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อนุภาคระดับนาโนเมตรของเงินและไอออนเงิน



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF MESOPOROUS SILICA MODIFIED WITH
3-MERCAPTOPROPYLTRIMETHOXYLANE FOR ADSORPTION OF
SILVER NANOPARTICLES AND SILVER ION

Miss Uma Pongkitdachoti



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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อนุภาคระดับนาโนเมตรของเงินถูกนำไปใช้งานอย่างแพร่หลายในผลิตภัณฑ์ต่าง ๆ เป็นสาเหตุให้เกิดการปนเปื้อนลงสู่แหล่งน้ำในสิ่งแวดล้อม โดยอนุภาคระดับนาโนเมตรของเงินสามารถปลดปล่อยไอออนเงิน และทั้งอนุภาคระดับนาโนเมตรของเงินและไอออนเงินเป็นอันตรายต่อสิ่งมีชีวิตและมนุษย์ ในงานวิจัยนี้ได้เตรียมตัวดูดซับซิลิกาที่มีรูพรุนขนาดใหญ่ด้วยวิธีการโซล-เจล โดยใช้ซิลิโคนไตรเมทิลแอมโมเนียมโบรไมด์ และกรดซิตริกเป็นเทมเพลต จากนั้นนำซิลิกาที่สังเคราะห์ได้ไปพิสูจน์เอกลักษณ์ด้วยเทคนิคเอ็กซ์เรย์ดิฟแฟรกชันและไนโตรเจนแอบซอร์บชันแอนาไลซิส ซึ่งผลการทดลองพบว่าซิลิกาที่สังเคราะห์โดยใช้กรดซิตริกเป็นเทมเพลต มีขนาดโพรงใหญ่ที่สุด (12.12 นาโนเมตร) และมีพื้นที่ผิวมากที่สุด (630.61 ตารางเมตรต่อกรัม) จากนั้นนำซิลิกานี้ไปตัดแปรผิวด้วย 3-เมอร์แคปโทโพรพิลไตรเมทอกซีไซเลน และพิสูจน์เอกลักษณ์ด้วยเทคนิคการวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยสมบัติทางความร้อน เมื่อนำซิลิกาที่ผ่านการตัดแปรผิวไปใช้ดูดซับไอออนเงินและอนุภาคระดับนาโนเมตรของเงิน ผลการทดลองพบว่าซิลิกาที่ผ่านการตัดแปรผิวสามารถดูดซับไอออนเงินและอนุภาคระดับนาโนเมตรของเงินได้ โดยสภาวะที่เหมาะสมสำหรับการดูดซับไอออนเงินคือ ค่าพีเอชของสารละลายเริ่มต้นเป็น 3 และเวลาที่เหมาะสมในการดูดซับคือ 120 นาที ในขณะที่เวลาที่เหมาะสมในการดูดซับอนุภาคระดับนาโนเมตรของเงินคือ 480 นาที พฤติกรรมการดูดซับไอออนเงินลงบนผิวของซิลิกา เป็นไปตามแบบจำลองทางจลนพลศาสตร์แบบปฏิกิริยาอันดับสองเทียมและแลงเมียร์ไอโซเทิร์ม โดยความจุสูงสุดของการดูดซับไอออนเงินเป็น 114.9 มิลลิกรัมต่อกรัม ส่วนพฤติกรรมการดูดซับอนุภาคระดับนาโนเมตรของเงิน เป็นไปตามแลงเมียร์ไอโซเทิร์ม โดยความจุสูงสุดของการดูดซับอนุภาคระดับนาโนเมตรของเงินเป็น 92.59 มิลลิกรัมต่อกรัม และส่วนสุดท้ายซิลิกาที่ได้จากสังเคราะห์และตัดแปรผิวสามารถนำไปใช้ดูดซับไอออนเงินและอนุภาคระดับนาโนเมตรของเงินในตัวอย่างน้ำเสียและผลิตภัณฑ์ที่มีส่วนผสมของอนุภาคระดับนาโนเมตรของเงินได้

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UMA PONGKITDACHOTI: SYNTHESIS OF MESOPOROUS SILICA MODIFIED WITH 3-MERCAPTOPROPYLTRIMETHOXYSILANE FOR ADSORPTION OF SILVER NANOPARTICLES AND SILVER ION. ADVISOR: ASST. PROF. FUANGFA UNOB, Ph.D., 50 pp.

Silver nanoparticles are widely used in nano-consumer products and it may cause the contamination in environmental water source. Silver nanoparticles and the released silver ions have adverse effect on living organism and human. In this research, silica that had large pore size was prepared by sol-gel method using CTAB and citric acid as templates. The materials were characterized by x-ray diffraction and nitrogen adsorption analysis. The results showed that the silica synthesized by using citric acid template had the largest pore size (12.12 nm) and highest surface area (630.61 m²/g). The obtained silica was modified with 3-mercaptopropyl trimethoxysilane and characterized by thermal gravimetric analysis. The modified silica was used to adsorb silver ions and silver nanoparticles. The results showed that this silica can remove silver ions and silver nanoparticles from solutions. The suitable condition for adsorption silver ions was the initial pH 3 and 120 min of contact time. The suitable contact time for adsorption silver nanoparticles was 480 min. The adsorption behavior of silver ions followed pseudo-second order kinetics model and Langmuir isotherm with maximum adsorption capacity of 114.9 mg/g and the adsorption behavior of silver nanoparticles followed Langmuir isotherm with maximum adsorption capacity of 92.59 mg/g. Finally, this silica was successfully used to adsorb silver ions and silver nanoparticles in wastewater and nano-consumer product.

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CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF FIGURES	x
LIST OF TABLES	xii
LIST OF ABBREVIATIONS	xiii
CHAPTER I INTRODUCTION.....	1
1.1 Statement of the problem	1
1.2 Objectives of the thesis.....	2
1.3 Scope of the thesis.....	2
1.4 The benefits of this thesis.....	2
CHAPTER II THEORY AND LITERATURE REVIEW	3
2.1 Information about silver.....	3
2.1.1 Silver ions and silver nanoparticles	3
2.1.2 Removal of silver ions in aqueous solution	3
2.2 Adsorbent	4
2.2.1 Information about silica	4
2.2.2 Synthesis of silica.....	4
2.3 Adsorption	6
2.3.1 Physical adsorption (physisorption)	6
2.3.2 Chemical adsorption (chemisorption).....	6

	Page
2.3.3 Adsorption kinetics.....	6
2.3.4 Adsorption isotherm	8
2.4 Literature review	9
CHAPTER III EXPERIMENTS.....	12
3.1 Apparatus.....	12
3.2 Chemicals and reagents	13
3.3 Synthesis of mesoporous silica.....	14
3.4 The functionalization of mesoporous silica by 3-mercaptopropyl trimethoxysilane (silica-MPTMS).....	15
3.5 Characterization of the obtained silica	16
3.6 Adsorption study.....	16
3.7 Application to real samples.....	19
CHAPTER IV RESULTS AND DISCUSSION	20
4.1 Characterization of mesoporous silica	20
4.1.1 X-ray diffraction (XRD)	20
4.1.2 Porosity and surface area of synthesized mesoporous silica.....	21
4.1.3 Thermal gravimetric analysis (TGA).....	24
4.1.4 Transmission electron microscopy (TEM).....	25
4.2 Adsorption study.....	26
4.2.1 Adsorption of silver ions	26
4.2.2 Adsorption of silver nanoparticles	35
4.3 Application in real samples	42
CHAPTER V CONCLUSION	43

	Page
REFERENCES	45
VITA.....	50



LIST OF FIGURES

	Page
Figure 2.1 Structure of silica surface	4
Figure 2.2 The sol-gel process.....	5
Figure 4.1 XRD pattern of mesoporous silica prepared by using CTAB (A), CTAB in dilute solution (B) and citric acid (C) as templates.....	21
Figure 4.2 Nitrogen adsorption-desorption isotherm of mesoporous silica using CTAB template (A) CTAB template in dilute solution (B) and citric acid template (C).....	22
Figure 4.3 Nitrogen adsorption-desorption isotherm of silica-MPTMS.	24
Figure 4.4 Pore size distributions of the unmodified and modified mesoporous silica.....	24
Figure 4.5 TGA curve of mesoporous silica and silica-MPTMS.....	25
Figure 4.6 TEM images of silica-MPTMS.	25
Figure 4.7 The effect of initial pH on the adsorption efficiency of silver ions by silica-MPTMS; initial silver concentration 45 mg/L.	27
Figure 4.8 The influence of contact time on the adsorbed amount onto silica-MPTMS; initial silver ion concentration 45 ppm, initial pH of solution 3.	28
Figure 4.9 The linear plot of pseudo-first order adsorption kinetics using experimental data.	30
Figure 4.10 The linear plot of pseudo-second order adsorption kinetics using experimental data.	30
Figure 4.11 The adsorption isotherm of silver ions adsorption on the silica-MPTMS; initial pH 3; contact time 120 min.....	32

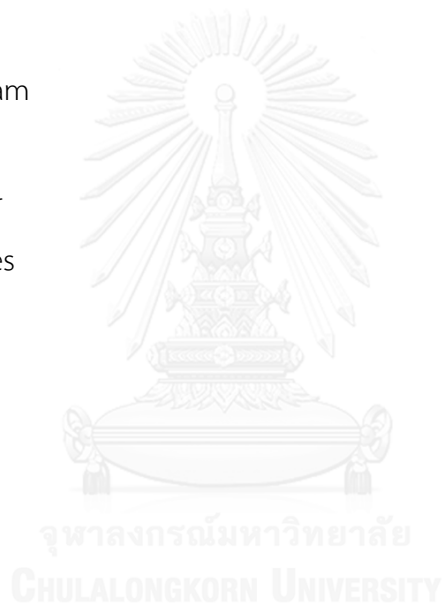
Figure 4.12	Linear Langmuir plot of silver ions adsorption on silica-MPTMS.....	33
Figure 4.13	Linear Freundlich plot of silver ions adsorption on silica-MPTMS.....	34
Figure 4.14	TEM images of silica-MPTMS-Ag with silver as dark spots on silica.	35
Figure 4.15	The effect of contact time on the adsorption of the silver nanoparticles and total silver (in the solution) onto silica-MPTMS.....	36
Figure 4.16	The pseudo-first order kinetics plot of silver nanoparticles adsorption.....	37
Figure 4.17	The pseudo-second order kinetics plot of silver nanoparticles adsorption.....	37
Figure 4.18	The adsorption isotherm of silver nanoparticles and total silver (in the solution) adsorption onto silica-MPTMS.....	39
Figure 4.19	Linear Langmuir plot using experimental data of silver nanoparticles adsorption on silica-MPTMS.....	39
Figure 4.20	Linear Freundlich plot using experimental data of silver nanoparticles adsorption on silica-MPTMS.....	40
Figure 4.21	TEM image of silica-MPTMS-AgNPs.....	41

LIST OF TABLES

	Page
Table 3.1: List of analytical apparatus	12
Table 3.2: List of chemicals.....	13
Table 3.3: The mole ratio of mixture for synthesis mesoporous silica	14
Table 4.1: The pore size range (average) and surface area of all mesoporous silica.....	23
Table 4.2: Langmuir isotherm parameter of the silver ions adsorption by silica-MPTMS	34
Table 4.3: Freundlich isotherm parameter of the silver ions adsorption by silica-MPTMS	34
Table 4.4 Pseudo-first order and pseudo-second order kinetics parameters of the silver nanoparticles adsorption by silica-MPTMS.....	38
Table 4.5: Langmuir isotherm parameter of the silver nanoparticles adsorption by silica-MPTMS	40
Table 4.6: Freundlich isotherm parameter of the silver nanoparticles adsorption by silica-MPTMS.....	40
Table 4.7: The results of application of silica-MPTMS in real samples	42
Table 5.1: The adsorption behavior and selected conditions for adsorption silver ions and silver nanoparticles.....	43

LIST OF ABBREVIATIONS

°C	degree Celsius
ICP-OES	inductively coupled plasma-optical emission spectrometry
XRD	X-ray diffractometer
TGA	thermogravimetric analysis
TEM	transmission electron microscopy
AgNPs	silver nanoparticles
MPTMS	3-mercaptopropyltrimethoxysilane
g	gram
mg	milligram
L	liter
mL	milliliter
min	minutes



CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Silver and its compounds are widely used in various applications e.g. currency, decorative item, mirror, etc. Recently, silver nanoparticles have also been increasingly used in many sectors. The well-known properties of silver nanoparticles are anti-bacterial and anti-fungal [1]. Hence, it is used in cosmetic, medical applications, laundry and home care products. Although, silver nanoparticles have many advantages, it can release silver ions and both are toxic to organs of human and some bacterial beneficial to ecology [2-4]. There are some researches investigating the leaching of silver nanoparticles and silver ions from nano-consumer products including sock, clothing, and washing machine. It was founded that silver nanoparticles and silver ions were released from these products [5, 6] and in this case, these species may enter into sewer systems. Therefore, silver nanoparticles and silver ions emission content should be controlled.

Adsorption is the one of most popular technique for removal of silver ions because it is simple and low cost. Silica is commonly used as adsorbent for heavy metals because it has high porosity and large surface area to volume ratio. [7-9]. Moreover, silica can be synthesized easily by sol-gel method and the pore size can be adjusted to suit the application by using different templates, such as citric acid and surfactants [10, 11]. Although many researchers have studied the removal of silver ions by adsorption process [12-14], few studies have been focused on the elimination of silver nanoparticles. Some researches proposed the use of hollow sphere silica for adsorption of silver nanoparticles [11].

In this research, we propose the preparation of mesoporous silica by sol-gel method using different templates including CTAB and citric acid and modification the surface of silica with 3-mercaptopropyltrimethoxysilane for adsorption of silver nanoparticles and silver ions.

1.2 Objectives of the thesis

The objective of the thesis are listed below,

- To synthesize mesoporous silica modified with 3-mercaptopropyl trimethoxysilane.
- To evaluate the efficiency in silver nanoparticle and silver ion adsorption by the proposed silica and investigate the effect of adsorption parameter.

1.3 Scope of the thesis

The scope of this thesis covers the preparation of mesoporous silica by sol-gel method using different templates including CTAB and citric acid and the modification the silica with 3-mercaptopropyltrimethoxysilane. The obtained silica was characterized by X-ray diffraction spectroscopy (XRD), nitrogen adsorption analysis, Infrared spectroscopy (IR) and thermogravimetric analysis (TGA).

Next, in the study of silver ions and silver nanoparticles adsorption, the effect of pH, adsorption kinetics, adsorption isotherms was studied. Finally, the obtained material was used to adsorb silver ions and silver nanoparticles from wastewater. The content of silver ions and silver nanoparticles were determined by ion selective electrode (ISE), inductively coupled plasma – optical emission spectrometry (ICP-OES) and UV-vis spectrophotometry.

1.4 The benefits of this thesis

To obtain an adsorbent for removal of silver nanoparticles and silver ions from wastewater

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Information about silver

2.1.1 Silver ions and silver nanoparticles

Elemental silver and silver compounds have been used in many applications including in industrial, medical and decoration sector [15]. Recently, silver nanoparticles have drawn a lot of interest due to its unique properties and a number of scientists have developed several easy methods for silver nanoparticles synthesis [16, 17]. Silver nanoparticles are particles of elemental silver that have diameter size between 1-100 nm. Among its benefits, silver nanoparticles are well known for its antibacterial and antiviral properties [1]. They are often added in cleaning product and cosmetics. The mechanism of antibacterial and antiviral is not clear and many different mechanisms are suggested. One of the proposed mechanisms [4] involves the penetration of silver nanoparticles into cell of bacterial or virus and the adverse effect of silver ions released from the particles. These silver ions (as soft Lewis acid) may bind with sulfur atom (S) or phosphorous atom (P) (as soft Lewis base) of cell component and cause cell death. Although silver nanoparticles have many benefits, silver nanoparticles that are released from nano-consumer product may cause good bacterial or virus in environment death and have undesirable effects to the ecology system [18]. Moreover, both of silver ions and silver nanoparticles also have adverse effect on human [2]. Therefore, the removal of silver nanoparticles and silver ions from wastewater is necessary.

2.1.2 Removal of silver ions in aqueous solution

Many researches proposed the removal of silver ions from aqueous solution by several methods including adsorption, ion exchange, membrane separation, coagulation and electrolysis [19-23]. Adsorption is one of the most commonly used techniques for removal of silver ions and silver nanoparticles due to its simplicity and low cost for operation.

2.2 Adsorbent

An adsorbent is a material that has the ability to extract target analyte from gases, liquids or solids. In this work, the adsorbents of interest are the materials that have large pore size and high surface-to-volume ratio and silica is chosen for silver nanoparticles adsorption.

2.2.1 Information about silica

Silica is an inorganic polymer that contains siloxane (Si-O-Si) in the main structure. The functional group on the surface of silica is silanol (Si-OH) that can be divided into 3 types; isolated, vicinal and geminal silanol groups as shown in figure 2.1 [24]. Silica is one of the commonly used adsorbents for adsorption process. It can be synthesized via a simple method and its pore size can also be adjusted depending on the method of synthesis [11]. Moreover, the surface of the silica can be modified with various functional groups in order to make it more specific to target analytes.

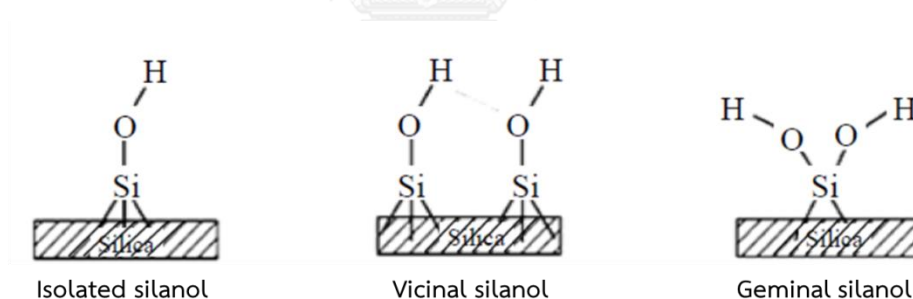


Figure 2.1 Type of silanol groups on silica surface [24]

2.2.2 Synthesis of silica

Silica can be obtained through several synthesis routes. The sol-gel process is one of the simple processes for synthesis of silica. The sol-gel method can be described as the formation of an oxide network through condensation reaction of silica precursor (e.g. tetraethyl orthosilicate, TEOS) in liquid phase. The steps of sol-gel process [25, 26] is shown below;

- Step 1: The different stable solutions of silica precursor in the solution are formed and this is called the sol process. The templates can be added in this step and the final product would have pore size related to the size of the template added.
- Step 2: This step is called gelation which is the formation of oxide network through the condensation reaction that results in a dramatic increase in the viscosity of the solution. The product from this step is small silica particles.
- Step 3: This step concerns the aging of gel. The condensation reactions continue until the gel transforms into a solid mass and the solvent in the gel pores are removed. This step is the aggregation of the particles and the growth of silica structure.
- Step 4: This step is the gel drying. Water and other volatile liquid are evaporated from the gel network. There are the fundamental changes in the structure of the gel.
- Step 5: In this step, the densification and decomposition can occur when the obtained product was calcined at high temperatures. The product network can be collapsed and remaining organic species including organic templates are volatilized.

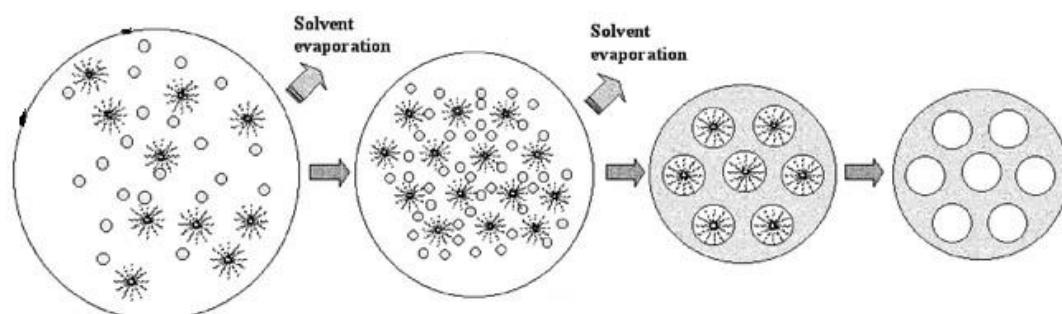


Figure 2.2 The sol-gel process [26]

2.3 Adsorption

Adsorption is the process that atoms, ions or molecules from gas or liquid phase (adsorbate) accumulate on the surface of adsorbent via mass transfer process [27]. The adsorption can be divided into 2 types; physical adsorption and chemical adsorption.

2.3.1 Physical adsorption (physisorption)

Physical adsorption is the process that occurs via intermolecular force or Van der Waals forces between adsorbate (atoms, ions or molecules) and surface of adsorbent. This interaction is not specific and the adsorbate can accumulate as multilayer on the surface of adsorbent.

2.3.2 Chemical adsorption (chemisorption)

Chemical adsorption is the process that occurs through chemical bond formation between adsorbate and the specific active site of adsorbent. This interaction is much stronger than those taking place in physical adsorption. The layer of adsorbates that accumulate on adsorbent surface would be monolayer and the adsorption would be irreversible (or slightly reversible) due to the bonding between the specific sites of adsorbent surface with adsorbate. Therefore, the adsorbed amount depends on the number of specific sites on the surface of adsorbent.

2.3.3 Adsorption kinetics

The kinetics of adsorption describes the uptake rate of adsorbate at liquid-solid interface [11, 28-30]. An order of kinetics is predicted by fitting the experimental results to the adsorption kinetics model and the kinetics parameters can be obtained by the calculations. It is used to design sorption system and describe the adsorption behaviors of the studied adsorbate on the adsorbent of interest.

i. Pseudo first order kinetics model

The pseudo first order kinetics model is demonstrated by the eq. 2.1 to 2.2;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.1)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2.2)$$

where, q_t is the sorption capacity at time t (mg/g)

q_e is the sorption capacity at equilibrium (mg/g)

k_1 is the rate constant of the pseudo-first order adsorption (min^{-1})

t is time (min)

A plot of $\log(q_e - q_t)$ versus t , gives a slope and intercept of $-k_1/2.303$ and $\log q_e$, respectively.

ii. Pseudo second order kinetics model

The pseudo-second order kinetics model was developed with assumption that the adsorption occurs via chemisorption and the pseudo-second order kinetics equation is given in eq. 2.3 to 2.6;

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.3)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (2.4)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2.5)$$

$$h = k_2 q_e^2 \quad (2.6)$$

where, q_t is the sorption capacity at time t (mg/g)

q_e is the sorption capacity at equilibrium (mg/g)

k_2 is the rate constant of the pseudo-second order adsorption (g/mg min)

h is the initial sorption rate (mg/g min)

t is time (min)

Plotting t/q_t against t , gives a slope and intercept of $1/q_e$ and $1/h$, respectively. Then, k_2 can be calculated by using eq. 2.6.

2.3.4 Adsorption isotherm

Adsorption isotherm is the adsorption of adsorbate on the surface of an adsorbent at thermodynamic equilibrium and constant temperature [11, 31]. Several adsorption isotherm models have been developed for describing the adsorption of adsorbate from aqueous solution on adsorbent at equilibrium including Langmuir and Freundlich model.

i. Langmuir isotherm

Langmuir model assuming the monolayer adsorption of adsorbates on homogeneous surface of adsorbent is expressed in eq. 2.7 and it can be rearranged to linear equation form as written in eq. 2.8;

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.7)$$

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2.8)$$

where, C_e is the equilibrium concentration of adsorbate in bulk solution

(mg/L) **CHULALONGKORN UNIVERSITY**

q is the adsorbed amount of adsorbate at equilibrium (mg/g)

q_m is the maximum adsorbed amount of adsorbate (mg/g)

K_L is Langmuir constant related to free energy adsorption (L/mg)

The values of q_m and K_L can be obtained from the slope and intercept of the linear plot between C_e/q against C_e , respectively.

ii. Freundlich isotherm

Freundlich isotherm model was developed based on the assumption of multilayer adsorption on heterogeneous surface. The Freundlich equation is shown in eq. 2.9 and the linear form of Freundlich equation is given in eq. 2.10;

$$q_e = K_f C_e^{1/n} \quad (2.9)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.10)$$

where, q_e is the adsorbed amount of adsorbate at equilibrium (mg/g)

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

K_f is Freundlich constant related to adsorption capacity (mg/g)

n is Freundlich constant related to adsorption intensity

The linear plot of $\log q_e$ versus $\log C_e$, gives a slope and intercept of $1/n$ and $\log K_f$, respectively.

2.4 Literature review

Recently, many researchers developed the method for determination of silver leaching from nano-consumer products including nano-sock fabrics and nano-washing machine.

Benn and Westerhoff [6] developed a method for determination of silver released from commercial nano-sock fabrics. They found that the product contained 31.3 mg of silver in sock. Then, this sock was immersed in 500 mL of deionized water and the observed concentration of silver leached from sock into water was 1.30 mg/L.

Farkas et al. [5] measured the concentration of silver that could be released from nano-washing machine. The result showed that the concentration of silver in runoff from nano-washing machine was 0.011 mg/L. Therefore, removal of silver nanoparticles and silver ions from wastewater is necessary.

Some researchers reported the removal of silver nanoparticles as shown as follows.

Khan et al. [32] investigated the removal of silver nanoparticles by *Aeromonas punctata*. *Aeromonas punctata* with dose of 1×10^7 CFU (colony forming unit) per mL was able to remove 4.42 mg/L of silver nanoparticles.

Gicheva and Yordanov [19] studied the removal of citrate-coated silver nanoparticles from aqueous solution using activated carbon. The maximum adsorbed amount of silver nanoparticles was 65 mg/g activated carbon.

Oh et al. [20] reported the removal of bare silver nanoparticles, citrate and polyvinylpyrrolidone stabilized silver nanoparticles using activated sludge. This activated sludge could remove silver nanoparticles in aqueous solution with maximum adsorbed amount of 89.09 mg silver nanoparticles/g.

Sim et al. [11] compared the efficiency of unimodal (small pore size, 2.3 nm) and bimodal (small and large pore size, 2.3 and 130 nm) nanoporous silica modified with aminopropyltriethoxysilane in the removal of silver nanoparticles. The result showed that the bimodal nanoporous silica could remove silver nanoparticles better than the unimodal nanoporous silica. It was because the bimodal nanoporous silica had large pore size (130 nm).

From the literature reviews, silver nanoparticles could be removed by several materials. Herein, we focused on the synthesis of silica that had large pore size. There were several researches reporting the synthesis of silica with large pores by sol-gel method using different template shown as follows.

Nguyen et al. [33] synthesized silica by modified stöber method using polystyrene sulfonate and polyacrylic acid. The obtained silica was hollow sphere with diameter of 100 to 300 nm.

Takahashi et al. [34] prepared silica by sol-gel method using citric acid template. The result showed that the obtained silica had high surface area (ca. 1000 m^2/g) and large pore size (ca. 10 nm). Lee et al. [10] also prepared silica by sol-gel method using citric acid template and the obtained silica has pore diameter of 2-15 nm.

Furthermore, Boonamnuyvitaya et al. [35] studied the synthesis of silica by sol-gel method using hexadecyltrimethylammonium bromide (CTAB) template. This obtained silica had pores with diameter of 1-100 nm.

There are several researches reporting the functionalized silica for silver ions removal as shown below.

Ladhe et al. [21] studied theoretical analysis of the pseudo-second order kinetics model of adsorption of silver ions onto mesoporous silica functionalized with thiol group. The result showed that this adsorption could fit with the model.

Lu et al. [15] used thiol-functionalized silica-mixed matrix membranes for adsorption of silver ions from aqueous solutions. The results showed that the maximum adsorption capacity of 227 mg/g was obtained.

Quang et al. [12] studied the adsorption of silver ions using silica gel grafted with thiol-functional groups. The maximum adsorption capacity of this silica was 75.8 mg/g.

In this work, mesoporous silica that had large pore size was prepared by sol-gel method using different templates including CTAB, CTAB in dilute solution and citric acid. The first method, was modified from stöber method [8] using CTAB template of which the micelles growth was obtained by sodium nitrate [36]. In the second method, silica was formed in dilute solution in the presence of CTAB and sodium nitrate. In the last method, silica was synthesized by sol-gel method using citric acid template.

After that, the silica that had largest pore diameter and highest surface was modified by 3-mercaptopropyltrimethoxysilane. Lastly, the obtained silica was used for adsorption of silver ions and silver nanoparticles from aqueous solution.

CHAPTER III

EXPERIMENTS

In this work, mesoporous silica modified with 3-mercaptopropyltrimethoxysilane for adsorption of silver ions and silver nanoparticles was prepared. The experimental section is divided into 2 parts:

- I. Preparation of mesoporous silica
 - Synthesis of mesoporous silica
 - Modification of mesoporous silica by 3-mercaptopropyl trimethoxysilane
 - Characterization of materials
- II. Adsorption study
 - Adsorption of silver ions
 - Adsorption of silver nanoparticles
 - Application to real samples

3.1 Apparatus

Table 3.1: List of analytical apparatus

Apparatus	Manufacturing/Models
Centrifuge	Sanyo/Centaur2
Inductively coupled plasma-optical emission spectroscopy (ICP-OES)	Thermo/iCAP 6000 Series
Ion selective electrode (ISE-Silver electrode)	In-house made electrode [37]
Surface area analyzer	BEL Japan/BELSORP-mini
Oven	Memmert/UM 500
pH meter	Mettler TOLEDO/Seven compact model
Thermal gravimetric analyzer	Perkin-Elmer/Pyris1

Table 3.1: List of analytical apparatus (continued)

Apparatus	Manufacturing/Models
Transmission electron microscope (TEM)	JOEL/JEM-2100
UV-visible spectrophotometer	Hewlett Packard/HP 8453
X-ray diffraction spectrometer (XRD)	Bruker AXS/Diffractometer D8

3.2 Chemicals and reagents

3.2.1 Chemicals

All chemicals used in this research were of analytical grade.

Table 3.2: List of chemicals

Chemicals	Supplies
Ammonium hydroxide (NH ₄ OH)	Merck
Citric acid (CA)	Carlo erba
Ethanol	Merck
Hexadecyltrimethylammonium bromide (CTAB)	Fluka
Nitric acid (HNO ₃)	Merck
Silver standard solution (1000 mg/L)	Merck
Sodium borohydride (NaBH ₄)	Sigma-aldrich
Sodium hydroxide (NaOH)	Merck
Sodium nitrate (NaNO ₃)	Carlo erba
Soluble starch	Merck
Tetraethyl orthosilicate (TEOS)	Sigma-aldrich
Toluene	Carlo erba
3-Mercaptopropyltrimethoxysilane (MPTMS)	Sigma-aldrich

3.2.2 Preparation of reagents

All of reagents were prepared by using milliQ water.

Silver solutions: silver solutions were prepared by dilution of 1000 mg/L stock standard solution to required concentrations.

Solution for pH adjustment: Nitric acid (HNO_3 , 1, 3 and 5%v/v) or sodium hydroxide (NaOH , 0.1 and 1 M) solutions were prepared daily by dilution of nitric acid 65% or dissolving appropriate amount of sodium hydroxide in milliQ water, respectively.

Sodium nitrate solution: Sodium nitrate solution (NaNO_3 , 0.05 M) used to control ionic strength of solution was prepared daily by dissolving calculated amount of NaNO_3 in milliQ water.

Soluble starch: Soluble starch (2%) used to stabilize silver nanoparticles was prepared daily by dissolving calculated amount of soluble starch in milliQ water.

Silver nanoparticles solution: Silver nanoparticles (AgNPs) were prepared by reducing silver ions from silver nitrate with sodium borohydride using starch as stabilizer [38].

3.3 Synthesis of mesoporous silica

Sol-gel method was used to synthesize mesoporous silica. In this work, hexadecyltrimethylammonium bromide (CTAB) and citric acid (CA) were used as template for pore formation in silica. The mole ratio of TEOS, NH_4OH and template in each method is shown in the table 3.3.

Table 3.3: The mole ratio of mixture for synthesis mesoporous silica

Method	TEOS	H_2O	EtOH	NH_4OH
CTAB template	1	60	-	0.3
CTAB template (in dilute solution)	1	2333.9	536.1	16.29
CA template	1	53.6	40.7	0.086

In CTAB template method, mesoporous silica was synthesized by using CTAB of which the micelles growth was induced by NaNO_3 [8, 36]. CTAB (79 mg) was dissolved in 0.01 M of sodium nitrate solution (template solution). TEOS (2.5 mL) and

NH_4OH (6 mL) was slowly dropped into the template solution and stirred at 30 °C for 30 min. Then, this mixture was stirred continuously at room temperature for 24 hr. After that, the mixture was dried in an oven at 120 °C for 12 h and calcined at 550 °C for 8 h to remove CTAB template.

In CTAB template in dilute solution system, mesoporous silica was synthesized by using CTAB of which the micelles growth was induced by NaNO_3 and silica was formed in dilute solution [8, 13, 36]. CTAB (300 mg) was dissolved in 0.5 M of sodium nitrate solution (template solution). TEOS (0.43 mL) was dissolved in ethanol (60 mL). This mixture and NH_4OH (1.2 mL) was slowly dropped into the template solution and stirred at 30 °C for 30 min. After that, the rest of the procedure was the same as performed in CTAB template method.

In citric template method [10], TEOS (2.23 mL) was dissolved in ethanol (23 mL). A solution of diluted NH_4OH (0.09 M) was prepared in milliQ water. Then, the solution of NH_4OH was added slowly into the solution of TEOS and the mixture was stirred vigorously at 50 °C for 3 h. After that, 1.9 g of citric acid was added into the mixture and stirred continuously at room temperature for 10 min. After that, the mixture was dried in an oven at 70 °C for 24 h and calcined at 500 °C for 2 h to remove citric acid template.

3.4 The functionalization of mesoporous silica by 3-mercaptopropyl trimethoxysilane (silica-MPTMS)

The thiol functionalized silica-MPTMS was prepared as follows [8]. A portion of 500 mg of mesoporous silica was dispersed into 125 mL of toluene and 1.8 mL of 3-mercaptopropyltrimethoxysilane was slowly dropped into the mixture. Then, the mixture was refluxed at 110-120 °C under continuous stirring for 5 h. The obtained thiol functionalized mesoporous silica was recovered by centrifugation and washed several times with ethanol and milliQ water, respectively.

3.5 Characterization of the obtained silica

X-ray diffraction technique (XRD) was used to observe the crystalline structures of the prepared mesoporous silica.

The porosity and surface area of the obtained mesoporous silica were measured by the nitrogen adsorption analysis and the adsorption data were fitted to Brunauer-Emmett-Teller (BET) model.

Thermal gravimetric analysis (TGA) was used to determine the thermal stability of the silica-MPTMS.

Transmission electron microscopy (TEM) was used to observe the morphology of silica-MPTMS before and after adsorption of silver nanoparticles.

3.6 Adsorption study

All experiments were performed in triplicate using batch method.

3.6.1 Adsorption of silver ions

Silver ions solution used in the investigation of the effect of various adsorption parameters was prepared from silver standard solution (1000 mg/L) and the solution ionic strength was controlled with 0.05 M of sodium nitrate solution. The adsorption experiment of silver ions was performed in triplicate using batch method. The mixture of silver ions solutions and silica-MPTMS was stirred at room temperature for a specific period of time and the solid was separated by centrifugation. The concentration of silver ions was determined by ICP-OES. The adsorption efficiency (Adsorption, %) and the adsorbed amount of silver ions (q , mg/g) were calculated using equation 3.1 and 3.2, respectively;

$$\text{Adsorption (\%)} = \frac{(C_0 - C)}{C_0} \times 100\% \quad (3.1)$$

$$q \text{ (mg/g)} = \frac{(C_0 - C)}{W} V \quad (3.2)$$

where C_0 is the initial concentration of silver ions in solution (mg/L)

C is the final concentration of silver ions in solution (mg/L)

V is the volume of solution (L)

W is the weight of silica-MPTMS (g)

(i) Effect of pH

The effect of initial pH on silver ions adsorption efficiency by silica-MPTMS was studied in a pH range from 1.0 to 7.0. The initial concentration of silver ions was 45 mg/L and the adsorption experiment was carried out using approximately 5 mg of silica-MPTMS and 10 mL of silver ions solution. The contact time of this experiment was 180 min. The initial pH of the solution was adjusted by using HNO_3 or NaOH solution.

(ii) Effect of contact time

The effect of contact time on silver ions adsorption onto silica-MPTMS was investigated using approximately 5 mg of silica-MPTMS and 30 mL of silver ions solution having an appropriate initial pH value determined previously. The contact time was varied in the range of 5 to 240 min.

(iii) Adsorption isotherm

The adsorption experiments were carried out at $29 \pm 1^\circ\text{C}$. The initial concentration of silver ions was varied in the range of 20 to 200 mg/L. The suitable adsorption condition (i.e. pH and contact time) determined previously was adopted. The obtained data was

used to study the adsorption behavior by fitting these data with Langmuir and Freundlich isotherm model.

3.6.2 Adsorption of silver nanoparticles (AgNPs)

The adsorption of AgNPs in aqueous solution by silica-MPTMS was studied using approximately 5 mg of silica-MPTMS in 10 mL of AgNPs solution. The mixture was stirred at room temperature for a specific period of time and the solid was separated by centrifugation. The nature of silver nanoparticles is that they can release silver ions in solution [39]. Thus, in order to correctly observe the adsorption of AgNPs, the amount of both silver ions and silver nanoparticles in silver nanoparticles solution were determined. The content of silver ions and total silver in AgNPs solution was analyzed by an in-house made silver ion selective electrode [37] and ICP-OES, respectively. The content of silver nanoparticles in solution was determined by subtraction the amount of total silver (by ICP-OES) with the amount of silver ions (by ISE). Then, this solution was used as standard of AgNPs to construct the standard curve for the determination of AgNPs by UV-Vis spectrophotometry. After adsorption, the residual concentration of AgNPs and total silver ions was determined by UV-Vis spectrophotometer and ICP-OES, respectively.

(i) Effect of contact time

The effect of contact time in the range of 10 to 480 min on AgNPs adsorption onto silica-MPTMS was studied.

(ii) Adsorption isotherm

The adsorption isotherm experiment was performed at $29 \pm 1^\circ\text{C}$. The initial concentration of AgNPs was varied in the range of 20 to 200 mg/L. The experimental data was used to study adsorption behavior by fitting the obtained data with Langmuir and Freundlich isotherm model.

3.7 Application to real samples

A wastewater containing silver ions was obtained from the laboratory of Gem and Jewelry Institute of Thailand (Public Organization). The adsorption of silver ions in the wastewater by silica-MPTMS was performed under the most suitable condition in silver ions condition.

Nano-consumer products were used as sources of AgNPs. The adsorption of AgNPs by silica-MPTMS was performed under the most suitable adsorption condition.

The content of total silver in all samples was determined before and after adsorption by ICP-OES.



CHAPTER IV

RESULTS AND DISCUSSION

In this work, mesoporous silica that had large pore size was prepared by sol-gel method using different templates including CTAB, CTAB in dilute solution and citric acid. The formation of pore and size of pore was controlled by the template added into the sol process. The three methods were used to prepare silica as shown below.

The first method was a modified stöber method [8]. In this method, the growth of CTAB micelles was obtained by using sodium nitrate in template solution [36].

In the second method, CTAB and NaNO_3 were used as template solution but silica was formed in diluted solution. It was an attempt to obtain thin wall of silica or large pore in the structure of silica [13].

For the last method, silica was synthesized by sol-gel method using citric acid template [10].

The physical properties such as crystallinity, porosity and surface area were observed. Then, the selected mesoporous silica was modified with 3-mercaptopropyl trimethoxysilane (silica-MPTMS) and used to adsorb silver ions and silver nanoparticles.

4.1 Characterization of mesoporous silica

4.1.1 X-ray diffraction (XRD)

X-ray diffraction was used to characterize the crystallinity of the obtained materials. The XRD patterns of mesoporous silica prepared by using CTAB, CTAB in dilute solution and citric acid as templates are shown in figure 4.1. All of patterns show a broad peak of amorphous phase silica.

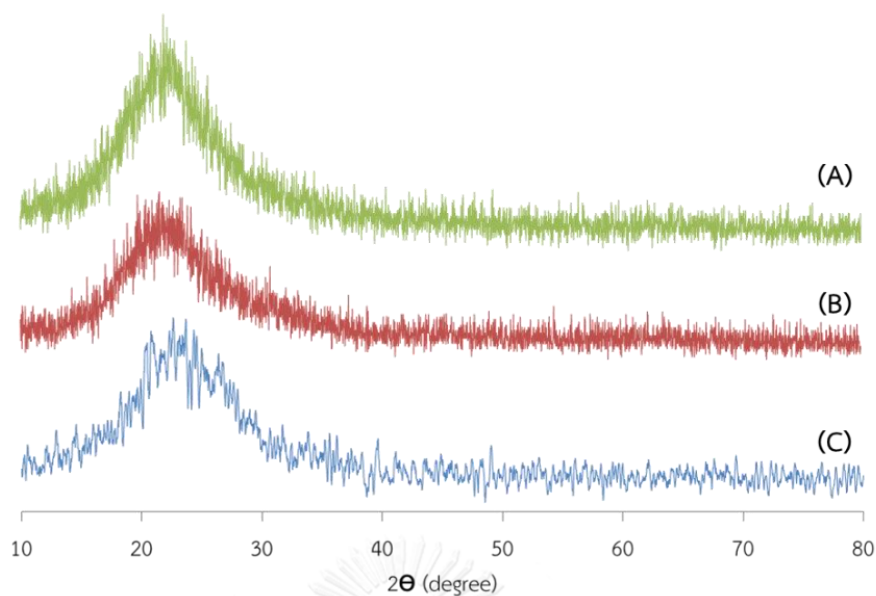


Figure 4.1 XRD pattern of mesoporous silica prepared by using CTAB (A), CTAB in dilute solution (B) and citric acid (C) as templates.

4.1.2 Porosity and surface area of synthesized mesoporous silica

Nitrogen adsorption analysis was used to determine the porosity and surface area of the synthesized mesoporous silica and silica-MPTMS. N_2 adsorption-desorption isotherm of all mesoporous silica are shown in figure 4.2. They exhibit a hysteresis loop of type-IV isotherm in the IUPAC classification of adsorption isotherm. It confirms that the obtained materials were mesoporous materials.

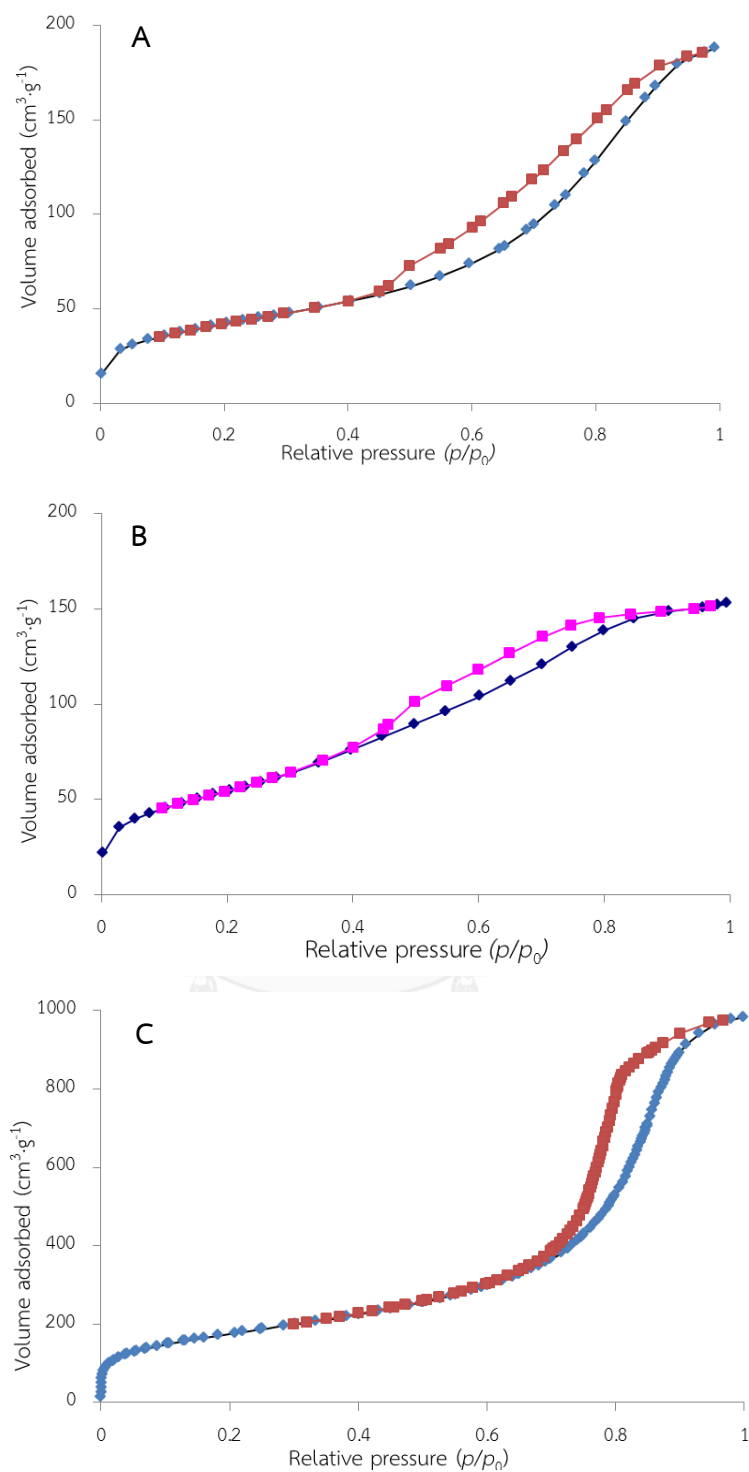
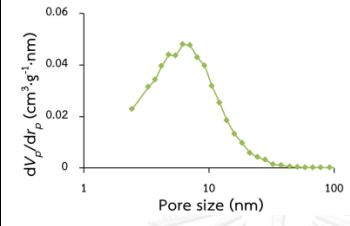
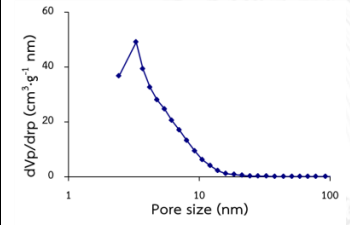
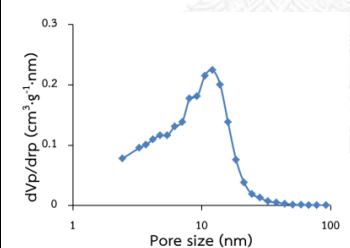


Figure 4.2 Nitrogen adsorption-desorption isotherm of mesoporous silica using CTAB template (A) CTAB template in dilute solution (B) and citric acid template (C)

Then, Brunauer-Emmett-Telle (BET) method was used to calculate the surface area of all mesoporous silica. Pore size and surface area of the materials are shown in table 4.1.

Table 4.1: The pore size and surface area of all mesoporous silica

Method	Pore size distributions	Pore size range (nm) (Average pore size)	Surface area (m^2/g)
CTAB template		2 – 80 nm (6.18 nm)	150.17
CTAB template (in dilute solution)		2 – 40 nm (3.28 nm)	199.83
Citric acid template		2 – 80 nm (12.12 nm)	630.61

From table 4.1, the results show that the product from the synthesis by using citric acid template had largest average pore size and high surface area. Thus, this method was chosen to synthesize mesoporous silica for further surface modification and use in the adsorption of silver ions and silver nanoparticles. After surface modification, the average pore size and surface area of the obtained material was 10.58 nm and $473.69 \text{ m}^2/\text{g}$, respectively. A reduction in surface area and pore size was probably the results from the coverage of 3-mercaptopropyltrimethoxysilane on the surface of mesoporous silica. N_2 adsorption-desorption isotherm of silica-MPTMS

is shown in figure 4.3 and the pore size distributions of the mesoporous silica before and after modification are further shown in figure 4.4.

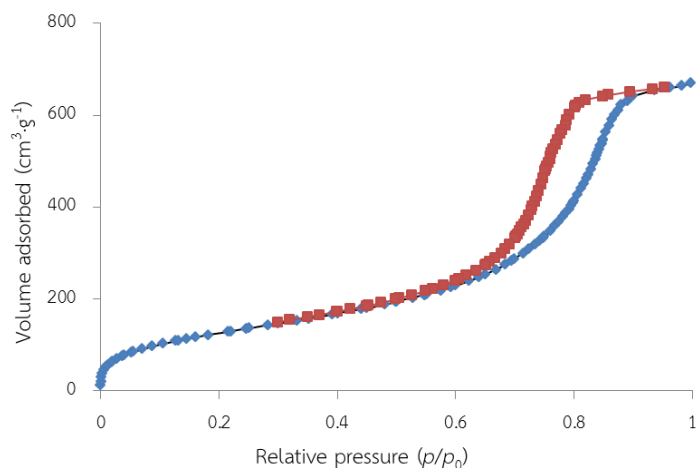


Figure 4.3 Nitrogen adsorption-desorption isotherm of silica-MPTMS.

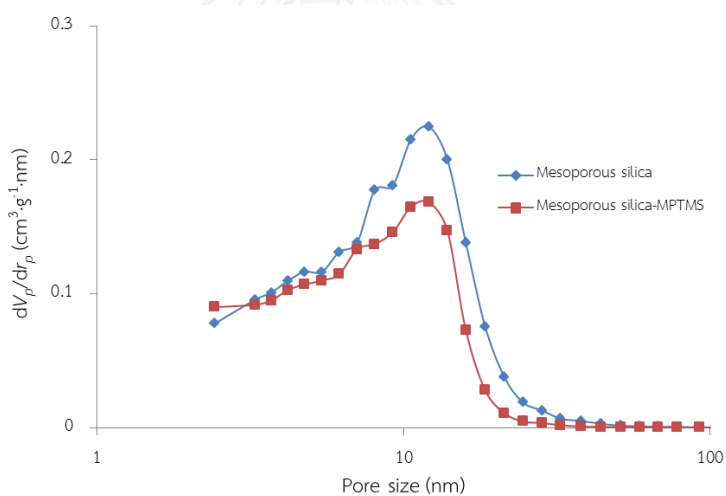


Figure 4.4 Pore size distributions of the unmodified and modified mesoporous silica.

4.1.3 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was used to evaluate the thermal stability of the mesoporous silica before and after the modification with 3-mercaptopropyl trimethoxysilane. It was operated in temperature range from 50°C to 600°C with a heating rate of 10°C/min.

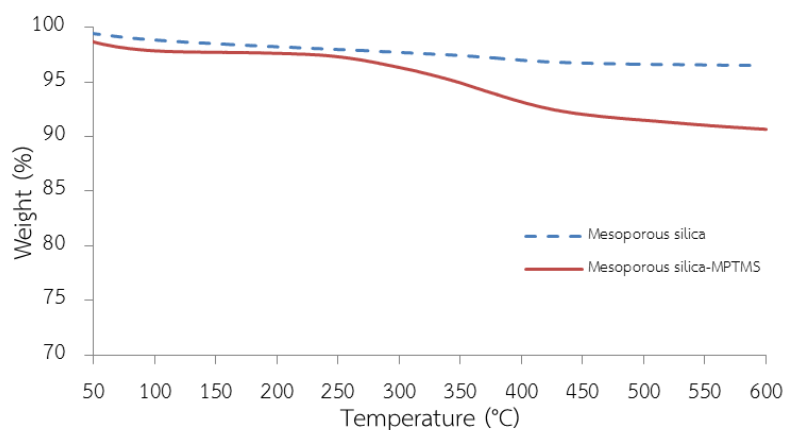


Figure 4.5 TGA curve of mesoporous silica and silica-MPTMS.

In figure 4.5, TGA curve of silica-MPTMS (solid line) is compared with that of mesoporous silica (dot line) and it shows different weight loss in temperature range from *ca.* 250°C to 450°C. It is attributed to the decomposition of 3-mercaptopropyltrimethoxysilane and this result confirms that 3-mercaptopropyl trimethoxysilane was successfully modified on the surface of mesoporous silica.

4.1.4 Transmission electron microscopy (TEM)

The morphology of silica-MPTMS was observed by TEM (figure 4.6). The images show the distribution of pores of different size in amorphous silica and large pores are also observed.

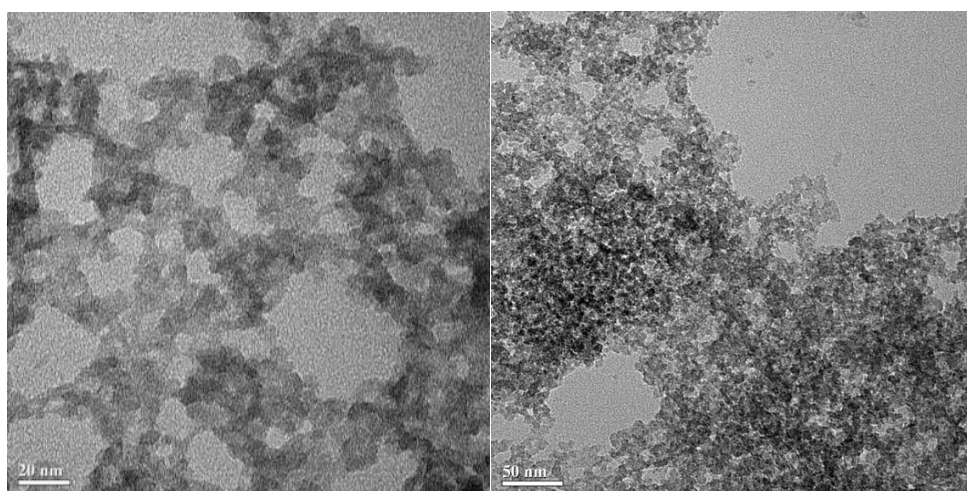


Figure 4.6 TEM images of silica-MPTMS.

4.2 Adsorption study

The adsorption behavior of silver ions and silver nanoparticles onto silica-MPTMS was investigated and the adsorption study was divided into 2 parts. In the first part, the effect of pH, contact time and initial concentration on the adsorption of silver ions onto silica-MPTMS was observed. In the second part, the adsorption behavior of silver nanoparticles onto silica-MPTMS was studied under the influence of different contact times and initial concentrations. Moreover, the kinetics of silver ions and silver nanoparticles adsorption and adsorption isotherms were studied.

The efficiency of silver ions and silver nanoparticles adsorption was presented in terms of adsorption efficiency (%) and adsorbed amount (q, mg/g) which was calculated by following equation 4.1 and 4.2, respectively;

$$\text{Adsorption (\%)} = \frac{(C_0 - C)}{C_0} \times 100\% \quad (4.1)$$

$$q \text{ (mg/g)} = \frac{(C_0 - C)}{W} V \quad (4.2)$$

where C_0 is the initial concentration of silver ions or silver nanoparticles in solution (mg/L)

C is the final concentration of silver ions or silver nanoparticles in solution (mg/L)

V is the volume of solution (L)

W is the weight of silica-MPTMS (g)

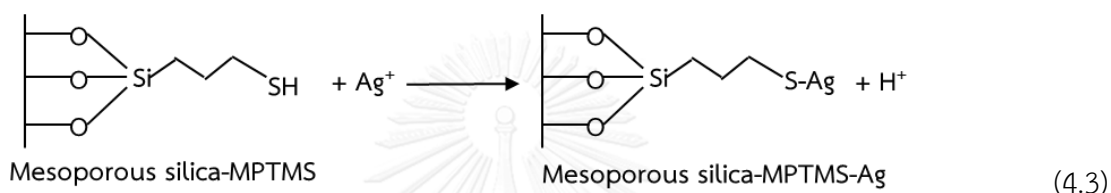
4.2.1 Adsorption of silver ions

(i) Effect of initial pH

The influence of initial pH of silver ions solution in the range of pH 1.0 to 7.0 was studied. In figure 4.7, the effect of initial pH on the adsorption efficiency of silver ions by silica-MPTMS is demonstrated. The results show that the pH did not affect the adsorption efficiency of silver ions and therefore, silica-MPTMS can be used in a

wide pH range. However, further experiment for adsorption study was performed in solution with initial pH of 3.

Furthermore, it was found that the equilibrium pH values observed in these solutions was *ca.* 3, despite different initial pH values. When considering the ability of silica-MPTMS to adsorb silver ions from these solutions, the formation of complex between silver ions and thiol-functional groups of MPTMS on mesoporous silica is likely to occur as shown in chemical reaction (4.3) [12].



From the reaction (4.3), it shows that proton (H^+) is the product of complex formation. When silica-MPTMS adsorbed silver ions in the solution, the pH of solution would decrease from its initial values.

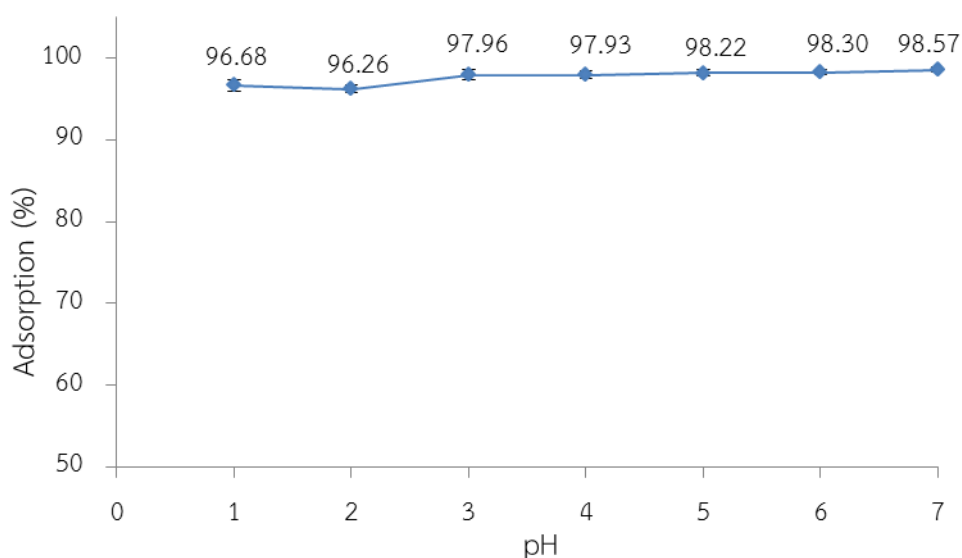


Figure 4.7 The effect of initial pH on the adsorption efficiency of silver ions by silica-MPTMS; initial silver concentration 45 mg/L.

(ii) Effect of contact time

In this experiment, the effect of contact time was studied in the range of 5 to 240 min and the experimental data was used to fit adsorption kinetics model in order to understand the adsorption behavior and to obtain kinetics parameters of analyte uptake rate at the solid-liquid interface. In figure 4.8, it shows that the adsorbed amount of silver ions increased sharply at the beginning of adsorption and reached relatively constant values after 15 min, indicating that the adsorption equilibrium was attained. The rapid adsorption was probably attributed to the porous structure of the mesoporous silica.

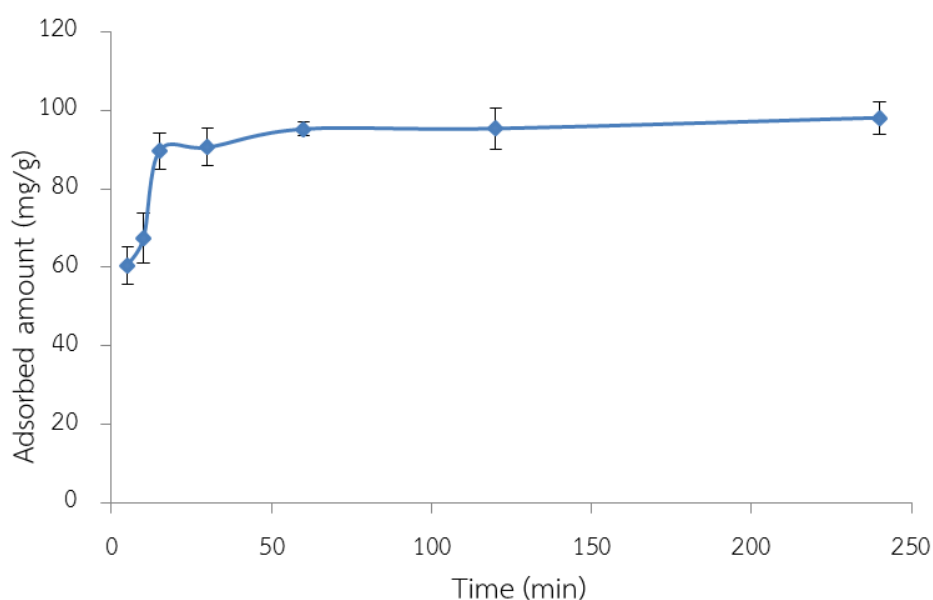


Figure 4.8 The influence of contact time on the adsorbed amount onto silica-MPTMS; initial silver ion concentration 45 ppm, initial pH of solution 3.

In order to investigate the adsorption kinetics, the experimental data were fitted to pseudo-first order and pseudo-second order kinetics model. These models were developed regarding the overall rate of analyte uptake by an adsorbent.

The linear form of pseudo-first order and pseudo-second order kinetics equation are expressed in equation 4.4 [40] and 4.5 [11], respectively;

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4.4)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4.5)$$

where, q_t is the adsorbed amount of silver ions at time t (mg/g)
 q_e is the adsorbed amount of silver ions at equilibrium (mg/g)
 k_1 is the rate constant of the pseudo-first order adsorption (min^{-1})
 h is the initial sorption rate (mg/g min)
 t is time (min)

The initial sorption rate (h) was calculated using the following equation (eq. 4.6) [11];

$$h = k_2 q_e^2 \quad (4.6)$$

where k_2 is the rate constant of the pseudo-second order adsorption (g/mg min)

The results of adsorption of silver ions onto silica-MPTMS were used in the linear plot following the linear equation of pseudo-first order and pseudo-second order kinetics model (figure 4.9 and 4.10). The result shows that the adsorption data fitted well to the pseudo-second order kinetics model ($R^2 > 0.99$). Therefore, the adsorption may follow the assumption of pseudo-second order adsorption kinetics that is the adsorption of silver ions onto silica-MPTMS may occur via chemisorption or the formation of complex between sulfur atom of the thiol groups on the surface of silica-MPTMS and silver ions as proposed in reaction (4.3).

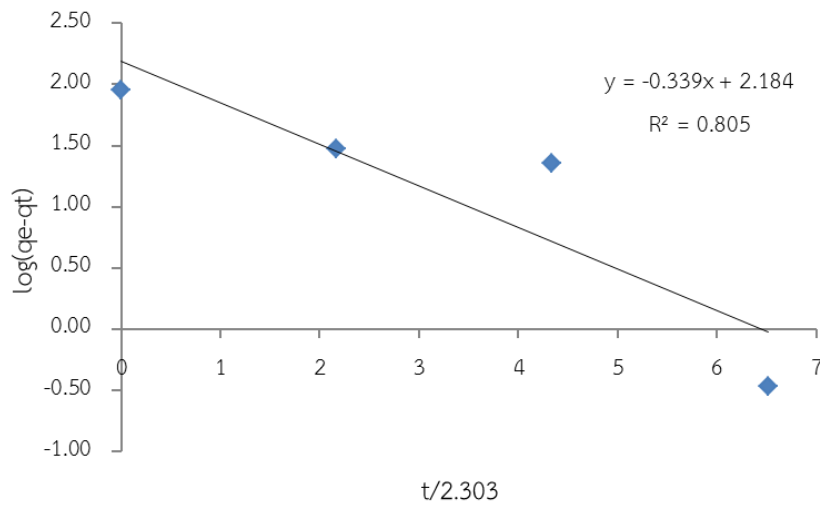


Figure 4.9 The linear plot of pseudo-first order adsorption kinetics using experimental data.

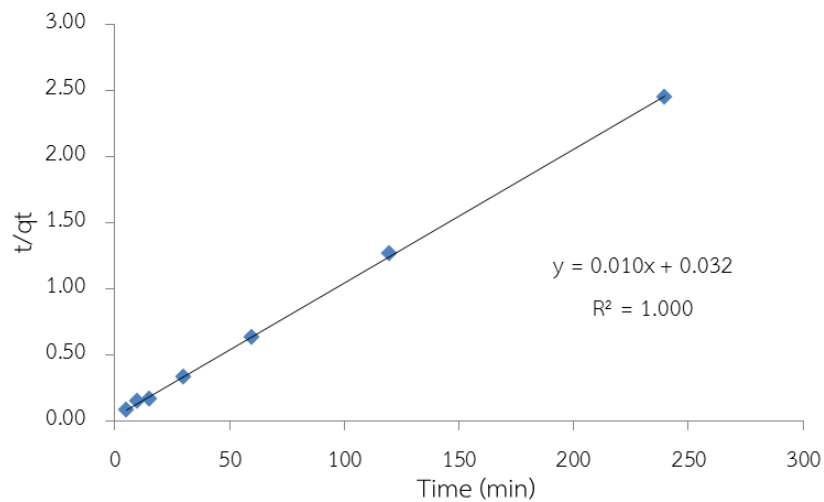


Figure 4.10 The linear plot of pseudo-second order adsorption kinetics using experimental data.

By plotting the data following equation 4.5, the amount of silver ions adsorbed on the adsorbent at equilibrium (q_e , mg/g) and the initial sorption rate (h) could be obtained from the slope and intercept of the plot between t/q_t versus t . The rate constant of adsorption could be calculated using equation 4.6. The adsorbed amount of silver ions at equilibrium from the calculation was 100 mg/g, while the experimental adsorbed amount of silver ions at equilibrium was 98 mg/g.

These values were in agreement which confirmed that the kinetics of silver ions adsorption could be described by pseudo-second order kinetics model. In addition, the initial sorption rate and the rate constant of adsorption were 31.25 mg/g min and 0.003125 g/mg min, respectively.

(iii) Adsorption isotherm

The adsorption behavior of silver ions onto silica-MPTMS at equilibrium can be described by the results from the adsorption isotherm study. In this experiment, fixed amount of silica-MPTMS (5 mg) was used in the adsorption of silver ions from solution of fixed volume (30 mL) containing various concentrations of silver ions (20-200 mg/L) with the initial pH value of 3 and contact time of 120 min (chosen from previous experiment) at room temperature. Long adsorption time was used in this study in order to assure that the equilibrium could be reached in solution at high concentration of silver ions. The data of adsorption at equilibrium were fitted with Langmuir and Freundlich isotherm models.

Langmuir isotherm model was developed based on the assumption of the monolayer adsorption on the specific or homogeneous surface of adsorbent with limited number of active sites. Only one sorbate can adsorb on each site of adsorbent via chemisorption. On the other hand, Freundlich isotherm model assumes that the adsorption of analytes would increase when increasing the concentration of analytes in solution. It is because sorbate can be adsorbed on these active sites of adsorbent surface as multilayer coverage [41].

The adsorbed amount of silver ions by silica-MPTMS observed when increasing the equilibrium concentration is shown in Figure 4.11. The adsorbed amount of silver ions increased when increased solution concentration and reached constant value *ca.* 110 mg/g despite of further increase in solution concentration, indicating that the active sites on the surface were saturated with silver ions.

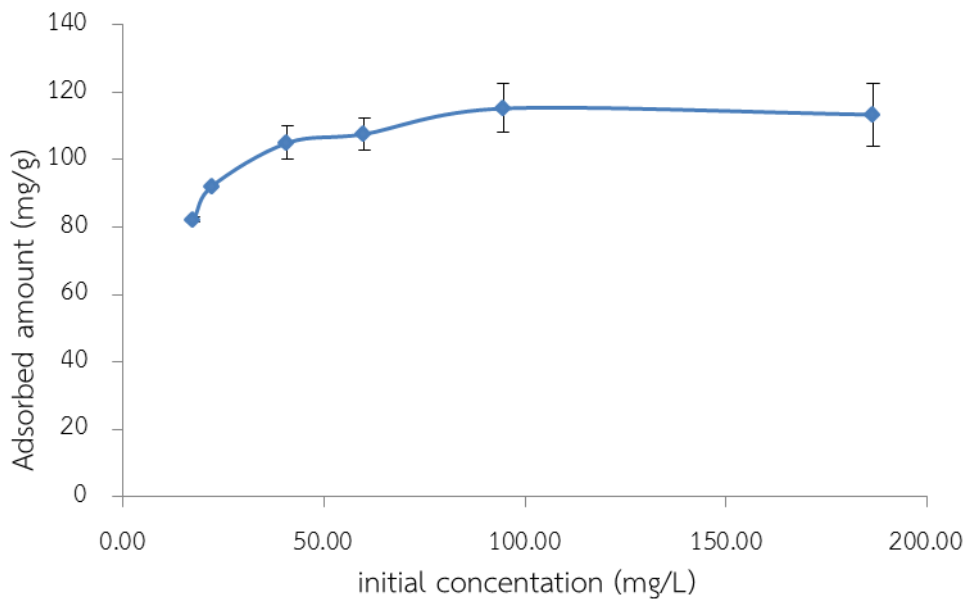


Figure 4.11 The adsorption isotherm of silver ions adsorption on the silica-MPTMS; initial pH 3; contact time 120 min.

The experimental data were used for the linear plotting following linear equation of Langmuir and Freundlich isotherm as shown in eq. 4.7 and 4.8, respectively [31];

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4.7)$$

where C_e is the equilibrium concentration of silver ions in the bulk solution (mg/L)

q is the adsorbed amount of silver ions at equilibrium (mg/g)

q_m is the maximum adsorbed amount of silver ions (mg/g)

K_L is Langmuir constant related to energy of adsorption (L/mg)

From the equation 4.7, the maximum adsorbed amount of silver ions (q_m) and Langmuir constant (K_L) can be calculated from slope and intercept of the linear equation obtained from a plot between C_e/q versus C_e (figure 4.12). The parameters of Langmuir isotherm for adsorption of silver ions were calculated and listed in the table 4.2.

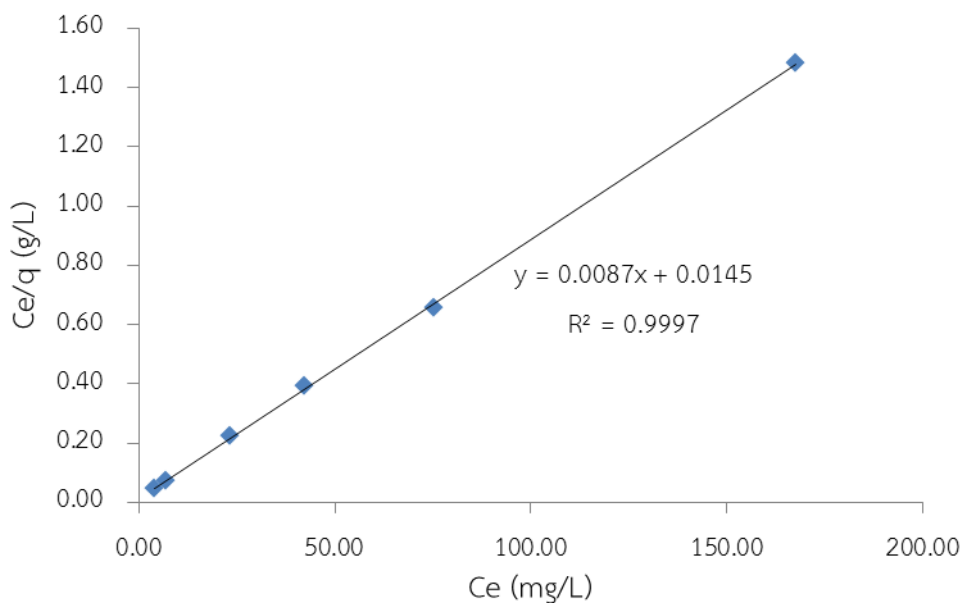


Figure 4.12 Linear Langmuir plot of silver ions adsorption on silica-MPTMS.

On the other hand, the linear form of Freundlich isotherm is presented by the following equation [41];

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (\text{eq. 4.8})$$

where, q is the adsorbed amount of silver ions at equilibrium (mg/g)

C_e is the equilibrium concentration of silver ions in the bulk solution (mg/L)

K_f is Freundlich constant related to adsorption capacity (mg/g)

n is Freundlich constant related to adsorption intensity

The data of equilibrium adsorption were used in linear plot following linear equation of Freundlich isotherm ($\log q$ versus $\log C_e$) as shown in figure 4.13. The parameters of Freundlich isotherm for adsorption of silver ions were calculated and listed in the table 4.3.

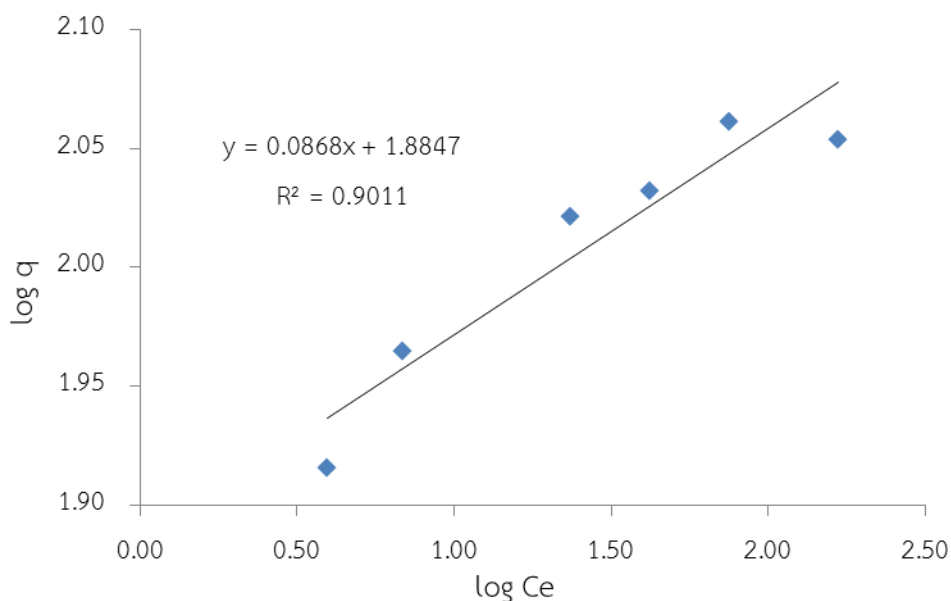


Figure 4.13 Linear Freundlich plot of silver ions adsorption on silica-MPTMS.

Table 4.2: Langmuir isotherm parameter of the silver ions adsorption by silica-MPTMS

Linear equation	R^2	K_L (L/mg)	$q_{m,cal}$ (mg/g)	$q_{m,exp}$ (mg/g)
$y = 0.0087x + 0.0145$	0.9997	0.600	114.9	115.2

Table 4.3: Freundlich isotherm parameter of the silver ions adsorption by silica-MPTMS

Linear equation	R^2	K_f (mg/g)	n
$y = 0.0868x + 1.8847$	0.9011	76.68	11.52

The results from linear regression as shown in table 4.2 and 4.3 indicate that the adsorption data could fit to Langmuir model ($R^2 > 0.99$) better than Freundlich model. Therefore, the behavior of silver ions adsorption on silica-MPTMS could be described by the assumption of Langmuir model. The Langmuir constant (K_L) was calculated to be 6.47×10^4 L/mol and the high value of Langmuir constant can be related to high adsorption energy that is usually observed in chemisorption. Therefore the adsorption of silver ions on silica-MPTMS probably occurred via the

coordination of silver ions with donor site of MPTMS (sulfur atom). The maximum adsorbed amount (q_m) calculated from the obtained linear equation was 114.9 mg/g. Moreover, the maximum adsorbed amount obtained from calculation is in agreement with the maximum adsorbed amount observed from experiment, confirming a good fitting of the experimental data with Langmuir isotherm.

(iv) Transmission electron microscopy (TEM) of silica-MPTMS-Ag

TEM images of silica-MPTMS after being used in silver ions adsorption are shown in figure 4.14. It shows a deposition of silver onto the silica-MPTMS. It confirmed that silver ions could be adsorbed onto the silica-MPTMS.

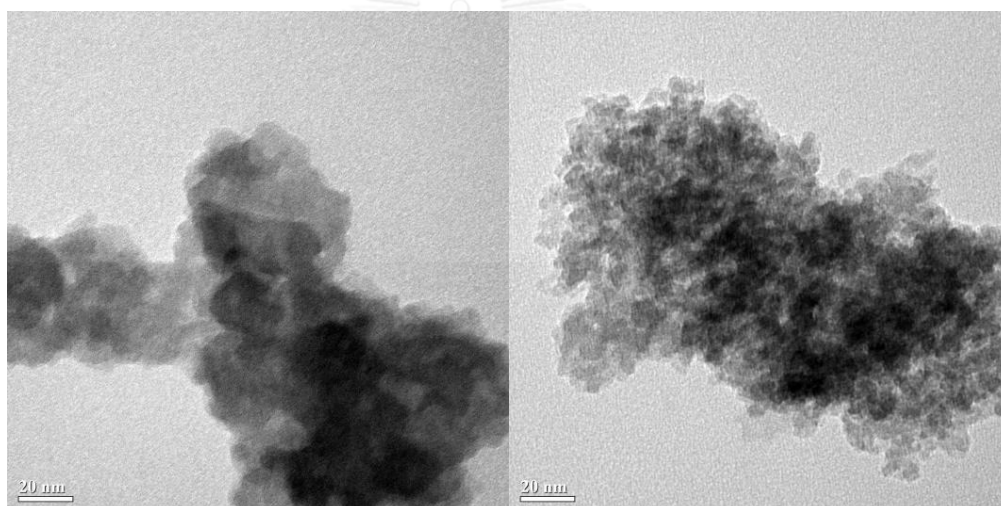


Figure 4.14 TEM images of silica-MPTMS-Ag with silver as dark spots on silica.

4.2.2 Adsorption of silver nanoparticles

In this part, the adsorption of silver nanoparticles was studied in the mixture system between silver nanoparticles and silver ions. It is because silver nanoparticles in solution can release silver ions and therefore, there would rarely be a pure silver nanoparticles solution. In this study, the content of silver nanoparticles in solution was determined by subtraction the amount of total silver (analyzed by using ICP-OES after sample digestion) with the amount of silver ions (obtained by using in-house made silver ion selective electrode). Then, the standard of known silver

nanoparticles concentration was used to construct calibration curve in the detection by UV-vis spectrophotometer. Furthermore, the concentrations of silver nanoparticles in samples before and after adsorption were determined by UV-vis spectrophotometry.

(i) Effect of contact time

The effect of contact time on the adsorption of silver nanoparticles was studied in the range of 10 to 480 min. The adsorbed amount of silver nanoparticles on silica-MPTMS slowly increased when increased the contact time and reached to relatively constant values after 360 min (Figure 4.15), indicating that the adsorption equilibrium was attained. Total silver concentration in solutions was also determined. Regarding the amount of total silver adsorbed by the adsorbent, the adsorbed amount was higher than that of silver nanoparticles, revealing that in the mixture system, the adsorption of both silver ions and silver nanoparticles occurred simultaneously. However, the adsorption of silver ions reached equilibrium rapidly as shown previously. Therefore, the adsorption of silver nanoparticles is likely to occur much more slowly than silver ions, probably due to its much larger size.

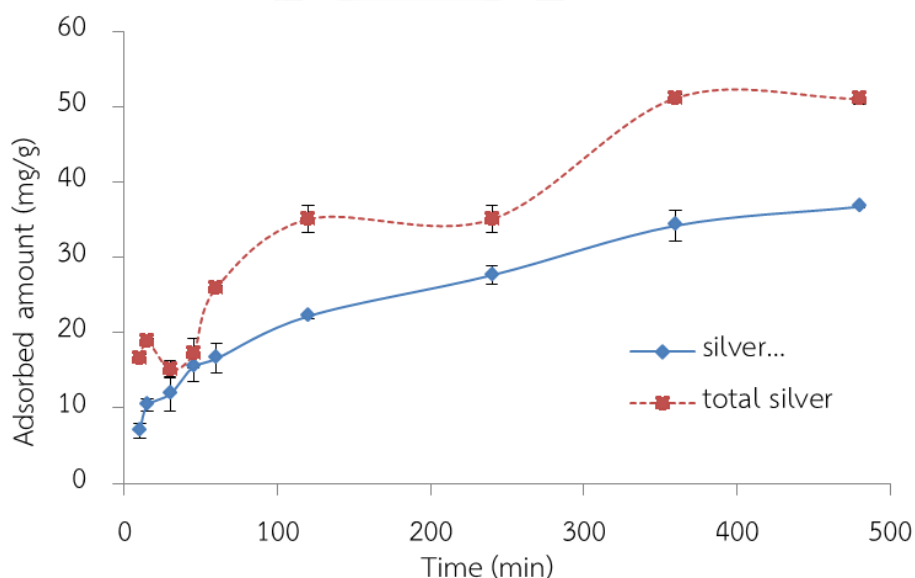


Figure 4.15 The effect of contact time on the adsorption of the silver nanoparticles and total silver (in the solution) onto silica-MPTMS.

The pseudo-first order and pseudo-second order kinetics model were adopted to determine the kinetics of silver nanoparticles adsorption onto the silica-MPTMS [40]. The experimental data were used to construct linear plot following equation 4.4 and 4.5 (figure 4.16-4.17). The parameter of pseudo-first order and pseudo-second order kinetics were calculated as summarized in table 4.4.

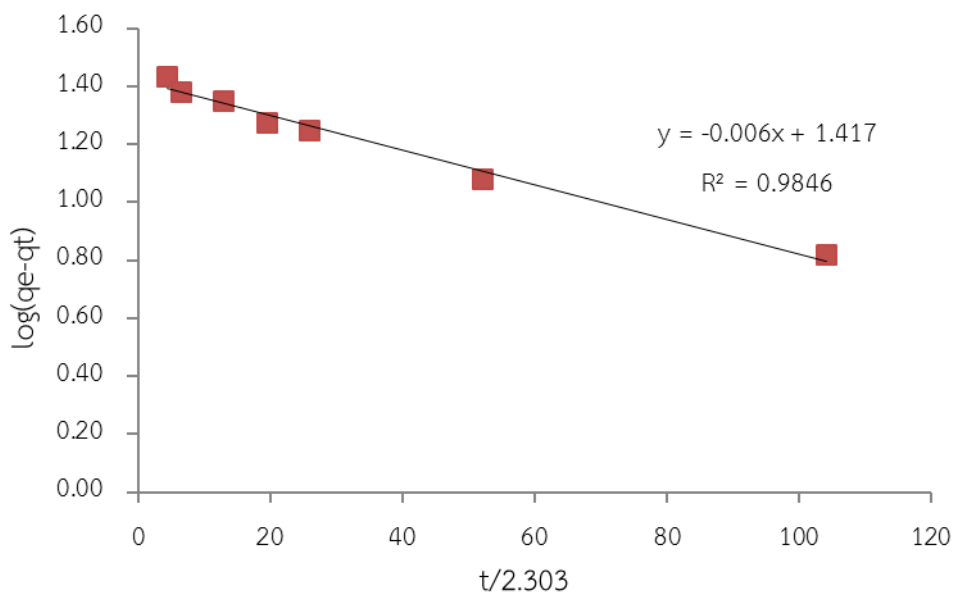


Figure 4.16 The pseudo-first order kinetics plot of silver nanoparticles adsorption.

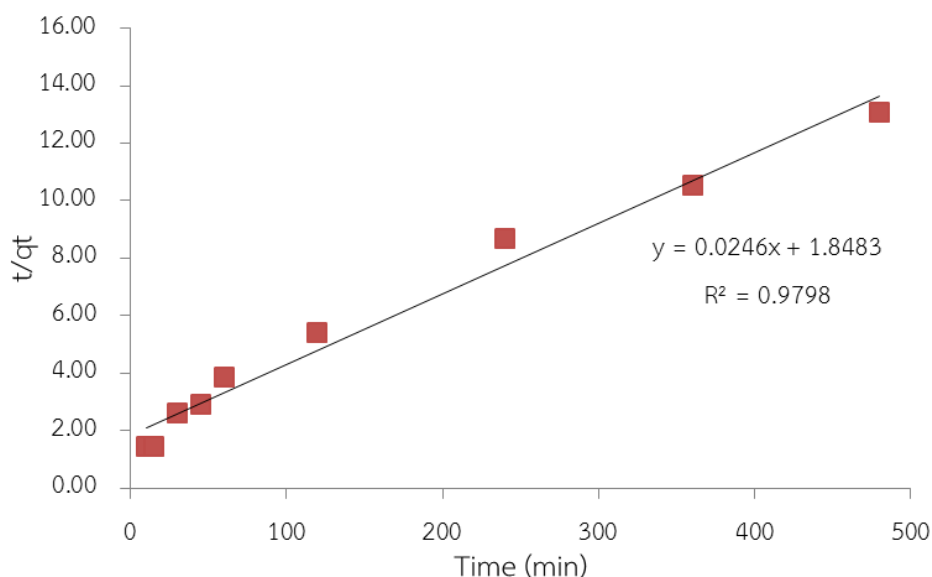


Figure 4.17 The pseudo-second order kinetics plot of silver nanoparticles adsorption.

Table 4.4 Pseudo-first order and pseudo-second order kinetics parameters of the silver nanoparticles adsorption by silica-MPTMS

Kinetic model	Linear equation	R^2	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)
Pseudo 1 st order	$y = -0.0064x + 1.4845$	0.9675	26.12	36.71
Pseudo 2 nd order	$y = 0.0246x + 1.8483$	0.9798	40.65	

The result shows that the kinetics of silver nanoparticles adsorption did not fit well to both pseudo-first order and pseudo-second order model regarding the correlation coefficient (R^2) that was not close to 1. It was probably because there may be competitive adsorption between silver ions and silver nanoparticles onto silica-MPTMS. Therefore, the adsorption of silver nanoparticles onto silica-MPTMS cannot be simply predicted by the uptake rate of silver nanoparticles from the mixture system.

(ii) Adsorption isotherm

The adsorption behaviors of silver nanoparticles on silica-MPTMS at equilibrium can be explained by the experimental data from adsorption isotherm. The adsorption experiment was performed by using fixed amount of adsorbent (5 mg) and fixed volume of solution (10 mL) containing different concentration of silver nanoparticles with contact time of 480 min at room temperature. In these experiments, the concentration ratio between silver nanoparticles and silver ions in the mixture system was around 3:1. In order to clearly observe the behavior of silver nanoparticles, the concentration of silver ions was reduced as much as possible. Langmuir and Freundlich isotherm models were used to describe the results of adsorption at equilibrium.

Figure 4.18 displays the adsorbed amount of silver nanoparticles on silica-MPTMS at different equilibrium concentration of silver nanoparticles. The adsorbed amount of silver nanoparticles rapidly increased when increased the solution

concentration and reached relatively constant value around 90 mg/g. It indicated that the active site of silica-MPTMS was saturated with silver nanoparticles.

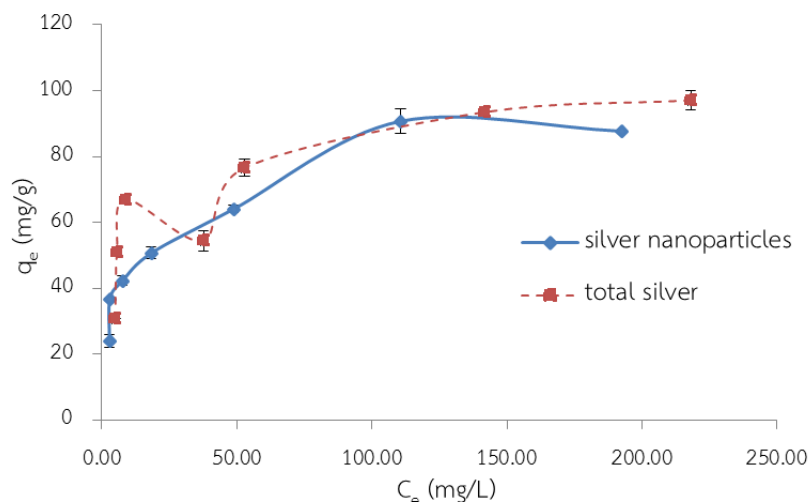


Figure 4.18 The adsorption isotherm of silver nanoparticles and total silver (in the solution) onto silica-MPTMS

The results of adsorption isotherm were used for the linear plotting using Langmuir and Freundlich isotherm model (equation 4.7 and 4.8) as shown in figure 4.19 and 4.20, respectively. The parameters of Langmuir and Freundlich isotherm for adsorption of silver nanoparticles were calculated from linear equation obtained from linear regression of adsorption data and listed in the table 4.5 and 4.6.

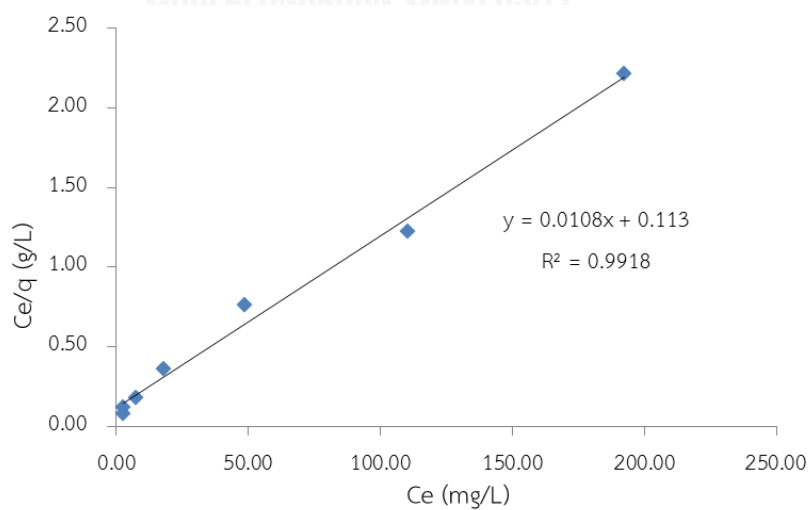


Figure 4.19 Linear Langmuir plot using experimental data of silver nanoparticles adsorption on silica-MPTMS.

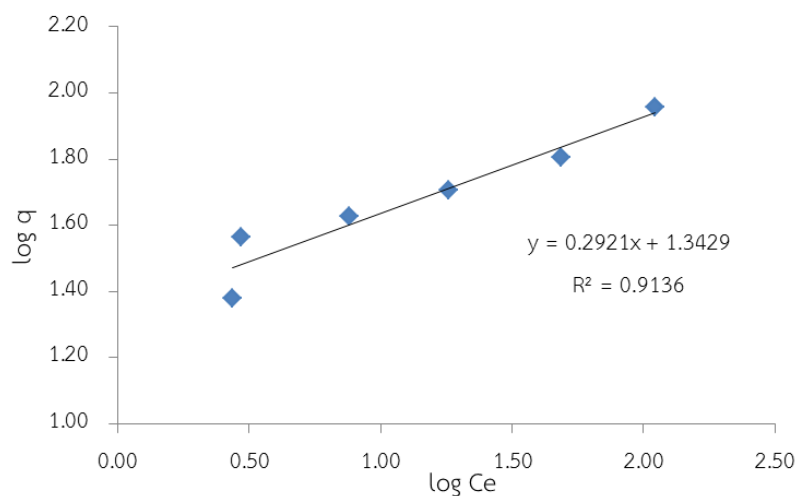


Figure 4.20 Linear Freundlich plot using experimental data of silver nanoparticles adsorption on silica-MPTMS.

Table 4.5: Langmuir isotherm parameter of the silver nanoparticles adsorption by silica-MPTMS

Linear equation	R^2	K_L (L/mg)	$q_{m,cal}$ (mg/g)	$q_{m,exp}$ (mg/g)
$y = 0.0108x + 0.113$	0.9918	0.0956	92.59	90.72

Table 4.6: Freundlich isotherm parameter of the silver nanoparticles adsorption by silica-MPTMS

Linear equation	R^2	K_f (mg/g)	n
$y = 0.2921x + 1.3429$	0.9136	22.02	3.42

The obtained data of silver nanoparticles adsorption at equilibrium followed Langmuir model ($R^2 > 0.99$) better than Freundlich model. Thus, the behavior of silver nanoparticles on silica-MPTMS could be described by Langmuir model assumption that silver nanoparticles were adsorbed as monolayer coverage on the surface. The Langmuir constant (K_L) was calculated to be 1.03×10^4 L/mol. This high value of Langmuir constant reveals the high adsorption energy that is usually observed in chemisorption. Therefore, the silver nanoparticles adsorption on silica-

MPTMS occurred through the coordination of silver nanoparticles with the donor site of active atom (sulfur atom). From the linear equation obtained, the maximum of adsorption capacity (q_m) was calculated to be 92.59 mg/g. The maximum of adsorbed amount from calculation is close to the value observed from experiment, confirming a good fitting of the results with Langmuir isotherm.

(iii) Transmission electron microscopy (TEM) of silica-MPTMS-AgNPs

TEM image of silica-MPTMS-AgNPs is shown in figure 4.21. It shows a deposition of silver nanoparticles onto silica-MPTMS.

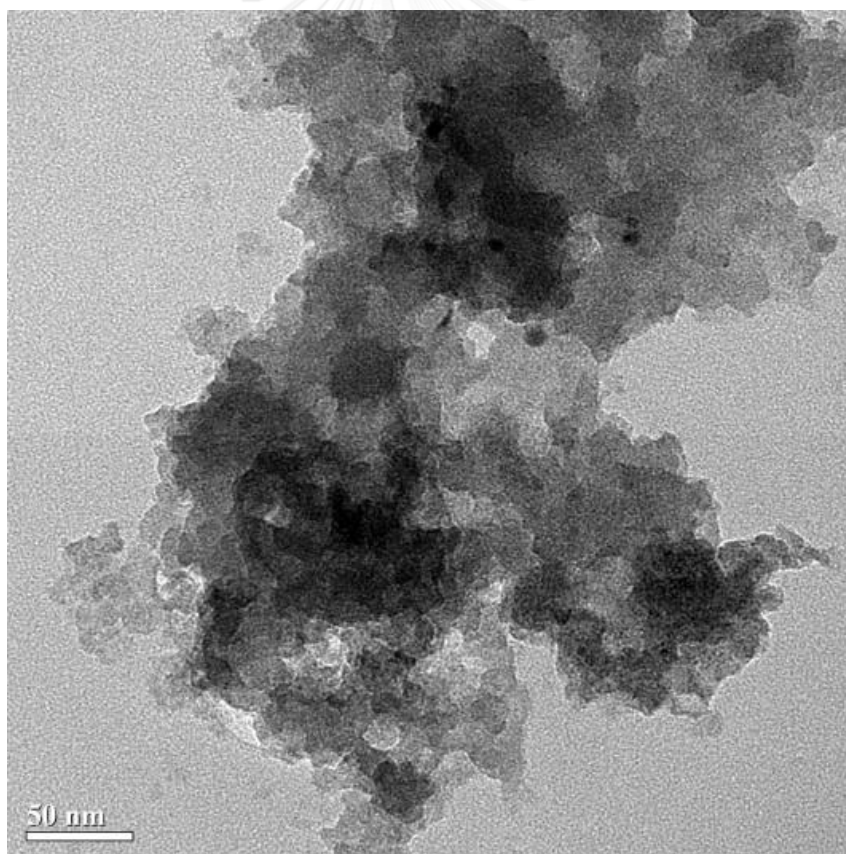


Figure 4.21 TEM image of silica-MPTMS-AgNPs.

4.3 Application in real samples

Silica-MPTMS was applied to remove silver ions and silver nanoparticles in water samples. In this work, a wastewater sample from the laboratory of Gem and Jewelry Institute of Thailand (Public Organization), silver nanoparticles wastewater from Environmental Analysis Research Unit (EARU) and nano-consumer products containing silver ions and silver nanoparticles were used in the adsorption experiments.

The adsorption experiment was performed in triplicate using 5 mg of silica-MPTMS in 10 mL of sample previously adjusted pH value to 3 (only for silver ions adsorption) for 120 min for silver ions adsorption or 480 min for silver nanoparticles adsorption.

The results of silver ions and silver nanoparticles adsorption from samples are shown in table 4.7. This result shows that silica-MPTMS can be used in real sample applications.

Table 4.7: The results of application of silica-MPTMS in real samples

Samples	Initial total silver concentration (mg/L)	Adsorbed amount (mg/g)	% silver adsorption
Ag-Wastewater	163.60	104.0 ± 3.0	31.8 ± 0.9
AgNPs-Wastewater	11.22	19.8 ± 0.2	88.2 ± 0.8
Nano-consumer product	20.56	37.9 ± 0.2	92.1 ± 0.4

CHAPTER V

CONCLUSION

Mesoporous silica was synthesized by sol-gel method using CTAB and citric acid template. The crystalline of the adsorbents were characterized by XRD. It was found these adsorbents are amorphous silica. The surface area analysis indicated that they are mesoporous materials. The silica prepared by citric acid template had the largest pore size and highest surface area compared to other products obtained. It was chosen for adsorption of silver ions and silver nanoparticles.

The adsorbent was successfully modified by 3-mercaptopropyl trimethoxysilane (silica-MPTMS) and characterized by TGA. The morphology of the adsorbents before and after adsorption of silver ions and silver nanoparticles was illustrated by TEM. It shows that silver ions and silver nanoparticles can adsorb on the adsorbent or into their pores.

Silica-MPTMS was used to adsorb silver ions and silver nanoparticles in aqueous solution using batch method. The effect of initial pH of solution (only silver ions adsorption), contact time and adsorption isotherm was investigated. It was found that the initial solution pH in a range of 1 to 7 did not have effect on the adsorption of silver ions. The adsorption behavior and suitable conditions for adsorption silver ions and silver nanoparticles is shown in table 5.1.

Table 5.1: The adsorption behavior and selected conditions for adsorption silver ions and silver nanoparticles

Parameter	Adsorption behavior	
	Silver ions	Silver nanoparticles
Contact time	120 min	480 min
Kinetics model	Pseudo 2 nd order	inconclusive
Adsorption isotherm	Langmuir isotherm	Langmuir isotherm
Maximum capacity	114.9 mg/g	92.59 mg/g

The adsorption of silver ions and silver nanoparticles onto silica-MPTMS is suggested to occur through the complexation of silver (Ag) and thiol-functional groups (-SH) on MPTMS. Finally, this adsorbent was successfully applied to adsorb silver ions and silver nanoparticles from the wastewater and nano-consumer product.

Suggestion of future work

- To study the reusability of adsorbent.
- To apply the adsorbent in large scale adsorption including wastewater treatment.



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