water and effluent have totally two principals. First is the destructive process like destructive oxidation and another one is the recuperative process for example, adsorption onto clay (Tsai et al., 2004).

2.2.1 Adsorption process of paraquat removal

The adsorption technique is investigated for paraquat removal. The various adsorbent are selected for paraquat treatment such as granular activated carbon or GAC, clay, rice husk and etc. The activated carbon is broadly used as an adsorbent because of its high efficiency for adsorption but the use of this material is not the cost effective way since the high cost of the spent carbon management (Tsai et al., 2005). Thus, the choosing of low cost material as an adsorbent is more attractive such as clay minerals. Clay minerals can adsorb paraquat better than the activated carbon because it has the proper particle size and has the negative charge on its surface whereas paraquat has cationic charge (Draoui et al., 1999). Mithyanta et al. investigated that the different type of clay minerals will have the different capacity for paraquat adsorption due to their C.E.C., the power of their negative charge and the presence of particular site for paraquat adsorption.

In the same way as clay minerals, rice husk from the rice milling industry is utilized as an adsorbent for contaminant removal including herbicide paraquat. The used of modified rice husk is initiated to increase the adsorption capacity. As a result, the modified rice husk with methacrylic acid is a good adsorbent which can adsorb paraquat effectively due to the carboxylic group which grafted on the rice husk’s surface area. This result will help the modified rice husk in order to adsorb paraquat ions in aqueous solution quickly. Moreover, the methacrylic acid-modified rice husk is improved the adsorption capacity of paraquat excellently (Hsu and Pan, 2007). However, the adsorption technique is not the best method for paraquat elimination because this method is a recuperative process and the herbicide paraquat will not be destroyed. Therefore, the treatment and disposal of the spent adsorbent after adsorption process will be required.

2.2.2 Microbial degradation process of paraquat removal

Microbial degradation is one of the techniques that can degrade paraquat gradually. The use of plant residues (such as rice straw, dropwort and Chinese milk vetch) is an applied method for paraquat microbial degradation. These three types of plant residues are used as a feasible site to sorb paraquat and ready to degrade in the soil environment and the highest of degradation rate is in rice straw, dropwort and Chinese milk vetch respectively (Lee et al., 1995). Moreover, paraquat can be degraded via the microbial degradation when this herbicide adsorbed to soil (Kanazawa, 1990). Nevertheless, the microbial degradation method is taking longer time than other methods and slowly degradation (Moctezuma et al., 1999). Thus, the other effective techniques like photocatalytic methods have been considered for paraquat removal.

2.2.3 Photocatalytic degradation process of paraquat removal

The photocatalytic process is one of the promising methods for removing the organic contamination with the presence of a catalyst and considering the catalytic reaction under the light proceeding (Lasa, 2005). The various advantages of this technique comparable to the microbial degradation process are listed below:

- Various organic compounds such as hydrocarbon fuels, halogenated solvent and hazardous organic chemicals can be eliminated by the photocatalytic process because the reaction of this technique is unspecific.
- The organic chemicals generally obtain the complete mineralization due to the strong oxidation process of photocatalytic degradation.
- Photocatalytic process tolerates toxic environment making it highly useful for the degradation of toxic compounds for example xenobiotics.
- The process is effective in both liquid and gaseous phase.

There are several kinds of semiconductor such as TiO_2, ZnO, or Fe_2O_3 have been analyzed for the photocatalytic degradation of environmental organic pollutants.

The photocatalytic process using titanium dioxide (TiO_2) for organic pollutants degradation is one of the interesting ways of pollution treatment in water and soils (Florencio et al., 2003). The applied use of titanium dioxide as a photocatalyst concerning for the degradation of herbicide like paraquat. The titanium dioxide (TiO_2) can degrade paraquat in aqueous solution under UV irradiation via the photocatalytic degradation technique. The photolysis degradation of paraquat solutions with the dissolved oxygen is slow. While in the absence of oxygen, paraquat solutions cannot be degraded under UV irradiation. Furthermore, the reaction rate and overall conversion of paraquat are strongly increased by adding TiO_2 to the system. At alkalinity condition, the photocatalytic process of paraquat can be completely degraded for less than three hours (Moctezuma et al., 1999).

To enhance the photocatalytic degradation method, the applied use of TiO_2 has been introduced to increase the efficiency of its photocatalytic properties by coating on the support or carrier such as plastic film, silica, alumina and etc. Many researchers tried to find the support that can encourage for paraquat degradation. The polythene and polypropylene films are utilized as a support with TiO_2 coating to prevent the photocatalyst separation but this technique makes the photodegradation rate of paraquat lower than usual due to the cause of the embedding of TiO_2 particles within the polymer and the attachment of TiO_2 on the plastic film (Tennakone and Kottegoda, 1996). Hence, another support like silica is used to increase the surface area and chemical inertness of the photocatalyst resulting in higher photodegradation rate. It was found that TiO_2-coated silica always present in high surface area, thermally stable and good mechanical properties of TiO_2 (Kim et al., 2003).

2.3 Adsorption

2.3.1 Principle of adsorption

Adsorption is a process of a substance that removes from one phase and sorb onto the surface of another phase by accumulation at the surface or interface between two phases (the original phase and separate or solid phase). Adsorbate is a substance that binds on the solid phase and the adsorbent is the material that holding the adsorbate on its surface (Faust and Aly, 1998).

2.3.2 Types of adsorption

The types of adsorption process are commonly categorized into two types. First is physisorption is a physical separation process that transfers the substance from the original phase to another phase without chemical transformation of the adsorbed substance or there is only the Van der Waals force of a molecule that sticks to the surface. The chemisorption is the adsorption process of material with the chemical change or has the other forces except the Van der Waals force between a molecule and the surface of adsorbed materials.

2.3.3 Factors affecting adsorption

1. Surface area of adsorbent

The adsorption capacity will increase with the more surface area of adsorbent.

2. Contact time

The adsorption process will be more complete when provided the longer contact time.

3. Solubility of adsorbate

Non-polar material tends to create more adsorption capacity than the polar material because it will be transferred in water easily.

4. Consideration between pore size and substance size

The adsorption capacity will decrease when large substances try to enter small pore because the substance is too big to penetrate into small pore.

5. Ionization's degree of adsorbate molecule

The adsorption capacity will be decreased with the higher degree of ionization of adsorbate molecule.

6. pH

The adsorption capacity depends on pH effect because it is the result of the ionization of adsorbate molecule.

2.3.4 Adsorption equilibrium

In the adsorption process, the solute which stick on the adsorbent surface will possible to desorb in the solution and the final rate between adsorption and desorption will be equal to obtain the adsorption equilibrium. The adsorption will proceed before reaching the equilibrium and at this point, the concentration of the molecule in solution and the concentration of the molecule in the adsorbed state will not change any longer.

Isotherm is generally used for the explanation of adsorption. There are various models have been investigated to describe the adsorption process. However, Langmuir isotherm and Freundlich isotherm are frequently used to explain the adsorption behavior.

1. Langmuir adsorption isotherm

The theories of Langmuir model include:

1. The adsorbent has the uniform surface pattern.
2. There is no move or interact of the adsorbed molecule on the adsorbent surface.
3. The mechanical of adsorption is the same throughout the process.
4. Each site of the adsorbed layer is a monolayer.

The equation of Langmuir isotherm is represented in the equation below:

$$q_e = \frac{bQC_e}{1+QC_e} \text{ or } \frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$

The Langmuir equation can be reformed into:

where:

q_e is the amount adsorbed per unit mass of adsorbent (mg/g)

Q is the maximum adsorption capacity (mg/g)

C_e is the equilibrium concentration of adsorbate in solution (mg/L)

b is a constant related to affinity of the binding sites (L/mg)

2. Freundlich adsorption isotherm

The Freundlich isotherm is described an empirical model for multi-site adsorption isotherm of coarse surfaces (Masel, 1996). The compound mixture can be investigated by using Freundlich model. The Freundlich equation is illustrated by:

$$q_e = K_F C_e^{1/n}$$

The Freundlich equation can be reformed into:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where:

K_F is the Freundlich equilibrium constant

n is the adsorption intensity

2.4 Heterogeneous photocatalysis

The photocatalysis technique is one of the promising methods for removing the organic contamination in aqueous effluent with the presence of a catalyst and considering the catalytic reaction under the light proceeding (Lasa, 2005). The heterogeneous photocatalytic reaction consists of three constituents to take place. These three factors are an emitted photon (with the proper wavelength), the surface of catalyst (especially a semiconductor particle such as TiO_2, ZnO, Cds), and a powerful oxidizing agent.

The process of heterogeneous photocatalytic mechanism (equations 1-1 to 1-10) is occurred when a photon of the photocatalyst (such as a semiconductor particle) has equal or higher than its band gap energy (E_{bg}) between the valence band (E_{vb}) and the conduction band (E_{cb}) to form the hole–electron pairs. The molecular excitation is obtained when the energy provided is larger than the band gap energy. Then electrons (e^-) in the conduction band and positive hole (h^+) in the valence band of a semiconductor or photocatalyst is initiated. The reduction process is obtained from the conduction band electron and the oxygen molecule (O_2) acceptor for forming the super-oxide anions (O_2^-) is called “the electron-transfer reaction” and the super-oxide anions (O_2^-) can consequently participate to form hydrogen peroxide (as shown in equation (1-6) and (1-7) respectively). In the other hand, the formation of $OH^{\bullet}$ free radical group is generated from the hydrogen peroxide photoconversion via the oxidation process (as illustrated by equation 1-9). These strong oxidizing agents are utilized for removing the organic pollutant on the catalyst’s surface especially $OH^{\bullet}$ radicals. The step of heterogeneous photocatalyst process is summarized as the following:

The first step is the generation of electrons (e^-) in the conduction band and positive holes (h^+) in the valence band of photocatalyst when E_{ph} is equal or greater than E_{bg}.

$$\text{Photocatalyst} \longrightarrow e^- + h^+ \qquad (1\text{-}1)$$

$$h^+ + RX_{ad} \longrightarrow RX^+_{ad} \qquad (1\text{-}2)$$

$$h^+ + H_2O_{ads} \longrightarrow OH^{\bullet}_{ads} + H^+ \qquad (1\text{-}3)$$

$$h^+ + OH^-_{ad} \longrightarrow OH^{\bullet}_{ad} \qquad (1\text{-}4)$$

The separation of H_2O molecule into ions is causing from OH^- in high concentration.

$$H_2O \longrightarrow OH^-_{ad} + H^+ \qquad (1\text{-}5)$$

The transferring from the electron charge to the oxygen molecule is occurred via the reaction of electron-transfer.

$$e^- + O_2 \longrightarrow O^-_2 \qquad (1\text{-}6)$$

$$O^-_2 + H^+ \longrightarrow HO^{\bullet}_2 \qquad (1\text{-}7)$$

$$H^+ + O^-_2 + HO^{\bullet}_2 \longrightarrow H_2O_2 + O_2 \qquad (1\text{-}8)$$

The free radical of $OH^{\bullet}$ group is also originated from hydrogen peroxide with the photoconversion reaction.

$$H_2O_2 + h_v \longrightarrow 2\ OH^{\bullet} \qquad (1\text{-}9)$$

$$HO^{\bullet}_{ad} + RX_{ad} \longrightarrow \text{Intermediate} \qquad (1\text{-}10)$$

2.4.1 Photocatalytic reactions of titanium dioxide (TiO_2)

From many recent studies, the applied use of titanium dioxide (TiO_2) or titania has been investigated as a photocatalyst for various application. TiO_2 is a semiconductor that has many useful properties for photodegradation technique like an innocuous substance, low-priced, stability, powerful band gap energy (3.0-3.2 eV), great absorption of UV, indissolvable in water, highly active under UV light and no visible light adsorption. Generally, the anatase phase of titanium dioxide is commonly used due to its good performance like high photocatalytic activity and stability. The mechanism process of TiO_2 is shown in the Figure 2.2 (Yasushiro and Takayuki, 2008)

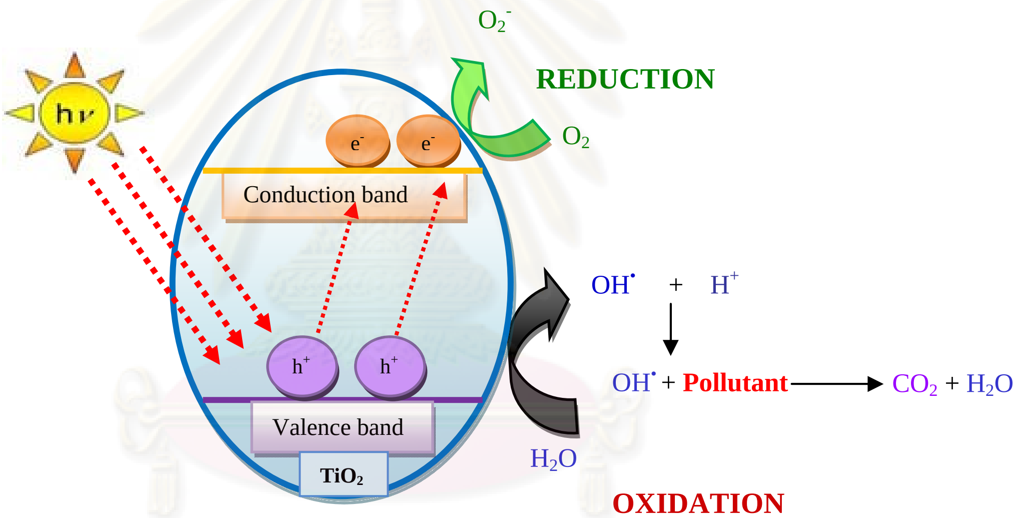


Figure 2.2 Mechanism of TiO_2 photocatalyst.

The heterogeneous photcatalytic process of TiO_2 is generated under the UV irradiation. This photocatalyst absorb a photon that contain the proper energy to its band gap (the energy band gap of TiO_2 in anatase phase is 3.2 eV) to promote electron-hole pair. The mechanism process of TiO_2 is shown in the equation below:

$$TiO_2 \xrightarrow{E_{ph} \geq E_{bg}\ (3.2\ eV)} e^-_{cb}(TiO_2) + h^+_{vb}(TiO_2) \qquad (2\text{-}1)$$

$$TiO_2\ (h_{vb}^+) + H_2O_{ads} \longrightarrow TiO_2 + OH^{\bullet}_{ads} + H^+ \qquad (2\text{-}2)$$

$$TiO_2\ (h_{vb}^+) + OH^-_{ads} \longrightarrow TiO_2 + OH^{\bullet}_{ads} \qquad (2\text{-}3)$$

$$TiO_2\ (h_{vb}^+) + D_{ads} \longrightarrow TiO_2 + D^+_{ads} \qquad (2\text{-}4)$$

$$TiO_2\ (e_{vb}^-) + A_{ads} \longrightarrow TiO_2 + A^-_{ads} \qquad (2\text{-}5)$$

$$TiO_2\ (e_{cb}^-) + O_{2ads} + H^+ \longrightarrow TiO_2 + HO_2^{\bullet} \longrightarrow O_2^{\bullet -} + H^+ \qquad (2\text{-}6)$$

$$TiO_2\ (e_{cb}^-) + HO_2^{\bullet} + H^+ \longrightarrow H_2O_2 \qquad (2\text{-}7)$$

$$H_2O_2 + hv \longrightarrow 2HO^{\bullet} \qquad (2\text{-}8)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow HO^{\bullet} + O_2 + HO^- \qquad (2\text{-}9)$$

$$H_2O_2 + TiO_2(e_{cb}^-) \longrightarrow HO^{\bullet} + HO^- + TiO_2 \qquad (2\text{-}10)$$

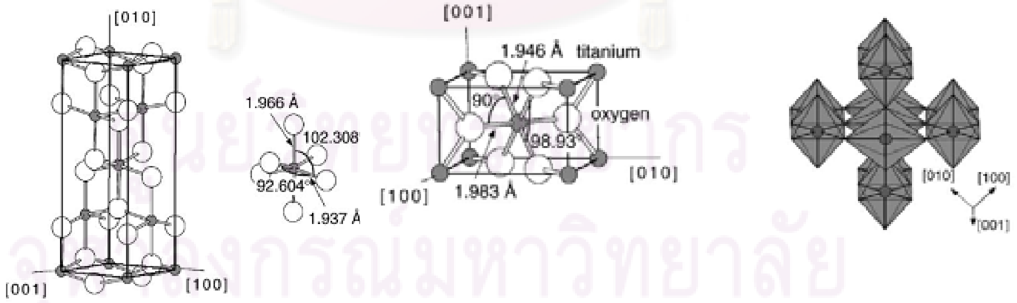
2.5 Titanium dioxide (TiO_2) photocatalysis

From many recent studies, the applied use of titanium dioxide (TiO_2) or titania has been investigated as a photocatalyst for various applications. TiO_2 is a semiconductor that has many useful properties for photodegradation tecnique like an innocuous substance, low-priced, stability, great absorption of UV, indissolvable in water, highly active under UV light and no visible light adsorption. Generally, the titanium dioxide has been presented in three main structures of their crystalline forms due to its arrangements of oxygen and titanium atom. The First form is anatase (tetragonal), which is the most extractively used as a result of its good performance like high photocatalytic activity and stability and the characteristics of TiO_2 in anatase form was shown in Table 2.2.

Table 2.2 Characteristics of anatase TiO_2 (Diebold, 2003)

Properties	**Anatase**
Crystalline form	Tetragonal
Band gab energy (eV)	3.200
Hardness (Mohs)	5.5-6.0
Density (g/cm^3)	3.894
Gibbs free energy, ΔG_f^o, (kcal/mol)	-211.4
Lattice constant, a (Å)	3.784
Lattice constant, c (Å)	9.515
Melting point (^{o}C)	Transformation to rutile at temperature above 800 ^{o}C

The density of anatase is 3.9 g/ml and its band gap energy is 3.2 eV. Rutile (tetragonal) is the second form of TiO_2, which has a density of approximately 4.26 g/ml or more and it is thermodynamic stability. The band gap energy of rutile phase is 3.0 eV. However, the anatase phase has higher photocatalytic activity than rutile and it is the most stable structure of titania. The last phase is brookite (orthorhombic), which is less stability. The arrangement of titanium dioxide crystal structures are shown in Figure 2.3



Anatase **Rutile** **Brookite**

Figure 2.3 Arrangement of TiO_2 crystal structures.

2.6 Amorphous rice husk silica

Rice husk is a byproduct from agricultural waste, which contain of organic materials, cellulose and silica content (Yalcin and Sevin, 2001). Silica or silicon dioxide is a metal oxide with the molecular weight of 60.1. Generally, the phases of silica are crystalline and amorphous form and it was found that amorphous rice husk silica is a good phase for silicon synthesis with the high purity (Ahmad and Adam, 2007). Many studied was shown that rice husks are the main source for amorphous rice husk silica extraction. The preparation of amorphous silica is done by using thermal treatment with the temperature of 500-700°C and the high surface area silica in powder form will be obtained (Chakraverty and Kaleemullah, 1991). Generally, the rice husk ash consists of silica around more than 90 percents by mass and the small amounts of others metallic components. Therefore, the pre-treating technique is required to remove the impurities before burning rice husk via the leaching technique with HCl, HNO_3 and NaOH.

Normally, the rice husk silica powder is used as an adsorbent and a support for the catalyst due to its high specific surface area (Ahmad and Adam, 2007). The properties of silica or silicon dioxide are shown in the Table 2.3.

Table 2.3 Properties of silicon dioxide

Properties	
Molecula formular	SiO_2
Molar mass	60.08 g mol^{-1}
Exact mass	59.96 g mol^{-1}
Density	2.648 $g \cdot cm^{-3}$
Melting point	1600-1725°C
Boiling point	2230°C
Solubility in water	0.079 g L^{-1}

2.7 Granular Formation

The photocatalyst in powder form is not the best way for practical use because it always disperses in the solution and difficult to reuse. Thus, the fabrication or formation technique has been recognized to form the photocatalyst in granular. There are several techniques for catalyst forming such as physical vapor deposition or PVD (Zeman and Takabayashi, 2003) and chemical vapor deposition or CVD (Kim et al., 2004) but these techniques will be required the complex material and high vacuum condition to operate (Yoshida et al., 2009). Hence, the mechanical coating or MCT will be concerned for catalyst formation due to its easy and cost effective to practice. It was found that the mechanical coating is a useful technique to fabricate the metallic film (TiO_2) on a spherical material (alumina balls). Therefore, the applied use of MCT technique will be selected to TiO_2/RH-SiO_2 formation.

Another technique for formation is using binder. It has been investigated that using binder is a technique to bind the components with the required chemical-physical properties. Thus, the applied use of binder will be investigated to form granular TiO_2/RH-SiO_2 catalyst.

CHAPTER III

METHODOLOGY

This chapter presents the preparation of modified TiO_2/RH-SiO_2 catalyst using in the synthetic waste water contaminated with paraquat. Performance on samples in both powder and forming phase of the samples are also explained.

3.1 Material

3.1.1 Chemicals

1. Titanium(IV) n-butoxide (TBOT, 99%); Acros Organics
2. Methyl viologen dichloride hydrate ($C_{12}H_{14}Cl_2N_2 \cdot xH_2O$, 98%); Sigma-Aldrich, Germany.
3. Nitric acid (HNO_3, 65%); Carlo Erba,
4. Hydrochloric acid (HCl, 37%); Carlo Erba
5. Sodium hydroxide (NaOH 99%); Merck
6. Alumina balls
7. Ultrabond P261

3.1.2 Equipments

1. Furnace
2. Hot air oven
3. Three-neck round bottom flask with condenser
4. Temperature controller with heater and thermocouple
5. Magnetic stirrer
6. pH meter
7. 400 W UV lamp
8. Circulating cooling system
9. Laboratory glasswares

3.2 Experimental procedures

3.2.1 Rice husk silica extraction

The preparation of amorphous silica was obtained from rice husk by using chemical treatment with acid leaching technique. First, the rice husk was cleaned with tap water to displace other contaminants. Then the cleaned husk was dried at 100^oC for 24 hours in an oven. Second, the dried husk was treated to remove the metal impurities with 3M HCl at 70^oC for 3 hours. After leaching, the husk was washed with water to obtain the neutral condition (pH 7.0). The neutralized husk was dried in an oven at 100^oC for 24 hours to remove the moisture content. Finally, the cleaned and dried husk was calcined in a muffle furnace to eliminate all organic compounds at 550^oC for 6 hours.

3.2.2 Synthesis of TiO_2/RH-SiO_2 catalyst

The TiO_2/RH-SiO_2 catalysts were prepared by impregnating TiO_2 colloid solution on RH-SiO_2 with the weight ratio of TiO_2: RH-SiO_2 as 5, 10, and 15 wt % TiO_2/RH-SiO_2. The method was started by adding desired amount of titanium(IV) n-butoxide into 40 ml of 3 M HNO_3 and stirred for 2 hours. After that the pH of mixture was adjusted to 3 by using 1 M NaOH. Then 3 g of RH-SiO_2 was added to the mixture and stirred for 2 hours. The mixture was centrifuged to separate solid sample and dried at 100^oC for 24 hours and calcined at 500^oC for 5 hours.

3.2.3 Fabrication of granular RH-SiO_2 and TiO_2/RH-SiO_2

The formation of materials in this study consists of two methods including the mechanical coating technique with the ranging diameter 1.2-2.0 mm of alumina balls under condition of 500^oC for 24 hours. The other technique is to use an inert binder to fabricate the material into granular form.

3.2.3.1 Fabrication of TiO_2/RH-SiO_2 with the mechanical coating technique

The 40 g of TiO_2/RH-SiO_2 powder and 60 g of alumina balls was added into 250 ml of pot mill and then rotated at 300 rpm for 15 hours. After the rotation, the TiO_2/RH-SiO_2 catalyst was calcined at 500^{o}C for 24 hours.

3.2.3.2 Fabrication of TiO_2 / RH-SiO_2 using an Ultrabond P261 with the extrusion technique

The granular TiO_2/RH-SiO_2 was prepared by using Ultrabond P261 binder. First, the 250 ml of P261 binder was added into 750 mg of TiO_2/RH-SiO_2 powder and then mixed together. After that, the syringe was used for the extrusion of the well-mixed sample. Finally, the extruded sample was dried at the room temperature for 24 hours.

3.2.4 Sample Characterizations

The physico-chemical properties of synthesized catalyst were analyzed by using XRD, XRF, BET, UV-Vis DRS, SEM and SEM-EDS techniques.

- The crystal structure and average crystallite size (*D*) of TiO_2/RH-SiO_2 catalyst were examined by X-ray Diffraction
- The surface areas of RH-SiO_2 and TiO_2/RH-SiO_2 catalyst were analyzed by BET method
- The composition of samples were investigated by X-ray fluorescence spectrometer
- The morphology of the particles of RH-SiO_2 and TiO_2/RH-SiO_2 catalyst were measured by Scanning Electron Microscopy
- The elementals composition of TiO_2/RH-SiO_2 catalyst were evaluated by Scanning Electron Microscopy-Energy Dispersive Spectroscopy

- The diffusion reflectance of RH-SiO_2 and TiO_2/RH-SiO_2 catalyst were measured by UV-Vis Diffuse Reflectance Spectroscopy

3.2.5 Adsorption Studies

A 200 mg of RH-SiO_2 was added into 200 ml of synthetic wastewater contaminated with paraquat. Paraquat concentration was set differently from 5, 10, 20, 30 and 40 ppm, respectively. The pH of mixture was adjusted to 7 by using 1 M NaOH. The adsorption was carried out with continuously mixed under the temperature of 25^{o}C throughout the process. The remained concentration of paraquat was measured by Jasco V630 UV-Vis spectrophotometer at 257 nm of the characteristic wavelength.

3.2.6 Photocatalytic degradation studies

For the photocatalytic activity, TiO_2/RH-SiO_2 catalyst was evaluated by the efficiency of paraquat degradation. The quantity of TiO_2/RH-SiO_2 catalyst was 1 g/L**.** The volume of paraquat solution was 200 ml with the pH of 7. The distance of the reactor to a 400 W UV lamp was fixed at 75 cm.

The TiO_2/RH-SiO_2 catalyst was added into paraquat solution 200 ml and stirred continuously throughout the photoreaction process. The 400 W of UV lamp was turned on to evaluate the photocatalytic performances. The Millipore disk (0.45 μm) was used to remove all TiO_2/RH-SiO_2 catalysts before measuring the concentration of paraquat by Jasco V630 UV-Vis spectrophotometer at 257 nm of the characteristic band. From the results of measurement, the effective ratio of photocatalyst was found.

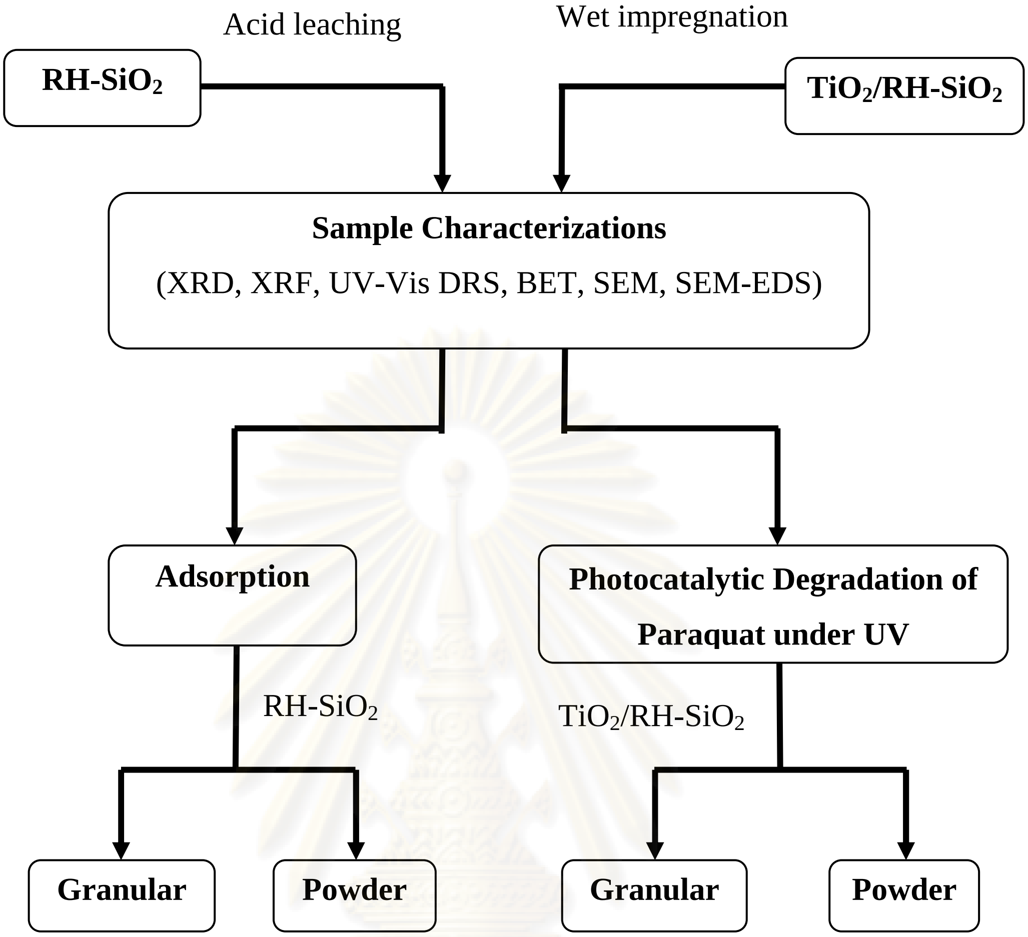


Figure 3.1 Scheme diagram of experiments.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the physico-chemical properties of prepared catalysts characterized by XRD, XRF, UV-Vis DRS, BET, SEM and SEM-EDS techniques. The adsorption capacity of rice husk silica (RH-SiO_2) and the photocatalytic activities of paraquat degradation using the catalysts (5, 10 and 15 wt % TiO_2/RH-SiO_2) under UV range are also discussed.

4.1 Adsorption of paraquat on rice husk silica

In this study, the adsorption capacities of RH-SiO_2 which was used as a support in both powder and granular form were investigated. To estimate the adsorption isotherm, the RH-SiO_2 powder was used as an absorbent and the initial paraquat concentrations were 5, 10, 20, 30 and 40 ppm. In case of granular form, the adsorption abilities of granular absorbents prepared via the mechanical coating and extrusion techniques were compared.

4.1.1 Adsorption in powder form

The removal and adsorption profiles of paraquat on RH-SiO_2 powder are shown in Figure 4.1. It was found that adsorption was steeply increased in the beginning phase of the contact time before reaching the adsorption equilibrium within 60 minutes. RH-SiO_2 is known as a good adsorbent. It is better to understand its adsorption capacity prior to the photocatalysis. Same patterns of adsorption can be observed in all studied initial concentrations (5, 10, 20, 30, and 40 ppm). In the low concentration (5, 10 ppm), the removal percentages were found to be of 75 and 60, respectively. Corresponding to the adsorption could not reach to their initial concentrations. For example, approximately 4 mg paraquat for every one gram was adsorbed under initial concentration of 5 ppm, and 6 mg paraquat for every one gram was adsorbed under initial; concentration of 10 ppm, respectively. It could be seen that 100 % adsorption could not be reached, even though RH-SiO_2 has high surface area. This might due to too low driving force (concentration difference between remained concentration in the solution and surface concentration) presented in the solution in the final stage.

In case of higher initial concentrations (20-40 ppm), the removal percentages were found to be of 40, 23 and 24, respectively. The higher initial concentration, the lower percent removals are. This would provide that adsorbent has its limitation of its own adsorption capacity. Corresponding to the adsorption capacity reached around 8.5-9.5 mg paraquat for every one gram of RH-SiO_2. The driving force in this case did not correspond to the concentration difference, but rely on the available surface area or active sites. According to the results above, two outcomes could be drawn out. One is an equilibrium time. Approximately 60 min was the suitable to ensure the adsorption was completed. This time will be set for the rest of adsorption tests. The other is that the phenomena of adsorption should follow Langmuir isotherm. However, the test on another type of isotherm (Freundlich isotherm) was also be evaluated.

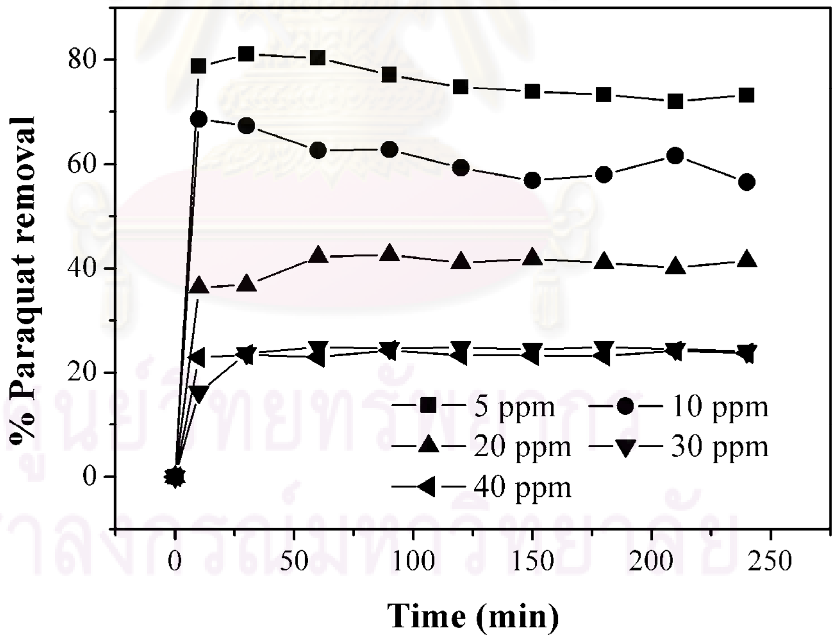


Figure 4.1 Percentage of paraquat removal.

To consider the adsorption behavior of paraquat removal over RH-SiO_2, the Langmuir and Freundlich isotherms were determined. The equation of Langmuir isotherm is presented in the equation below;

$$q_e = \frac{bQC_e}{1+QC_e}$$

The equation can be linearized as

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$

Where;

C_e is the equilibrium adsorption of solution concentration (mg/l)
Q is the maximum adsorption capacity (mg/g)
q_e is the amount adsorbed per unit mass of adsorbent (mg/g)
b is a constant related to affinity of the binding sites (L/mg)

The adsorption isotherm of paraquat on RH-SiO_2 in Figure 4.2 is illustrated. The paraquat equilibrium concentration increases from 0 to 12 mg/L with the paraquat adsorption capacity increases. For the capacity of paraquat under support's powder was about 9 mg/g at the equilibrium paraquat concentration of 12 mg/L. The adsorption isotherm of rice husk silica in powder form was modeled to Langmuir isotherm with an R^2 value of 0.999. The evaluations of constant values for the isotherm are the Q value of 9.8039 mg/g and the value of b of approximately 0.63 L/mg, obtained from Figure 4.3(b). The isotherm was plotted explicitly as shown in Figure 4.3(a)

On the other hand, the adsorption isotherm of Freundlich isotherm had an R^2 value of 0.950 with the n value of 4.31 and the K_F value was around 4.45, obtained from linearization of Figure 4.4. In addition the data might be also close to fit to Freundlich isotherm. This might be due to the concentrations used in the study were low.

From overall results, the adsorption of paraquat using RH-SiO_2 was fitted very well and better on the Langmuir isotherm. Hence, it suggested that the mechanism of adsorption is the same throughout the process or a monolayer form and the adsorbent or RH-SiO_2 adsorbed the paraquat pollutant on its surface at the certain sites

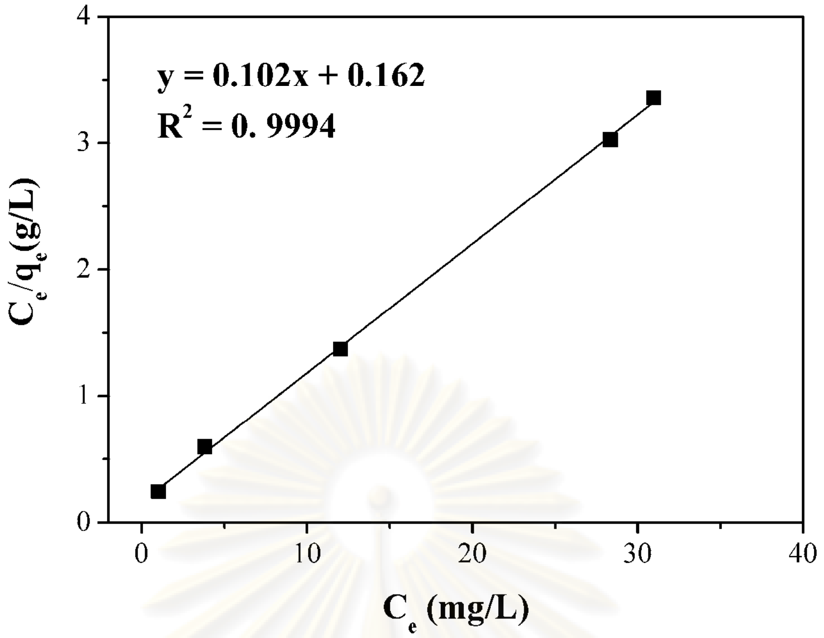
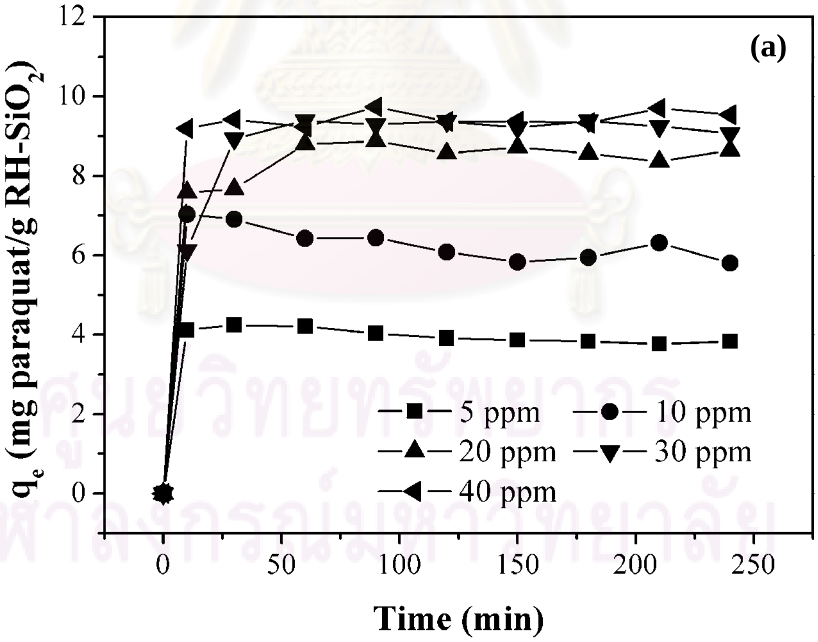


Figure 4.2 Linearized paraquat adsorption based over powder on Langmuir isotherm.



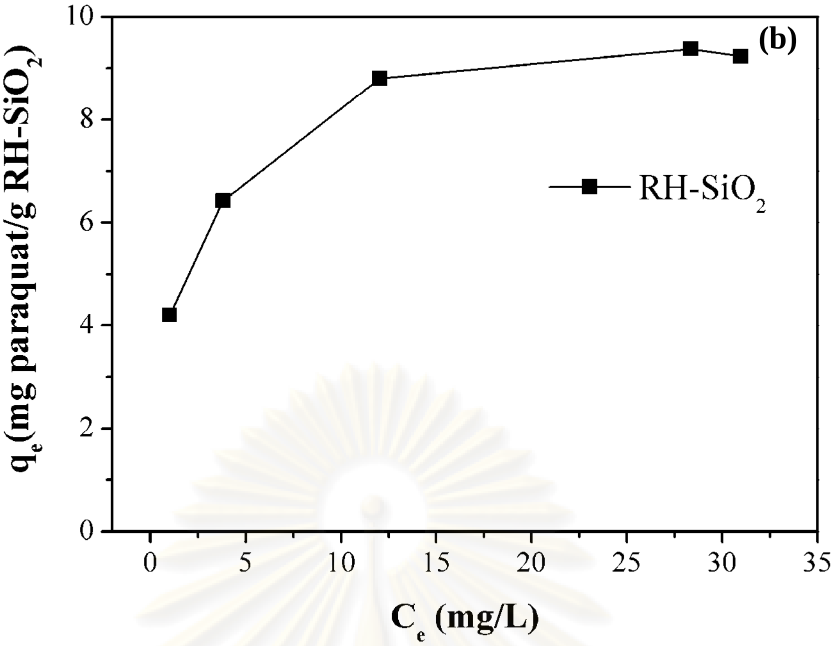


Figure 4.3 Adsorption a) With respect to time b) With respect to equilibrium concentration.

The Freundlich equation is illustrated by

$$q_e = K_F C_e^{1/n}$$

and after the linearization, the equation becomes

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where;

K_F is the Freundlich equilibrium constant
n is the adsorption intensity

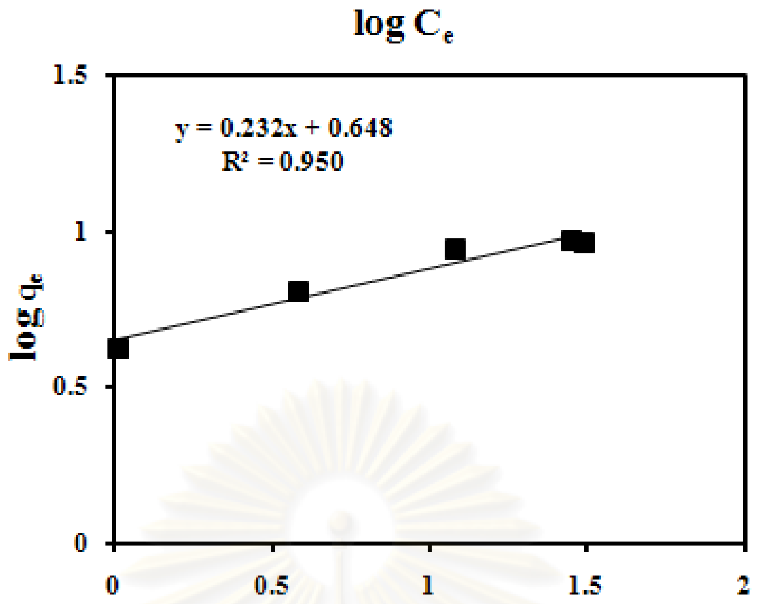


Figure 4.4 Linearized paraquat adsorption based over powder on Freundlich isotherm.

4.1.2 Granular rice husk silica

The adsorption efficiencies of granular RH-SiO_2 between the mechanical coating and extrusion techniques are compared and shown in Figure 4.5. The adsorption capacity of the RH-SiO_2 granular from two techniques was estimated by a monolayer-base set up and the initial paraquat concentration of 5 ppm. The results revealed that the mechanical coating absorbent was being able to adsorb paraquat higher than the extruded absorbent. According to the results, BET surface areas of the granules were required to measure. However, the isotherms on both granules were not considered.

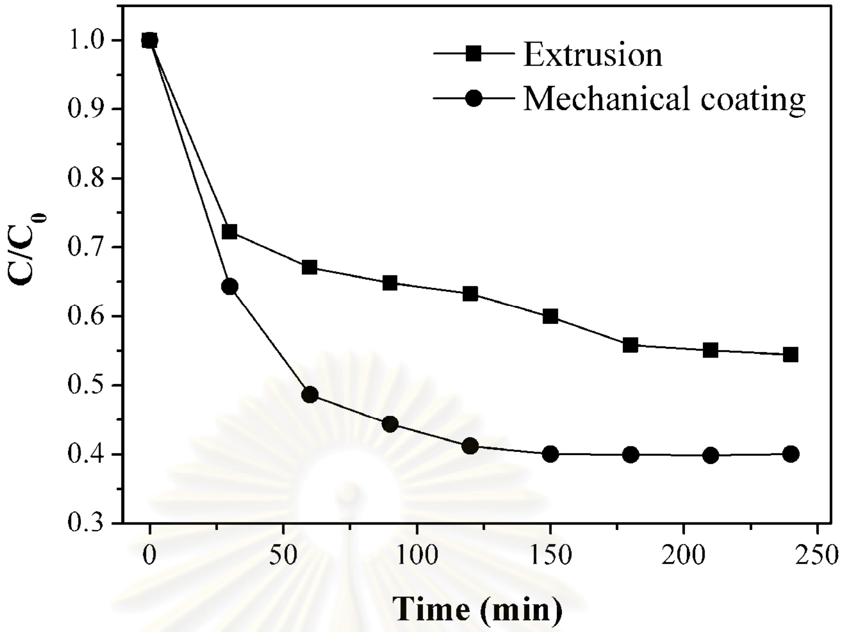


Figure 4.5 Concentration profiles of paraquat over granular RH-SiO_2 by two forming techniques.

For the BET surface area analysis of samples in granular form preparing using both of mechanical coating and extrusion techniques are tabulated in Table 4.1. As the results of granular RH-SiO_2 from the two techniques, it was found that the granular RH-SiO_2 prepared by the mechanical coating technique provided higher surface area than the sample which obtained via the extrusion method. This result had the same trend of granular 10 wt % TiO_2/RH-SiO_2 catalyst. The reason to select 10 wt % TiO_2/RH-SiO_2 was discussed in section 4.2. The sample formulated using the extrusion technique had to add some inactive/inert binder to agglomerate powder together. Thus, these binders which using to hold the samples might trap the pores of prepared powders, leading to decrease the surface area.

In contrast to the mechanical coating method, this technique used an inactive material (for this study, alumina ball was used.) to support the powder. Therefore, this technique reduced a little amount of sample surface area. This result was possibly due to the particles of titanium dioxide were well dispersed onto the surface of RH-SiO_2 and had the potential to block the pore of RH-SiO_2 surface. Hence, the surface areas of 5, 10, 15 wt % TiO_2/RH-SiO_2 catalysts were reduced respectively. The well dispersion of TiO_2 will be presented by SEM-EDS analysis, in section 4.2.1.5.

Table 4.1 BET surface areas of samples in granular form

	BET area (m^2g^{-1})	
Samples	**Mechanical coating**	**Extrusion**
RH-SiO_2	127	48
10 wt% TiO_2/ RH-SiO_2	119	12

4.2 Photocatalytic decomposition of paraquat

Prior to work on photocatalytic reaction, the characterizations on all catalyats were done.

4.2.1 Characterization results

4.2.1.1 X-Ray Diffraction (XRD)

The XRD patterns of titania supported rice husk silica (TiO_2/ RH-SiO_2) with the ratios of 5, 10 and 15 wt % TiO_2/RH-SiO_2 catalysts are displayed in Figure 4.6. It was observed that the main peaks of catalyst were shown at around 22° and 25°. The results revealed only the characteristic peak of titanium dioxide in an anatase phase (25°) accompanied with the amorphous rice husk silica, named as RH-SiO_2 (22°). This regards to an impregnation technique which maintained both support and active species after the synthesis. The XRD pattern of RH-SiO_2 was confirmed by a diffuse peak of amorphous rice husk silica reported by Della et al., 2002, and titanium dioxide in an anatase phase was confirmed by Thamapat et al., 2008.

As the results of XRD peaks, the sample of 5 wt % TiO_2/RH-SiO_2 contributed the highest peak of silica with the lowest peak of titanium dioxide in an anatase phase and these results were in contrast to the sample of 15 wt % TiO_2/RH-SiO_2. It is reasonable that the higher content of titanium dioxide, the higher intensity of anatase phase will be presented while the lower intensity of amorphous rice husk silica was shown.

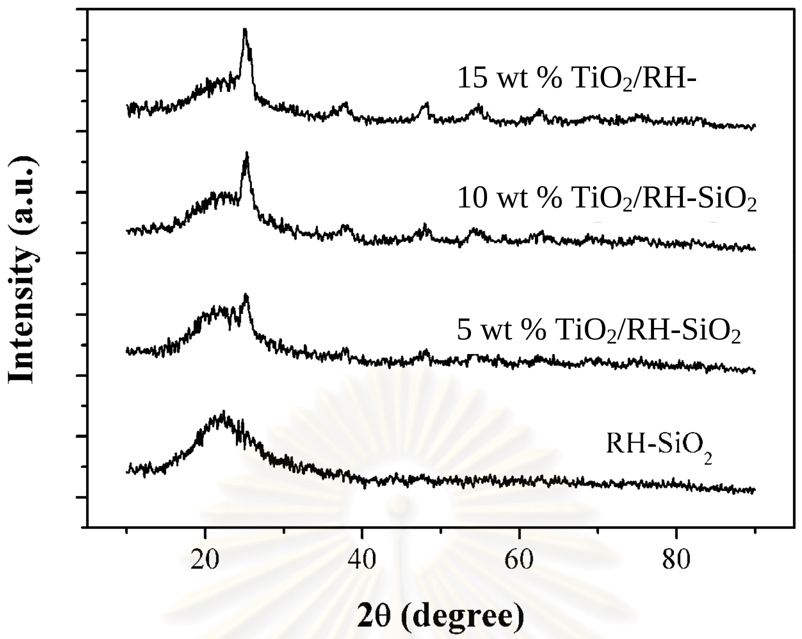


Figure 4.6 XRD patterns of 5, 10 and 15 wt % of TiO_2/RH-SiO_2 catalysts.

4.2.1.2 X-ray fluorescence spectrometer (XRF)

The X-ray fluorescence analysis determination was used to measure the elemental composition of solid samples. The results from XRF spectrometer are provided in Table 4.2. This was to confirm the quantitative analysis of the RH-SiO_2 and 5, 10 and 15 wt % TiO_2/RH-SiO_2 (catalysts) which were prepared from the acid leaching technique, and from the impregnation method, respectively.

It was investigated that the acid leaching technique could extract SiO_2 from the husk and gave 97.36% content of SiO_2. This value was quite high so it was possible to imply that the acid leaching was an applicable technique for RH-SiO_2 extraction. As known, rice husk is abundant in Thailand. It is suitable for SiO_2 for any related applications. For the titanium dioxide loading confirmation, the catalysts of 5, 10 and 15 wt % TiO_2/RH-SiO_2 were measured. As can be seen from the table, 5 wt % TiO_2/RH-SiO_2 was contributed the lowest content of titanium dioxide in the substrate element and this substrate content was gradually higher for 10 wt % TiO_2/RH-SiO_2 and 15 wt % TiO_2/RH-SiO_2 showed the highest value of titanium dioxide. The amounts of Ti content were consistent to those by the preparation. Hence, it can be summarized that the catalyst preparation using the impregnation technique can trap the particle of titanium dioxide on the RH-SiO_2 and this result was leading to increase the surface area of titanium dioxide by using RH-SiO_2 as a support.

Table 4.2 Elemental contents of studied samples

Samples	**SiO_2**	**Ti**
RH-SiO_2	97.36	-
5 wt% TiO_2/ RH-SiO_2	89.70	5.952
10 wt% TiO_2/ RH-SiO_2	84.27	9.264
15 wt% TiO_2/ RH-SiO_2	77.40	13.344

4.2.1.3 UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The UV-Vis DRS results are shown in Figure 4.7. The DR spectra presented the adsorption values of samples under UV region raised with an increasing quantity of TiO_2. As can be observed, 15 wt % TiO_2/RH-SiO_2 catalyst contained the highest adsorption value in the UV region, following with 10 wt % TiO_2/RH-SiO_2, 5 wt % TiO_2/RH-SiO_2 and RH-SiO_2, respectively. These results were reflected as the elemental analysis on each sample. In general, the RH-SiO_2 has no adsorption value in UV region whereas titanium dioxide has the property to reflect under UV light. Therefore, the consideration from UV-Vis DR spectra was illustrated the sample with a higher content of titanium dioxide would provide higher capability to response under UV range. These results led to the conclusion that all wt % TiO_2/RH-SiO_2 catalysts had the potential to apply for the photocatalytic degradation under UV region while the pure RH-SiO_2 without titanium dioxide content did not have.

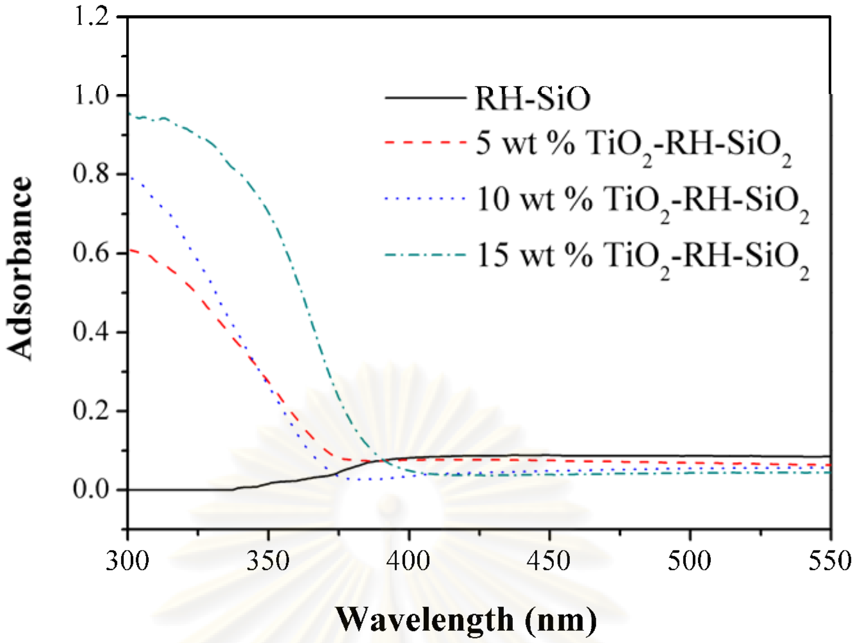


Figure 4.7 UV-Vis DR spectra of catalysts.

4.2.1.4 Scanning Electron Microscope (SEM)

The scanning electron microscopy was used to investigate the prepared materials' morphologies. RH-SiO_2 surface is quite rough (Figure 4.8 (a)). As seen for all TiO_2/RH-SiO_2 samples (Figure 4.8 (b-d)), TiO_2 fakes are scattered on the RH-SiO_2 surface. A sample of 15 wt % TiO_2/RH-SiO_2 seems to have the highest amount of titanium dioxide onto the surface area of RH-SiO_2 (as shown in Figure 4.8 (d)). From the overall results of SEM morphology, it can be linked to the BET surface area results for the decrease amount of sample surface area with more titanium dioxide content. As illustrated in Figure 4.8, the more titanium dioxide content was added, the more RH-SiO_2 surface area was blocked. Hence, the SEM analysis can be used to reconfirm the results of BET measurement technique.

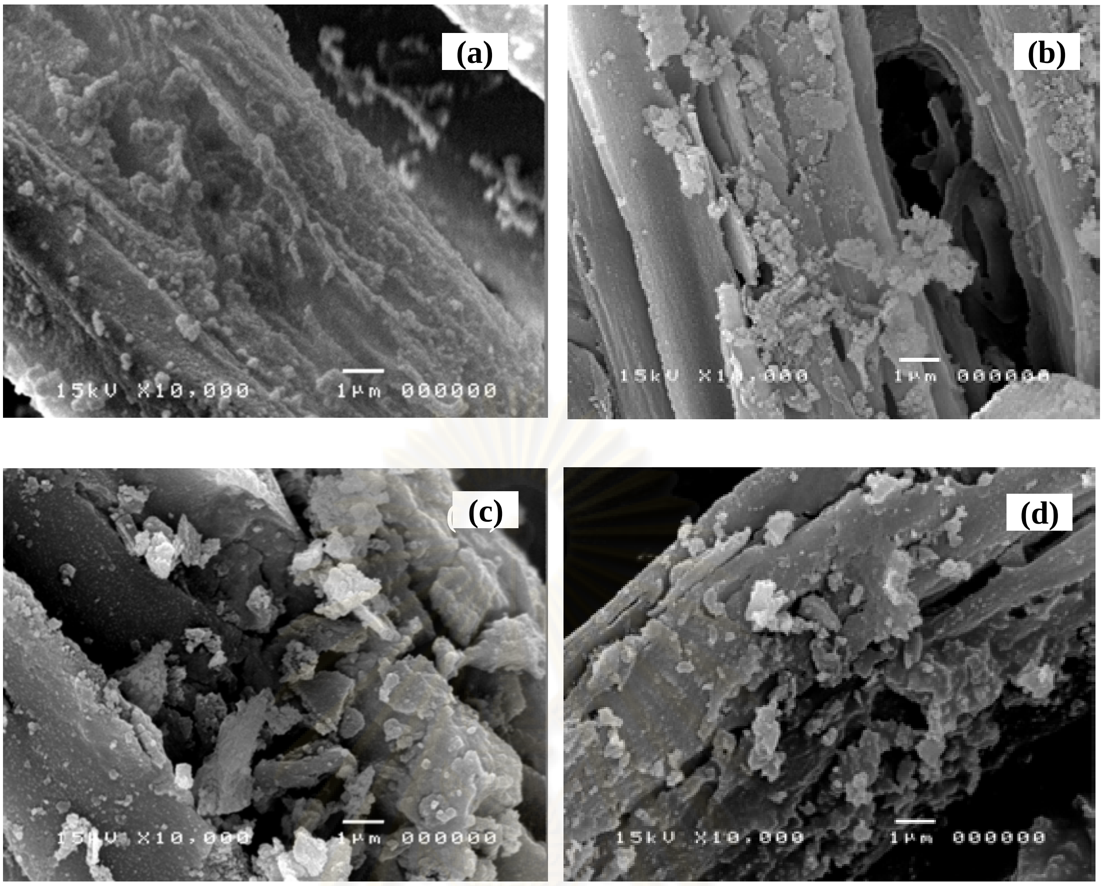
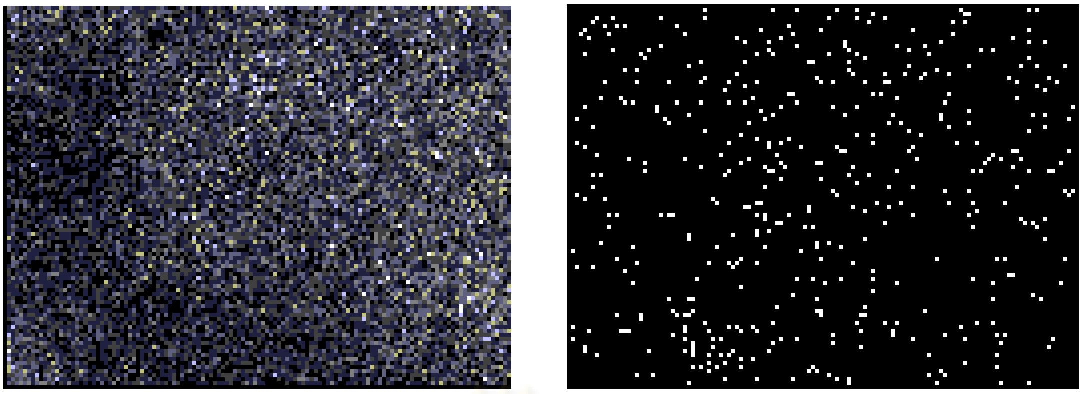


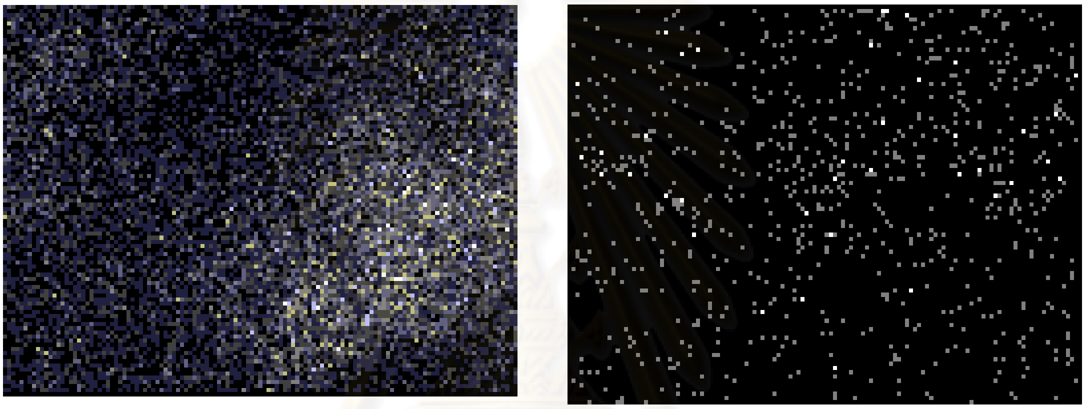
Figure 4.8 Scanning Electron Microscopy (SEM) images of (a) RH-SiO_2, (b) 5 wt % TiO_2/RH-SiO_2, (c) 10 wt % TiO_2/RH-SiO_2 and (d) 15 wt % TiO_2/RH-SiO_2 catalysts.

4.2.1.5 Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

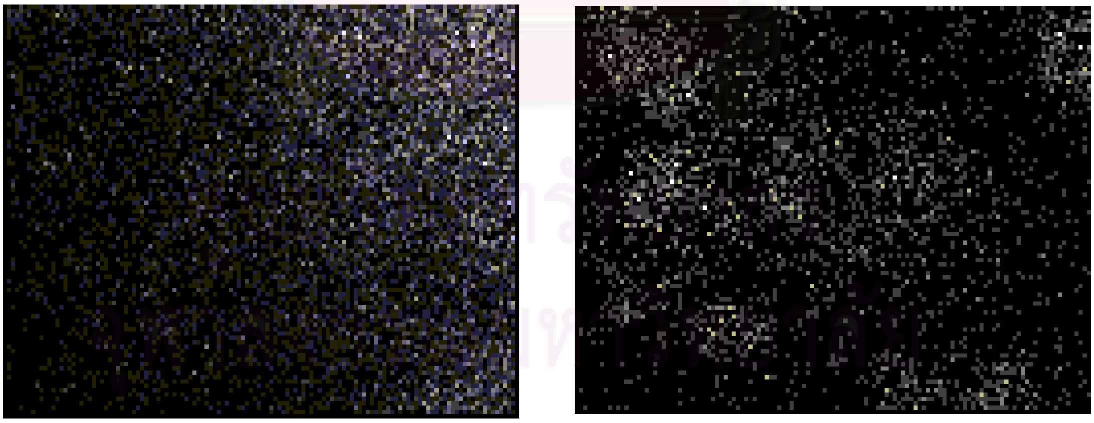
The SEM-EDS results of 5, 10, 15 wt % TiO_2/RH-SiO_2 catalysts are displayed in Figure 4.9. The morphology from the SEM-EDS technique showed the well-dispersion of each element (including Si and Ti) on the supported TiO_2/RH-SiO_2. This was to confirm the applicability of catalyst preparation technique.



a) 5 wt % TiO_2/RH-SiO_2 (Si)   b) 5 wt % TiO_2/RH-SiO_2 (Ti)



c) 10 wt % TiO_2/RH-SiO_2 (Si)   d) 10 wt % TiO_2/RH-SiO_2 (Ti)



e) 15 wt % TiO_2/RH-SiO_2 (Si)   f) 15 wt % TiO_2/RH-SiO_2 (Ti)

Figure 4.9 Dispersion of element images obtained by EDS.

4.2.2 Paraquat removal testing

TiO_2 was loaded onto the support in both powder and granular forms. However, before the photocatalytic activity evaluation, the photolysis was carried out to determine whether it affected to the overall decomposition. 10 wt % TiO_2 was selected for this study.

Figure 4.10 shows the profiles of paraquat concentrations based on three studies. One was for photolysis, meaning that there was no catalyst placing in the solution. The other two tests were carried out with catalysts placing in the solution under conditions of light-on and light-off. Considering photolytic work, there was insignificant reduction of paraquat concentration along 6 h time on stream. It indicated that paraquat required long time to degrade itself naturally, which was not comparably as fast as the following technique. When TiO_2/RH-SiO_2 is placed in the solution, two levels of reduction could be observed as shown in Figure 4.10. With the light off condition, less reduction (26%) was observed while higher reduction (80%) was presented with light on condition. It was expected that the reduction of concentration might be due to the adsorption phenomena as well as the photocatalysis. The portions were calculated between two phenomena. It was obvious that higher portion of photocatalysis could be observed rather than adsorption.

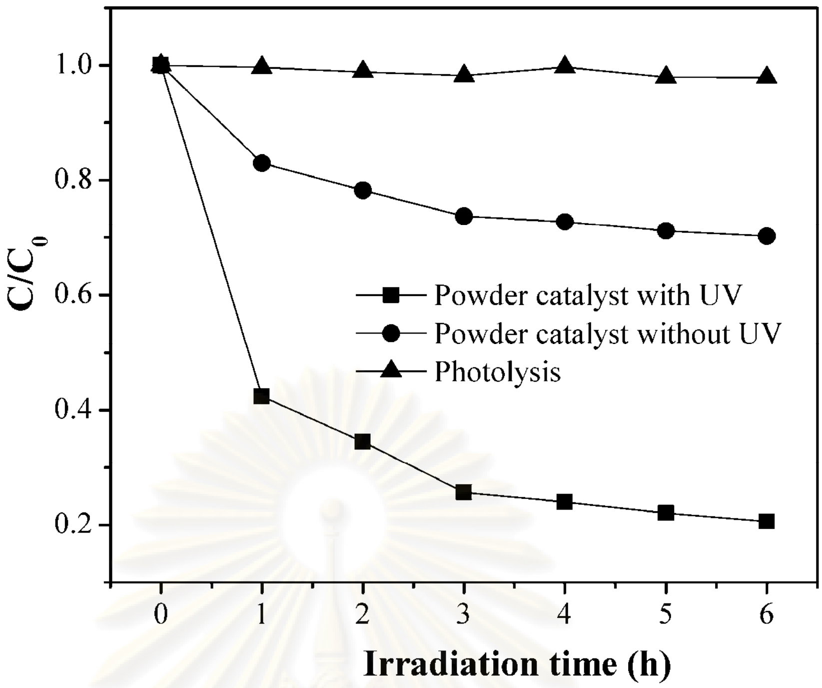


Figure 4.10 Photocatalytic degradation of paraquat (Initial concentration 5 ppm) using 10 wt % TiO_2/RH-SiO_2 with the presence and absence of UV light and photolysis.

BET surface of samples should be used to explain the results. Table 4.3 shows that BET surface area after the RH-SiO_2 was loaded with TiO_2 10 wt % is dropped from 286 to 188 m^2/g. The surface area became less when higher leading was prepared.

Table 4.3 BET surface areas of samples in powder form

Samples	**BET area (m^2g^{-1})**
RH-SiO_2	286
5 wt% TiO_2/RH-SiO_2	216
10 wt% TiO_2/RH-SiO_2	188
15 wt% TiO_2/RH-SiO_2	122

The results of paraquat removal are studied on 10 wt % TiO_2/RH-SiO_2 compared to P25 and shown in Figure 4.11. The study was done based on the same amount of TiO_2 being used. It was found that10 wt % TiO_2/RH-SiO_2 catalyst gave a higher reaction capacity than the commercial TiO_2 or P25. As a result, adsorption by RH-SiO_2 should be a key role of the reduction. This would be due to higher surface area of 10 wt % TiO_2/RH-SiO_2 catalyst (188 m^2g^{-1}) compared to the pure TiO_2 (50 m^2g^{-1}).

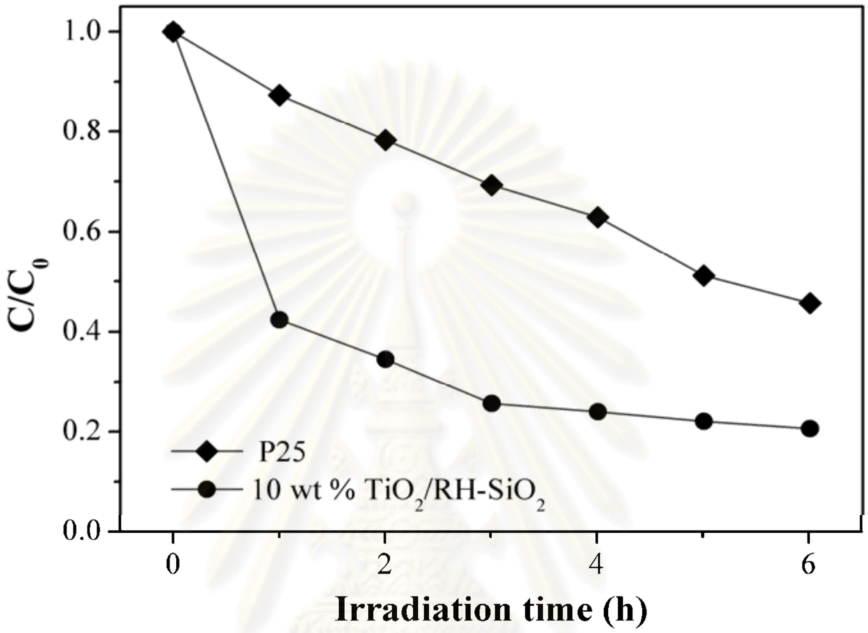


Figure 4.11 Photocatalytic degradation of paraquat (Initial concentration 5 ppm) using 10 wt % TiO_2/RH-SiO_2 and TiO_2 as a function of UV irradiation time.

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was applied to the photocatalytic degradation of paraquat and the LHHW equation was shown as following:

$$-r_A = \frac{k^*C}{1+KC}$$

Where;

$$k^* = (k)\bullet(K)$$

and after the linearization, the equation becomes

$$\frac{1}{-r_A} = \frac{1}{k*C} + \frac{1}{k}$$

Where;

r_A = reaction rate

A = paraquat

C = concentration of paraquat

K = adsorption rate constant

$k*$ = apparent rate constant

The photocatalytic of paraquat over 10 wt % TiO_2/RH-SiO_2 can be explained by Langmuir-Hinshelwood-Hougen-Watson kinetic model. The relationship of 1/(-r_A) and 1/C shows a straight line as presented in Figure 4.12. The adsorption constant (K) and the apparent rate constant ($k*$) of paraquat degradation at low concentration ($C_0 \geq$ 5 ppm) can be calculated from slope and intercept values fitted into Langmuir-Hinshelwood-Hougen-Watson equation, which are 0.4 ppm and 0.5327 hr^{-1}, respectively. The value of K was high compared to other reaction, indication that the adsorption was also an important phenomenon in the degradation. The results corresponded to the concentration profile obtained under the condition without UV, in Figure 4.10.

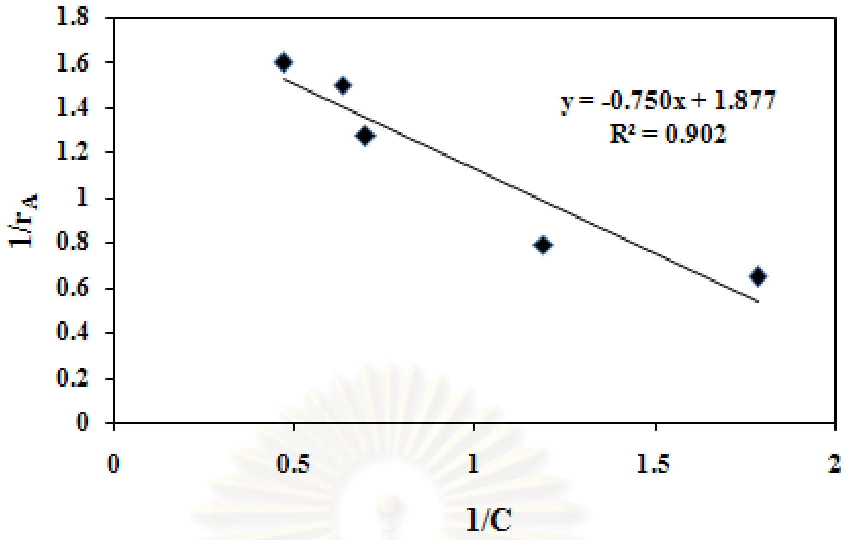


Figure 4.12 Langmuir-Hinshelwood-Hougen-Watson model for photocatalytic degradation of paraquat over 10 wt % TiO_2/RH-SiO_2.

4.2.3. Granular TiO_2/RH-SiO_2

Granular TiO_2/RH-SiO_2 images from two techniques are illustrated in this section. Smooth surface on one chemical coating material was observed. The photocatalytic degradation of 10 wt % TiO_2/RH-SiO_2 granular catalyst prepared by the extrusion and mechanical coating techniques are expressed in Figure 4.12. The result revealed that this catalyst obtained by the mechanical coating technique yielded higher degradation than the extrusion technique. This might be due to higher BET surface area, as already explained previously.

The reliability of both forms was studied. It was found that one by the mechanical coating might not be appropriate for the use, since the dissolve of coated titanium dioxide to the water was observed. It was based on hydrophilic property of TiO_2. However, it was not observed any peeling out of TiO_2 from the 10 wt % TiO_2/RH-SiO_2 catalyst via the extrusion technique. Based on the ease of preparation, the reuse reliability and the degradation potential, catalyst via the extrusion could be attractive for the photocatalysis.

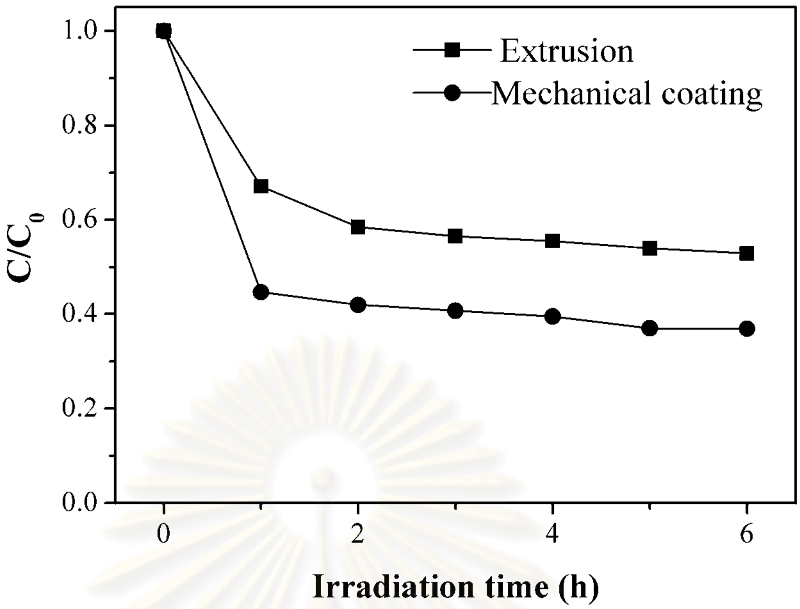


Figure 4.13 Photodegradation efficiency over granular TiO_2/RH-SiO_2 by two forming techniques.

CHAPTER V

CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

- The acid leaching method was an effective technique for the rice husk silica (RH-SiO_2) extraction and it gave 97.36% of SiO_2, providing surface area of 286 m^2g^{-1}.
- The adsorption equilibrium of paraquat over RH-SiO_2 was fitted with the Langmuir isotherm with an R^2 value of 0.9994. The maximum adsorption capacity value was 9.8039 mg/g.
- The titania supported rice husk silica (TiO_2/RH-SiO_2) catalysts were successfully prepared via impregnation method. Moreover, the titanium dioxide (TiO_2) particles were well-dispersed onto RH-SiO_2.
- After impregnation of TiO_2 with the calcined temperature of 500^{o}C for 5 h, the result revealed only the characteristic peak of TiO_2 in an anatase phase accompanied with the amorphous RH-SiO_2.
- In powder form, TiO_2/RH-SiO_2 contained TiO_2 more than 10 wt % caused the big decrease of surface area. The granular RH-SiO_2 using the mechanical coating technique had a surface are of 127 m^2g^{-1} and 48 m^2g^{-1} by extrusion technique.
- The adsorption capacities of paraquat solution at the concentration of 5, 10, 20, 30 and 40 ppm were observed by using RH-SiO_2 as an absorbent. At 5 ppm of paraquat concentration yielded the highest adsorption efficiency.
- Photocatalyst presented high adsorption in UV light region. The paraquat removal under photocatalytic reaction required adsorption simultaneously with the reaction. LHHW was fitted with R^2 value of 0.905.
- The test of catalyst pelletization was not good by mechanical coating.

5.2 Recommendations

- The Fourier Transform Infrared Spectroscopy (FT-IR) should be used in this study to identify the functional groups of the samples.
- The position set up of UV lamp should be on the top of the reactor for studying the photocatalytic efficiency of paraquat solution by a monolayer-base set up.
- Since only one step of photocatalytic reaction, has been studied, it is recommended to work on its reliability of the catalyst in several loops.

REFERENCES

Ahmad, A.E., and Adam, F. Indium incorporated silica from rice husk and its catalytic activity. Microporous and Mesoporous Materials 103 (2007): 284–295.

Cantavenera, M.J., Catanzaro, I., Loddo, V., Palmisano, L., and Sciandrello, G. Photocatalytic degradation of paraquat and genotoxicity of its intermediate products. Journal of Photochemistry and Photobiology A: Chemistry 185 (2007): 277-282.

Chakraverty, A., and Kaleemullah, S. Conversion of rice husk silica and combustible gas. Energy conversion Management 32 (1991): 565-570.

Danish, M., Sulaiman, O., Rafatullah, M., Hashim, R., and Ahmad, A. Kinetics for the removal of paraquat dichloride from aqueous solution by activated date (phoenix dactylifera) stone carbon. Bioresource, Paper and Coatings Technology Division 31(2010): 248-259.

Della, V.P., Kuhn, I., and Hotza, D. Rice husk ash as an alternate source for active silica production. Materials Letter 57 (2002): 818-821.

Diebold U. (2003), The surface science of titanium dioxide, Surface Science Reports, 48: 53-229.

Draoui, K., Denoyel, R., Chgoura, M., and Rouquerol, J. Adsorption of paraquat on minerals: a thermodynamic study. Journal Therm. Anal. Cal. 58 (1999): 597–606.

Enright, P., Novel photoelectrochemical cell for theremediation of organic compounds in water. Doctoral Dissertation, Department of Chemical and Pharmaceutical Sciences. Faculty of Science Dublin Institute of Technology, 2008.

Faust, S.D., and Aly, O.M. Chemistry of Water Treatment. 2nd edition. Florida: CRC Press LLC, 1998.

Florencio, M.H., Pires, E., Castro, A.L., Nunes M.R., Borges, C., and Costa, F.M. Photodegradation of diquat and paraquat in aqueous solutions by titanium dioxide: evolution of degradation reactions and characterization of intermediates. Chemosphere 55 (2004): 345-355.

Gao, J.C., Zou, J., Tan, X.W., and Wang, Y., Characteristics and properties of surface coated nano-TiO_2. Transaction of nonferrous metals society of China 16 (2006): 1252-1258.

Hashimoto, K., Irie, H., and Fujishima, A., TiO_2 Photocatalysis: A Historical Overview and Future Prospects. Japanese journal of applied physics 44 (2005): 8269-8285.

Hsu, S.T., and Pan, T.C. Adsorption of paraquat using methacrylic acid-modified rice husk. Bioresource Technology 98 (2007): 3617-3621.

Kanazawa, J. Behavior of herbicides with long-term application to soil. Shokucho 24 (1990): 388.

Kim, K.D., Bae, H.J., and Kim, H. T. Synthesis and growth mechanism of TiO_2-coated SiO_2 fine particles. Colloids and Surfaces A: Physicochem. Eng. Aspects 22 (2003): 163-173.

Kim, B.H., Lee, J.Y., Choa, Y.H., Higuchi, M., and Mizutani, N. Preparation of TiO_2 thin film by liquid sprayed mist CVD method. Materials Science and Engineering B 107 (2004): 289–294.

Kubiak, P., Geserick, J., Husing, N., and Mehrens, M.W. Electrochemical performance of mesoporous TiO_2 anatase. Electrochemical Performance of Mesoporous TiO_2 Anatase 175 (2008): 510-516.

Lasa, H.D., Serrano, B., and Salaices, M. Photocatalytic reaction engineering. 1th edition. New York: Springer Science and Business Media, Inc., 2005.

Lee, J.C., et al., Removal of Paraquat in Aqueous Suspension of TiO_2 in an Immersed UV Photoreactor. Journal of Chemical Engineering 20 (2003): 862-868.

Lee, S.J., Katayama, A., and Kimura, M. Microbial degradation of paraquat sorbed to plant residues. Journal of Agricultural Food Chemistry 43 (1995): 1343-1347.

Leyva, E., Moctezuma E., Hernández A., Palestino G., and H. Zamarripa. Photocatalytic Degradation of the Herbicide “Paraquat”. Chemosphere 39 (1999): 511-517.

Masel, R.I. Principles of Adsorption and Reaction of Solid Surfaces. New York: John Wiley & Sons, Inc., 1996.

Moctezuma, E., Leyva, E., Monreal, E., Villegas, N., and Infante, D. Photocatalytic degradation of the herbicide "paraquat". Chemosphere 39 (1999): 511-517.

Tennakone, K., and Kottegoda, I.R.M. Photocatalytic mineralization of paraquat dissolved in water by TiO_2 supported on polythene and polypropylene films. Journal of Photochemistry and Photobiology A: Chemistry 93 (1996): 79-81.

Thamaphat, K., Limsuwan, P. and Ngotawornchai, B. Phase characterization of TiO_2 powder by XRD and TEM. Kasetsart Journal (Nat. Sci.) 42(2008): 357 – 361.

Tsai, W.T., La, C.W., and Hsien, K.J. Adsorption kinetics of herbicide paraquat from aqueous solution onto activated bleaching earth. Chemosphere 55 (2004): 829-837.

Tsai, W.T., Hsien, K.J., Chang, Y.M., and Lo, C.C. Removal of herbicide paraquat from an aqueous solution by adsorption onto spent and treated diatomaceous earth. Bioresource Technology 96 (2005): 657-663.

Yasushiro, S., and Takayuki, H. Selective organic transformations on titanium oxide-based photocatalysts. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 9 (2008): 157-170.

Yalcin, N., and Sevinc, V. Studies on silica obtained from rice husk. Ceramics International 27 (2001): 219-224.

Yoshida, H., Lu, Y., Nakayama, H., and Hirohashi M. Fabrication of TiO_2 film by mechanical coating technique and its photocatalytic activity. Journal of Alloys and Compounds 475 (2009): 383–386.

Zeman, P., and Takabayashi, S. Nano-scale photocatalytic TiO_2 thin films prepared by magnetron. Thin Solid Films 433 (2003): 57–62.

APPENDIX

1. Calibration curve of paraquat

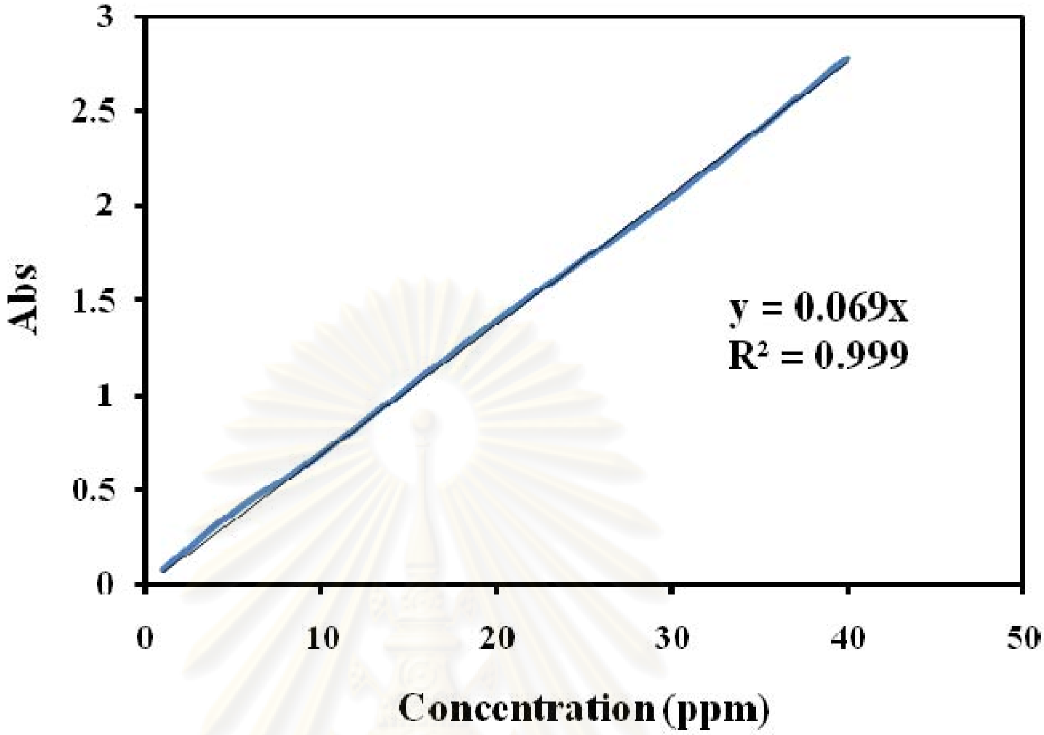


Figure A-1 Calibration curve of paraquat.

2. Adsorption capacity of paraquat with various concentrations over rice husk silica powder

Table A-1 Adsorption efficiency of 5 ppm paraquat solution using RH-SiO_2

5 ppm	Adsorption	ppm	q_e
0	0.3606	5.226087	0
10	0.0766	1.110145	4.115942
30	0.0682	0.988406	4.237681
60	0.0707	1.024638	4.201449
90	0.0824	1.194203	4.031884
120	0.0909	1.317391	3.908696
150	0.0942	1.365217	3.86087
180	0.0963	1.395652	3.830435
210	0.101	1.463768	3.762319
240	0.0966	1.4	3.826087

Table A-2 Adsorption efficiency of 10 ppm paraquat solution using RH-SiO_2

10 ppm	Adsorption	ppm	q_e
0	0.707	10.24638	0
10	0.2221	3.218841	7.027536
30	0.2307	3.343478	6.902899
60	0.264	3.826087	6.42029
90	0.2627	3.807246	6.43913
120	0.2875	4.166667	6.07971
150	0.3046	4.414493	5.831884
180	0.2967	4.3	5.946377
210	0.2714	3.933333	6.313043
240	0.3066	4.443478	5.802899

Table A-3 Adsorption efficiency of 20 ppm paraquat solution using RH-SiO_2

20 ppm	**Adsorption**	**ppm**	**q_e**
0	1.4383	20.84493	0
10	0.9146	13.25507	7.589855
30	0.9086	13.16812	7.676812
60	0.831	12.04348	8.801449
90	0.8256	11.96522	8.87971
120	0.847	12.27536	8.569565
150	0.8363	12.12029	8.724638
180	0.8472	12.27826	8.566667
210	0.8612	12.48116	8.363768
240	0.842	12.2029	8.642029

Table A-4 Adsorption efficiency of 30 ppm paraquat solution using RH-SiO_2

30 ppm	Adsorption	ppm	q_e
0	2.605	37.75362	0
10	2.1824	31.62899	6.124638
30	1.9883	28.81594	8.937681
40	1.9568	28.35942	9.394203
60	1.9638	28.46087	9.292754
90	1.9582	28.37971	9.373913
120	1.9692	28.53913	9.214493
150	1.9574	28.36812	9.385507
180	1.9669	28.5058	9.247826
210	1.979	28.68116	9.072464
240	2.605	37.75362	0

Table A-5 Adsorption efficiency of 40 ppm paraquat solution using RH-SiO_2

40ppm	Adsorption	ppm	qe
0	2.7743	40.20725	0
10	2.1401	31.01594	9.191304
30	2.1242	30.78551	9.421739
60	2.1372	30.97391	9.233333
90	2.1026	30.47246	9.734783
120	2.1277	30.83623	9.371014
150	2.1274	30.83188	9.375362
180	2.1305	30.87681	9.330435
210	2.1047	30.5029	9.704348
240	2.1161	30.66812	9.53913

3. Photocatalytic degradation of 5 ppm paraquat solution using TiO_2/RH-SiO_2 catalysts in powder form

Table A-6 Photocatalytic degradation of 5 ppm paraquat solution using 5 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	0.3464	5.02029	1
1	0.1378	1.997101	0.397806
2	0.1269	1.83913	0.366339
3	0.1243	1.801449	0.358834
4	0.1193	1.728986	0.3444
5	0.1085	1.572464	0.313222
6	0.1042	1.510145	0.300808

Table A-7 Photocatalytic degradation of 5 ppm paraquat solution using 10 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	0.3472	5.031884	1
1	0.1471	2.131884	0.423675
2	0.1197	1.734783	0.344758
3	0.089	1.289855	0.256336
4	0.0832	1.205797	0.239631
5	0.0766	1.110145	0.220622
6	0.0715	1.036232	0.205933

Table A-8 Photocatalytic degradation of 5 ppm paraquat solution using 15 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	0.3607	5.227536	1
1	0.1339	1.94058	0.371223
2	0.1099	1.592754	0.304685
3	0.0867	1.256522	0.240366
4	0.0816	1.182609	0.226227
5	0.0782	1.133333	0.216801
6	0.078	1.130435	0.216246

3. Photocatalytic degradation of 40 ppm paraquat solution using 5, 10, and 15 wt% TiO_2/RH-SiO_2 catalysts in powder form

Table A-9 Photocatalytic degradation of 40 ppm paraquat solution using 5 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	2.7179	39.38986	1
1	2.1542	31.22029	0.792597
2	1.862	26.98551	0.685088
3	1.6155	23.41304	0.594393
4	1.4311	20.74058	0.526546
5	1.3317	19.3	0.489974
6	1.1801	17.1029	0.434196

Table A-10 Photocatalytic degradation of 40 ppm paraquat solution using 10 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	2.7656	40.08116	1
1	1.9086	27.66087	0.690121
2	1.5594	22.6	0.563856
3	1.2164	17.62899	0.439832
4	0.9373	13.58406	0.338914
5	0.9021	13.07391	0.326186
6	0.8769	12.7087	0.317074

Table A-11 Photocatalytic degradation of 40 ppm paraquat solution using 15 % wt TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	2.7019	39.15797	1
1	2.0233	29.32319	0.748843
2	1.6377	23.73478	0.606129
3	1.4204	20.58551	0.525704
4	1.2341	17.88551	0.456753
5	1.0948	15.86667	0.405196
6	1.015	14.71014	0.375662

4. Photocatalytic degradation of paraquat (Initial concentration 5 ppm) using pure TiO_2 as a function of UV irradiation time and photolysis

Table A-12 Photocatalytic Degradation of 5 ppm paraquat solution using P25 catalysts.

Time	Adsorption	ppm	C/Co
0	0.3905	5.65942	1
1	0.3409	4.94058	0.872983
2	0.3057	4.430435	0.782843
3	0.2707	3.923188	0.693214
4	0.2456	3.55942	0.628937
5	0.1998	2.895652	0.511652
6	0.1783	2.584058	0.456594

Table A-13 Photolysis study of 5 ppm paraquat solution

Time	Adsorption	ppm	C/Co
0	0.3662	5.307246	1
1	0.3649	5.288406	0.99645
2	0.362	5.246377	0.988531
3	0.3597	5.213043	0.98225
4	0.3651	5.291304	0.996996
5	0.3587	5.198551	0.979519
6	0.3585	5.195652	0.978973

Table A-14 Photocatalytic degradation of 5 ppm paraquat solution using 10 wt % TiO_2/RH-SiO_2 catalysts with the absence of UV irradiation

Time	Adsorption	ppm	C/Co
0	0.3238	4.692754	1
1	0.2686	3.892754	0.829524
2	0.2387	3.45942	0.737183
3	0.2534	3.672464	0.782582
4	0.2356	3.414493	0.72761
5	0.2304	3.33913	0.71155
6	0.2275	3.297101	0.702594

5. Photocatalytic degradation of 5 ppm paraquat solution using the extruded 5 wt % TiO_2/RH-SiO_2 catalyts in granular form

Table A-15 Photocatalytic degradation of 5 ppm paraquat solution using the extruded 10 wt % TiO_2/RH-SiO_2 catalysts

Time	Adsorption	ppm	C/Co
0	0.3456	5.008696	1
1	0.2316	3.356522	0.670139
2	0.2021	2.928986	0.58478
3	0.1955	2.833333	0.565683
4	0.1918	2.77971	0.554977
5	0.1865	2.702899	0.539641
6	0.1828	2.649275	0.528935

BIOGRAPHY

Name: Miss Navaporn Kanjanasiranont

Date of Birth: December 22, 1986

Nationality: Thai

Education: 2005-2008, Bachelor Degree of Environmental Science, Faculty of Environment and Resource Studies, Mahidol University

Conference: The 17th Regional Symposium on Chemical Engineering (RSCE 2010)