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เมทิลไทโอไกลโคเลตสำหรับการสกัดไอออนทอง (III)

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PREPARATION OF POLYETHYLENEIMINE-COATED CARBON NANOTUBES  
MODIFIED WITH METHYL THIOGLYCOLATE FOR  
EXTRACTION OF GOLD(III) IONS

Mr. Kittipong Sanuwong

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science  
Faculty of Science  
Chulalongkorn University  
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Thesis Title	PREPARATION OF POLYETHYLENEIMINE-COATED CARBON NANOTUBES MODIFIED WITH METHYL THIOGLYCOLATE FOR EXTRACTION OF GOLD(III) IONS
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กิตติพงษ์ สาณวงษ์ : การเตรียมคาร์บอนนาโนทิวบ์ที่เคลือบด้วยพอลิเอทิลีนอิมินดัดแปรด้วยเมทิลไทโอไกลโคเลตสำหรับการสกัดไอออนทอง (III). (PREPARATION OF POLYETHYLENEIMINE-COATED CARBON NANOTUBES MODIFIED WITH METHYL THIOGLYCOLATE FOR EXTRACTION OF GOLD(III) IONS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.เฟื่องฟ้า อุ่นอบ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : อ.ดร.นิปกา สุขพิรมย์, 56 หน้า.

ทำการเตรียมคาร์บอนนาโนทิวบ์ที่เคลือบด้วยพอลิเอทิลีนอิมินแบบเชื่อมขวาง และดัดแปรพื้นผิวด้วยเมทิลไทโอไกลโคเลตเพื่อนำไปใช้เป็นตัวดูดซับไอออนทอง โดยเริ่มจากการเคลือบพอลิเอทิลีนอิมินบนผิวของคาร์บอนนาโนทิวบ์โดยอาศัยการดูดซับทางกายภาพ และใช้กลูทารัลดีไฮด์เป็นสารเชื่อมขวางทำให้โมเลกุลของพอลิเอทิลีนอิมินยึดติดเข้าด้วยกัน จากนั้นดัดแปรด้วยเมทิลไทโอไกลโคเลตเพื่อเพิ่มความจำเพาะในการดูดซับของ พิสูจน์เอกลักษณ์ของตัวดูดซับที่ได้ด้วยกล้องอิเล็กตรอนแบบส่องกราดที่ผนวกกับเครื่องวิเคราะห์ธาตุบนพื้นผิว ฟลูออโรสแกนพอร์มอินฟราเรดสเปกโทรเมตรี ฟลูออโรสแกนพอร์มรามานสเปกโทรเมตรี การวิเคราะห์ทางความร้อน และทดสอบด้วยปฏิกิริยาของนินไฮดริน ปริมาณพอลิเอทิลีนอิมินและเมทิลไทโอไกลโคเลตที่เหมาะสมในการเตรียมตัวดูดซับ คือ  $2.00 \times 10^{-4}$  และ 17.86 มิลลิโมลต่อกรัม ตามลำดับ จากนั้นศึกษาปัจจัยที่มีผลต่อประสิทธิภาพการดูดซับไอออนทองของตัวดูดซับ พบว่า ตัวดูดซับนี้ใช้เวลาในการสกัดทองเพียง 10 นาที โดยที่ค่า pH ของสารละลายในช่วง 1.5 ถึง 7 ไม่มีผลต่อการดูดซับ ไอโซเทอมของการดูดซับเป็นแบบแลงเมียร์ซึ่งคำนวณค่าความจุสูงสุดของการดูดซับทองได้เท่ากับ 203.7 มิลลิกรัมต่อกรัม ทั้งนี้สามารถชะทองออกจากตัวดูดซับที่ใช้แล้วได้โดยใช้ไทโอยูเรียความเข้มข้น 0.5 โมลาร์ที่ละลายใน 2 % กรดไฮโดรคลอริก

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KEYWORD : GOLD / CARBON NANOTUBES / POLYETHYLENEIMINE / METHYL THIOGLYCOLATE / ADSORPTION

KITTIPONG SANUWONG : PREPARATION OF POLYETHYLENEIMINE-COATED CARBON NANOTUBES MODIFIED WITH METHYL THIOGLYCOLATE FOR EXTRACTION OF GOLD(III) IONS. ADVISOR: ASST. PROF. FUANGFA UNOB, Ph.D., CO-ADVISOR: NIPAKA SUKPIROM, Ph.D., 56 pp.

Polyethyleneimine-coated carbon nanotubes modified with methyl thioglycolate (CNTs-PEI-MTG) were prepared and used as adsorbent for Au(III) extraction. Carbon nanotubes (CNTs) were coated with polyethyleneimine (PEI), via physical adsorption. The PEI molecules were attached together using glutaraldehyde as crosslinking agent and subsequently modified with methyl thioglycolate (MTG) to improve the adsorption selectivity toward gold ions. The obtained products were characterized by scanning electron microscope equipped with energy dispersive X-ray analyzer (SEM-EDX), Fourier transforms infrared spectrometer (FTIR), Raman spectrometer (FT-Raman), thermal gravimetric analyzer (TGA), and ninhydrin test. The optimum amounts of PEI and MTG for CNTs coating were  $2.00 \times 10^{-4}$  and 17.86 mmol/g CNTs, respectively. The effect of certain parameters on Au(III) adsorption by the adsorbents was evaluated. Adsorption equilibrium was reached in 10 minutes. The solution pH in the range of 1.5-7 did not have any effect on the adsorption efficiency. The adsorption behavior followed Langmuir isotherm with the calculated maximum adsorption capacity of 203.7 mg Au/g. The desorption of Au(III) ions from the used adsorbent was achieved using 0.5 M thiourea in 2%(v/v) HCl solution.

Field of Study: Petrochemistry and Polymer science Student's Signature.....

Academic Year: 2554 Advisor's Signature.....

Co-advisor's Signature.....

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## LIST OF ABBREVIATIONS

°C	degree Celsius
cm <sup>-1</sup>	unit of wavenumber
CNTs	carbon nanotubes
CNTs-PEI	polyethyleneimine-coated carbon nanotubes
CNTs-PEI-MTG	polyethyleneimine-coated carbon nanotubes modified with methyl thioglycolate
FAAS	flame atomic absorption spectrometry
FT-IR	Fourier transform infrared spectrometry
ICP-OES	inductively couples plasma optical emission spectrometry
MTG	methyl thioglycolate
PEI	polyethyleneimine
SEM-EDX	scanning electron microscopy and energy dispersive X-Ray spectroscopy
TGA	thermogravimetric analysis

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of the problem

Gold is one of the precious metals which are widely used in various applications including jewelry and electronic industries. Day by day, the demand of gold has increased along with increasingly high price. It contrasts with the amount of gold in the nature that is limited and has steadily decreased as a result from mining in large scale. It should find ways to reuse gold from every possible resource. Many different methods such as precipitation, ion exchange and electrolysis have been used to recover gold. Among these methods, chelating adsorption is one of promising approaches of solid–liquid separation due to its good selectivity in gold extraction.

Polyethyleneimine (PEI) is a water-soluble polyamine containing a large number of amino groups which has chelation ability with metal ions [1-3]. PEI was successfully coated on many solid supports including silica gel [4, 5], polymer [2], activated carbon [6] and carbon nanotubes (CNTs) [7, 8]. CNTs have been drawing interest in field of materials development due to their high mechanical strength and chemical resistance. Many reports have demonstrated the possible method to attach PEI molecules on the CNTs surface and its use as adsorbent [7, 8].

Coating of carbon nanotubes with polyethyleneimine that has hydrophilic property, allows carbon nanotubes to disperse better in aqueous solutions. PEI was attached on CNTs surface via weak physical interaction and tends to leach out from the surface. Glutaraldehyd is then used as crosslinking agent to attach PEI molecules together improving adsorbent stability and preventing the polymer leaching. In order to increase efficiency in Au(III) adsorption, methyl thioglycolate (MTG) was modified on PEI coated carbon nanotubes. Amine groups of PEI on adsorbent surface can form amide bond with ester groups of the modified MTG and this MTG molecule also contains sulfur atom that has affinity to gold (III) ions.

This research focuses on the preparation of polyethyleneimine-coated carbon nanotubes modified with methyl thioglycolate and the application as adsorbent for gold (III) extraction from water.

## **1.2 Objectives**

1.2.1 To prepare and characterize polyethyleneimine-coated carbon nanotubes and modified with methyl thioglycolate (CNTs-PEI-MTG).

1.2.2 To evaluate the efficiency in Au(III) adsorption by CNTs-PEI-MTG and the effect of certain parameters on Au(III) adsorption efficiency.

## **1.3 Scopes of this research**

The scope of this research is firstly to prepare of polyethyleneimine-coated carbon nanotubes and modify with methyl thioglycolate (CNTs-PEI-MTG) by using the optimized amount of PEI and MTG in modification process. Then, the obtained adsorbents are characterized by scanning electron microscope equipped with energy dispersive X-ray analyzer (SEM-EDX), Fourier transforms infrared spectrometer (FT-IR), Raman spectrometer (FT-Raman), thermal gravimetric analyzer (TGA), and ninhydrin test. Thereafter, the influences of experimental parameters including solution pH, contact time and co-existing ions on the efficiency in Au(III) adsorption by CNTs-PEI-MTG were investigated. The adsorption isotherms and reusability of the adsorbents were also studied. Finally, the modified adsorbent was applied to extract Au(III) in real wastewater.

## **1.4 The benefit of this research**

This research provides a method for preparation and modification of polymer coated carbon nanotubes and its application as adsorbent for Au(III) extraction.

## **CHAPTER II**

### **THEORY AND LITERATURE REVIEW**

#### **2.1 Carbon nanotubes**

Carbon nanotubes (CNTs) are allotropes of carbon that are shaped like a cylinder with diameter of the order of few nanometers. Carbon nanotubes are categorized into two types, single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), depending on the number of layers on the tube. There are many techniques that have been developed to produce desired quality of nanotubes, including arc discharge, laser ablation, high-pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD) [9].

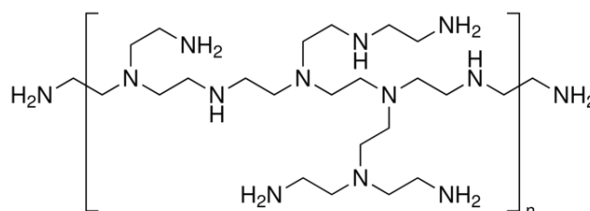
Carbon nanotubes have been gaining increasing recognition for their adsorption capabilities. This is due to their extremely small size, uniform pore distribution and large specific surface area that can be functionalized or modified by various reagents such as oxidizing agent, metals, metal oxides, polymer or other organic compounds, [10] to increase the efficiency of the CNTs in the adsorption applications. In addition, their high chemical and thermal stability also make CNTs an attractive adsorbent.

#### **2.2 Polyethyleneimine**

Polyethyleneimine (PEI) is a water-soluble polyamine which acts as a weak base in aqueous solution. PEI is a cationic polyelectrolyte due to the presence of a large number of amine groups in molecular chains, these amine groups has affinity to form hydrogen bond with others and can be protonated at pH lower than 9 [11-13]. PEI appears in different molecular masses and forms, but in commercial, it is usually available in branched form that contains primary, secondary and tertiary amino groups as shown in Figure 2.1. PEI is widely used for protein separation and purification



[14], CO<sub>2</sub> capturing [4, 5], and also well known for its metal chelation property [1-3] due to the presence of a large number of amine groups.



**Figure 2.1** Structure of branched polyethylenimine (PEI).

Amine groups on PEI act as borderline-soft Lewis base in HSAB theory [15, 16], it prefers to forming complexes with soft Lewis acid species such as Cu(II), Cd(II), Zn(II) ions. Moreover, the protonated amine groups can interact with negatively charged species such as Au(III) and Cr(VI) anion species. However, PEI is still not suitable for practical use as metal adsorbent because PEI is in liquid form at room temperature. It requires solid support to anchor. Many researchers reported the successful coating of PEI on many solid supports including silica gel [4, 5], polymer [2], activated carbon [6] and also carbon nanotubes [7, 8].

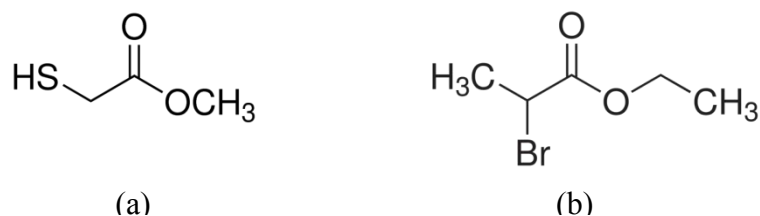
Due to the high mechanical strength and chemical resistance of CNTs as mentioned before, this work is focused on the attachment PEI molecules on the CNTs surface and use as adsorbent. However, PEI is believed to mainly attach on CNTs surface via weak physical interaction and tend to leach out from the surface. Glutaraldehyd is used as crosslinking agent to attach PEI molecules together. This will improve adsorbent stability and prevent the polymer leaching. Furthermore, the PEI coated adsorbent will disperse well in aqueous solution due to an increase in surface hydrophilic property and will result in high adsorption efficiency.

### 2.3 Methyl thioglycolate

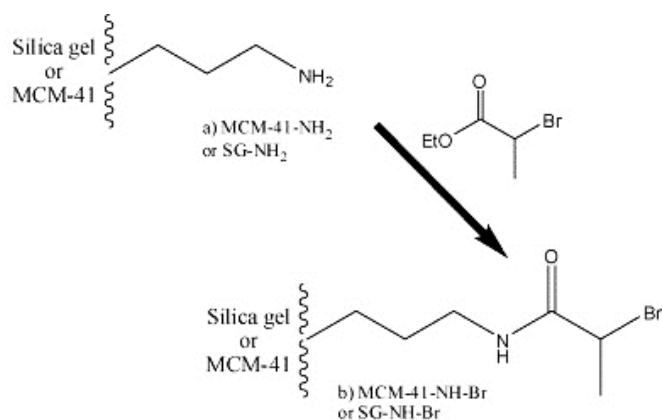
In order to increase selectivity of Au(III) adsorption to the adsorbent, the modification with specific reagent is recommended. Methyl thioglycolate (MTG), also called methyl mercaptoacetate, is a molecule which has two reactive functional

groups i.e. thiol group that prefers to forming complex with Au(III) species and ester group that can react with various compounds. The example of MTG application was reported by Aryal *et al.* [17]. MTG was used in drug released application by stabilizing AuNPs with its thiol site and ester site could react with the drug segment. It seems that MTG was used to be a linker between two different substances [18].

To modify MTG onto PEI coated CNTs, the reaction between amine group of PEI and ester part of MTG is expected. Puanggam and Unob [19] proposed the modification of their adsorbents via reaction between ethyl-2-bromo propionate with aminopropyl modified silica (Figure 2.3), and the modification was a success. Therefore, in this study, the ester group of MTG that has similar structure to ethyl-2-bromo propionate would possibly interact with amine group on PEI attached on the CNTs surface.



**Figure 2.2** Structure of methyl thioglycolate (a) and ethyl-2-bromo propionate (b).



**Figure 2.3** The possible interaction between ester group and amine group [19].

## **2.4 Adsorption**

Adsorption is the phenomenon of the sorption that occurs between the liquid or gas phase and solid phase. Adsorbed substance, also called adsorbate, is transferred from liquid or gas phase to accumulate at the interface between that phase and a solid phase or adsorbent. Adsorption mechanism is generally classified as physical and chemical adsorption [20, 21].

### **Physical adsorption**

Physical adsorption or physisorption is a process that caused by weak electrical attraction, called van der Waals force, between the adsorbed atoms or molecules and the active sites on adsorbent. The adsorbates are adsorbed increasingly on surface in multilayer regime and the number of layers depends on the concentration of adsorbate. Most of the physical adsorption is not specific which means that adsorbed molecules/atoms can freely move over the surface. Physical adsorption is generally reversible and the reversibility depends on the strength of attraction between the adsorbed molecules and active sites of the adsorbent.

### **Chemical adsorption**

Chemical adsorption or chemisorption occurs via chemical reaction between adsorbates and specific active sites on adsorbents that is stronger than van der Waals force. The interaction involves chemical interactions such as ionic and covalent bond that is irreversible. The adsorbates molecules usually occupy certain specific active sites on the surface and can form adsorption layer on adsorbent as monolayer adsorption.

## 2.5 Adsorption isotherms

In the adsorption process, the adsorbed molecules tend to be desorbed from adsorbent into solution before they are adsorbed again. When the rate of adsorption and rate of desorption reach to steady state, there is no change in the concentration of adsorbate on the surface and in solution and it is called adsorption equilibrium. The adsorption equilibrium that occurs at a constant temperature is called adsorption isotherms. There are several isotherm models that are used to describe the relationship between adsorbate and adsorbent at the equilibrium [22-24].

### Langmuir isotherm

Langmuir adsorption model is based on the assumption that adsorbate is adsorbed as the monolayer adsorption on homogeneous surface of adsorbent with limited number of active sites. Each site can adsorb only one target metal ion via chemisorption. The Langmuir equation is given in Eq. (2.1) and its linear form in Eq. (2.2).

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (2.1)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2.2)$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g),  $C_e$  the equilibrium concentration of the adsorbate in the bulk solution (mg/L),  $q_m$  the maximum adsorption capacity (mg/g), and  $b$  is the constant related to the free energy of adsorption (L/mg). Using linearized form of Langmuir equation, the maximum adsorption capacity ( $q_m$ ) and Langmuir constant ( $b$ ) can be obtained by plotting  $C_e/q_e$  versus  $C_e$ .

### Freundlich isotherm

Freundlich adsorption model is based on the assumption that the adsorption occurs on surface bearing different active sites with different adsorption energy and these active sites can adsorb target metal ions as multilayer on surface of adsorbent. The relation of the Freundlich model is given in Eq. (2.3) and its linearized form in Eq. (2.4).

$$q_e = K_F C_e^{1/n} \quad (2.3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2.4)$$

The linear form of Freundlich equation is generally used where  $K_F$  is a constant related to adsorption capacity of the adsorbent ( $\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$ ) and  $n$  is Freundlich constant indicated to the adsorption intensity.  $C_e$  and  $q_e$  are the same parameters as used in Langmuir equation.

### Elovich isotherm

Elovich adsorption model isotherm is commonly used to describe the adsorption behaviour with a rapid equilibrium rate in the early period, while it slows down in later periods of the adsorption process. It is expressed by the relation in Eq. (2.5) and (2.6);

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right) \quad (2.5)$$

$$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \quad (2.6)$$

where  $K_E$  is the Elovich equilibrium constant ( $\text{L/mg}$ ) and  $q_m$  is the Elovich maximum adsorption capacity ( $\text{mg/g}$ ). If the adsorption behaviour at equilibrium obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and the intercept of the linear plot of  $\ln (q_e/C_e)$  versus  $q_e$  as shown in Eq. (2.6).

## 2.6 Literature review

Chanda and Rempel [25] developed and prepared the adsorbent for uranium and iron adsorption by coating polyethyleneimine (PEI) on the surface of silica gel after using Cu(II) ion as the host ion. Glutaraldehyde was subsequently used to cross-link PEI molecules together by changing  $\text{-NH}_2$  group of polyethyleneimine to  $\text{>N-CH(OH)}$  group. Then the host ion was removed by leaching with sulfuric acid. They found that the coated PEI enhanced the adsorption efficiency of uranium and iron.

Yin *et al.* [6] prepared adsorbent from palm shell activated carbon that was impregnated with different molecular weight polyethyleneimine and used the adsorbents to adsorb Cd(II) ions in solution. They observed that the adsorption of low molecular weight PEI on the micropores of activated carbon as monolayer led to a reduction in specific surface area while high molecular weight PEI did not significantly affect the reduction of specific surface area. In addition, it was found that only low molecular weight PEI appeared to enhance Cd(II) adsorption capacity of the activated carbon.

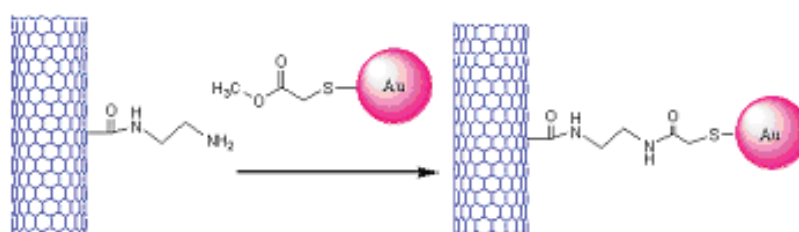
From these researches, it reveals that polyethyleneimine can be coated on both organic and inorganic materials. Thus, it is possible to prepare adsorbent by using polyethyleneimine attached on carbon nanotubes and some researchers have been successfully prepared such materials. For example, Hu *et al.* [26] synthesized the composite of multi-walled carbon nanotubes (MWNTs) and gold nanoparticle. This method began with the attachment of PEI on MWNTs surface via physical and electrostatic interaction and used this PEI to adsorb Au(III) ions followed by heating the solid to reduce Au(III) to  $\text{Au}^0$ . The MWNTs composite which attached with gold nanoparticles can be used in optic and electrocatalytic applications.

Lei *et al.* [27] proposed the method to synthesize carbon nanotube/CdSe composite. Polyethyleneimine (PEI) was coated on multi-walled carbon nanotubes (MWNTs) through electrostatic interaction, followed by grafting with polyacrylonitrile (PAN) on PEI molecules via atom transfer radical polymerization (ATRP), then coupling CdSe nanoparticles to  $\text{-CN}$  group of PAN molecules. The composite of CdSe particles attached on the sidewalls of MWNTs was obtained.

Etika *et al.* [28] studied the dispersibility of single wall carbon nanotube (SWNT) in water using pH-responsive polymers to stabilize aqueous SWNT suspensions. The result showed that SWNT coated with polyanion *i.e.* poly(acrylic acid) and poly(methacrylic acid) dispersed well in high pH solution whereas aggregated and bundled in low pH solution. SWNT that was coated with polycation *i.e.* poly(allylamine) and polyethyleneimine had a contrast result.

Zhang *et al.* [29] prepared Fe<sub>3</sub>O<sub>4</sub>-MWNT composite for bionanoscience application. First, MWNT was impregnated in polyethyleneimine solution and dried, then, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were formed on the sidewalls of the as-modified MWCNTs through solvothermal method. The obtained composite has electrical conductivity higher than original MWNT and has magnetic saturation similar to Fe<sub>3</sub>O<sub>4</sub>.

Above mentioned researches show that polyethyleneimine can be coated on surface of carbon nanotubes. Bifeng *et al.* [18] demonstrated the preparation of the hybrid material of carbon nanotubes anchored with gold nanoparticles via covalent interactions between methyl thioglycolate capping AuNPs and -NH<sub>2</sub> end group of ethylenediamine grafted on CNTs as shown in Figure 2.4. It was found that ester group (-COOR) of methyl thioglycolate can form amide bond with amine group (-NH<sub>2</sub>).



**Figure 2.4** Synthesis of AuNPs-CNTs hybrid material.

Thus, this research aims to prepare polyethyleneimine-coated carbon nanotubes adsorbent modified with methyl thioglycolate using interaction between amine group (-NH<sub>2</sub>) of polyethyleneimine and ester group (-COOR) of methyl thioglycolate. The thiol end groups of methyl thioglycolate have affinity toward Au(III) ions and the obtained adsorbents were used for Au(III) adsorption in aqueous solutions.

# **CHAPTER III**

## **EXPERIMENTS**

### **3.1 Apparatus**

#### **Flame Atomic Adsorption Spectrometer (FAAS)**

Flame atomic adsorption spectrometer (Perkin-Elmer, AAnalyst 100) was used for determination of metal concentration in solution using hollow cathode lamps (HCL) as a radiation source with air/acetylene fuel.

#### **Fourier Transform Infrared Spectrometer (FT-IR)**

Fourier Transform Infrared Spectrometer (Thermo Scientific, Nicolet 6700) was used to characterize the functional groups of adsorbents. The infrared spectra were recorded from 400 to 4000  $\text{cm}^{-1}$  in transmittance mode with KBr pellet technique.

#### **Fourier Transform Raman Spectrometer (FT-Raman)**

Fourier Transform Raman Spectrometer (Perkin-Elmer, Spectrum GX) was used for characterization of adsorbents by detecting the functional groups of materials.

#### **Scanning Electron Microscope with EDS (SEM-EDS)**

Scanning Electron Microscope (JEOL, JSM-6400) was used to analyze and photograph the images of surface adsorbents. Energy Dispersive Spectrometry (Oxford, Link ISIS 300) was equipped with SEM for measurements of elements on the surface.



**Thermogravimetric Analyzer (TGA)**

Thermogravimetric Analyzer (Perkin-Elmer, Pyris 1 TGA) was used to measure weight loss of adsorbents as a function of temperature. This technique was performed in the temperature range of 50 – 900°C at a heating rate of 10°C/min under nitrogen atmosphere.

**pH meter**

The pH meter (Hanna instrument, pH 211) was used for all pH measurements.

**Centrifuge**

Centrifuges (Hettich, EBA 20 and Sanyo, Centaur 2) were used for liquid-solid separation in all experiments.

## 3.2 Chemical and reagent

### 3.2.1 Chemicals

All chemicals were analytical reagent grade and listed in Table 3.1

**Table 3.1** Chemicals list and suppliers

<b>Chemicals</b>	<b>Suppliers</b>
Carbon nanotubes	Chiang Mai University
Dichloromethane	Carlo Erba Reagents
Ethanol	Merck KGaA
Glutaraldehyde solution (5.6M)	Fluka
Hydrochloric acid fuming 37%	Merck KGaA
Methyl thioglycolate 95%	Aldrich Chemistry
Nitric acid 65%	Merck KGaA
Polyethyleneimine 50%wt. (Mw 750000)	Aldrich Chemistry
Potassium hydroxide	Merck KGaA
Sodium acetate anhydrous	Carlo Erba Reagents
Sulfuric acid 95–97%	Merck KGaA
Thiourea 99.0%	Sigma–Aldrich
Toluene *	Carlo Erba Reagents
Au standard solution (1000 mg/L)	Merck KGaA
Cu standard solution (1000 mg/L)	Merck KGaA
Fe standard solution (1000 mg/L)	Merck KGaA
Ni standard solution (1000 mg/L)	Merck KGaA
Zn standard solution (1000 mg/L)	Merck KGaA

\* For moisture elimination, toluene was drying with calcium hydride and freshly distilled under nitrogen atmosphere before use.

### **3.2.2 Preparation of reagents**

All reagents were prepared by using deionized (DI) water.

#### **Working metals standard solution**

All working standard solutions were prepared by dilution of 1000 mg/L stock standard solutions to the desired concentrations.

#### **pH adjusted solution**

For pH adjustment, both of hydrochloric acid (HCl) and potassium hydroxide (KOH) solution were used and prepared in concentration of 1%v/v. HCl solution was prepared by dilution of concentrate acid solution. KOH solution was dissolved from calculated amount in DI water.

#### **Sodium acetate buffer solution**

Sodium acetate buffer solution was dissolved from desired amount in DI water and used to be pH buffer and ionic strength controller of working metal solution.

#### **Glutaraldehyde solution**

The crosslink agent was prepared by dilution of 5.6 M stock glutaraldehyde solution to the desired concentrations.

#### **Ninhydrin solution**

Ninhydrin solution was prepared by dissolved the appropriate amount of ninhydrin in ethanol.

#### **Thiourea**

The required amounts of thiourea were dissolved in 2%v/v HCl to prepare the desorbing solution in concentration range of 0.5 – 2.0 M thiourea.

### 3.3 Adsorbent preparation

#### 3.3.1 Purification of carbon nanotubes (CNTs)

For removing the remained metal catalyst that was used in synthesized process, carbon nanotubes (CNTs) were purified by refluxing with concentrate acid. Firstly, CNTs were sonicated with 100 mL of mixed acid (conc. nitric acid and conc. sulfuric acid by 1:3 volume ratio) for an hour. The CNTs became black slurry. Then the mixture was transferred in to a two neck round bottom flask and refluxed at 85°C for 5 hours. The black slurry was centrifuged and washed with DI water several times until pH reached to neutral. Finally, the treated CNTs was dried at 60 °C and kept for further use.

#### 3.3.2 Preparation of polyethyleneimine-coated CNTs (CNTs-PEI)

About 100 mg of treated CNTs was put into a test tube with desired amounts of polyethyleneimine (PEI). Then, 10 mL of DI water was subsequently added and mixed by magnetical stirrer. After 2 hours, the mixture was centrifuged and decanted the centrifugate off. About 10 mL of glutaraldehyde which acted as crosslinking agent was added to the remained solid and the mixture was stirred again for 30 minutes. In order to have free amine groups left on the surface, glutaraldehyde was fixed at 1:2 by mole PEI. After that, the mixture was centrifuged and washed twice with 5 mL of each DI water, ethanol and dichloromethane, respectively. The obtained solid was dried and kept at room temperature. The product was labeled as polyethyleneimine-coated carbon nanotubes (CNTs-PEI).

In order to optimize the amount of PEI, adsorbents were prepared by varying the amount of polymer from  $0.67 \times 10^{-4}$  to  $5.33 \times 10^{-4}$  mmol/g CNTs and the Au(III) adsorption capacities of obtained CNTs-PEI were determined. The adsorption efficiency  $q$  (mg/g) was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{m} \quad (3.1)$$

where  $C_i$  and  $C_f$  are the initial and final concentration of Au(III) in solution (mg/L), respectively.  $V$  is the volume of Au(III) solution (L) and  $m$  is the weight of sorbents (g).

### 3.3.3 Modification with methyl thioglycolate (CNTs-PEI-MTG)

In modification step, 100 mg CNTs coating with the optimized PEI amount and the desired amount of methyl thioglycolate (MTG) were added into a two neck round bottom flask with 50 mL dry toluene as solvent. Then the flask was placed in a sand baht at 60°C under nitrogen atmosphere for 5 hours. The obtained product was separated by centrifugation and washed twice with 5 mL of each dry toluene, ethanol and dichloromethane, respectively. The resulting solid was dried at room temperature. The product was called polyethyleneimine-coated carbon nanotubes modified with methyl thioglycolate (CNTs-PEI-MTG). The optimized amount of MTG was also evaluated by varying the amount of methyl thioglycolate from 1.79 to 26.78 mmol/g CNTs and their Au(III) adsorption efficiency was determined.

The modified adsorbent which was prepared by using the optimized amount of PEI and MTG, was used for further experiments.

## 3.4 Characterization of adsorbents

The products from each preparation step were characterized by scanning electron microscope equipped with energy dispersive X-ray analyzer (SEM-EDX), thermal gravimetric analyzer (TGA), Fourier transforms infrared spectrometer (FT-IR), Fourier transforms Raman spectrometer (FT-Raman) and ninhydrin test.

### **3.5 Au(III) adsorption study**

Working Au(III) solution using in various adsorption parameters, was prepared from stock Au(III) standard solution (1000 mg/L) and controlled an ionic strength with 0.05 M of sodium acetate buffer solution. All adsorption experiments were performed in triplicate using batch method in test tube as follow.

#### **3.5.1 Effect of pH**

The effect of pH on Au(III) adsorption efficiency of adsorbents was studied in the pH range of 1.0 – 7.0 by using 1% HCl and 1% KOH solution for pH adjustment. About 5 mL of Au(III) solution (80 mg/L) was added in test tube contained 5 mg of CNTs-PEI-MTG and magnetically stirred at room temperature for 2 hours. The remained solution was separated by centrifugation and measured Au(III) amount by flame atomic adsorption spectrometer (FAAS). The Au(III) adsorption efficiency of CNTs-PEI-MTG in various pH values was compared with the unmodified adsorbents (CNTs-PEI).

#### **3.5.2 Effect of adsorption time**

The effect of adsorption time on Au(III) adsorption efficiency of adsorbents was investigated using 80 mg/L Au(III) solution with the optimized pH value from previous experiment. About 5 mL of Au(III) solution was added in test tube contained 5 mg of CNTs-PEI-MTG and magnetically stirred at room temperature. The adsorption time was varied in the range of 10 – 120 minutes. The remained solution was separated by centrifugation and determined Au(III) concentration by FAAS. The effect of adsorption time on Au(III) adsorption efficiency of CNTs-PEI-MTG was compared with the unmodified adsorbents (CNTs-PEI).

### **3.5.3 Effect of co-existing ions**

The effect of co-existing ions on selectivity of adsorbents was investigated using binary metal solution of Au(III) with other metals i.e. Fe(III), Cu(II), Zn(II) or Ni(II). About 5 mg of CNTs-PEI-MTG was mixed with 5 mL of the binary metals solution using the optimized adsorption condition (pH and contact time). The remained solution was separated by centrifugation and measured Au(III) amount by FAAS. The Au(III) adsorption efficiency of CNTs-PEI-MTG was compared with the unmodified adsorbents (CNTs-PEI).

### **3.5.4 Adsorption Isotherm**

The adsorption isotherm experiments were performed at  $25\pm 1^\circ\text{C}$ . About 5 mg of CNTs-PEI-MTG was magnetically stirred with 5 mL of various initial concentrations of Au(III) solution in the range of 50 – 400 mg/L using optimal condition (pH and contact time). The remained solution was separated by centrifugation and determined Au(III) concentration by FAAS. Langmuir, Freundlich and Elovich model were adsorption isotherm models that used to study adsorption behaviour and calculate the maximum adsorption capacity of the adsorbent.

## **3.6 Au(III) desorption study**

Au(III) solution which was used in desorption studies, was prepared as same as solution in the adsorption studied part. All desorption experiments were performed in triplicate using batch method in a test tube as follow.

### **3.6.1 Type of desorbing solution**

About 5 mg of CNTs-PEI-MTG was magnetically stirred with 5 mL of Au(III) solution pH 4 for an hour. Then the solution was separated for measurement of the remaining Au(III) amount. After washing adsorbent with DI water, 5 mL of various

types and concentration of desorbing solution i.e. DI water, HCl, and acidic thiourea solution was added and stirred for an hour. The remained solution was separated by centrifugation and determined Au(III) amount by FAAS. The suitable eluent was used for further experiment.

### **3.6.2 Volume of desorbing solution**

Similarity to the procedure in 3.6.1, but the Au(III) adsorbed CNTs-PEI-MTG were desorbed with different volume from 2 to 5 mL of the suitable desorbing solution for an hour. The amount of Au(III) in the solution was determined by FAAS.

## **3.7 Reusability of the adsorbent**

In adsorption step, CNTs-PEI-MTG was mixed with 5 mL of Au(III) solution at pH 4 for an hour. Once the adsorbent was separated and washed with DI water, the suitable volume of the desorbing solution, which obtained from desorption studies, was added and stirred for an hour. The adsorbent was separated and washed twice with DI water and repeated to adsorption step again for 4 times. The amount of Au(III) in solution was determined by FAAS.

## **3.8 Real sample**

Au(III) wastewater which was obtained from the Gem and Jewelry Institute of Thailand (Public Organization) was performed adsorption efficiency of CNTs-PEI-MTG using the optimized adsorption time. The remained amount of Au(III) and other ions in solution was measured by FAAS and ICP-OES, respectively.

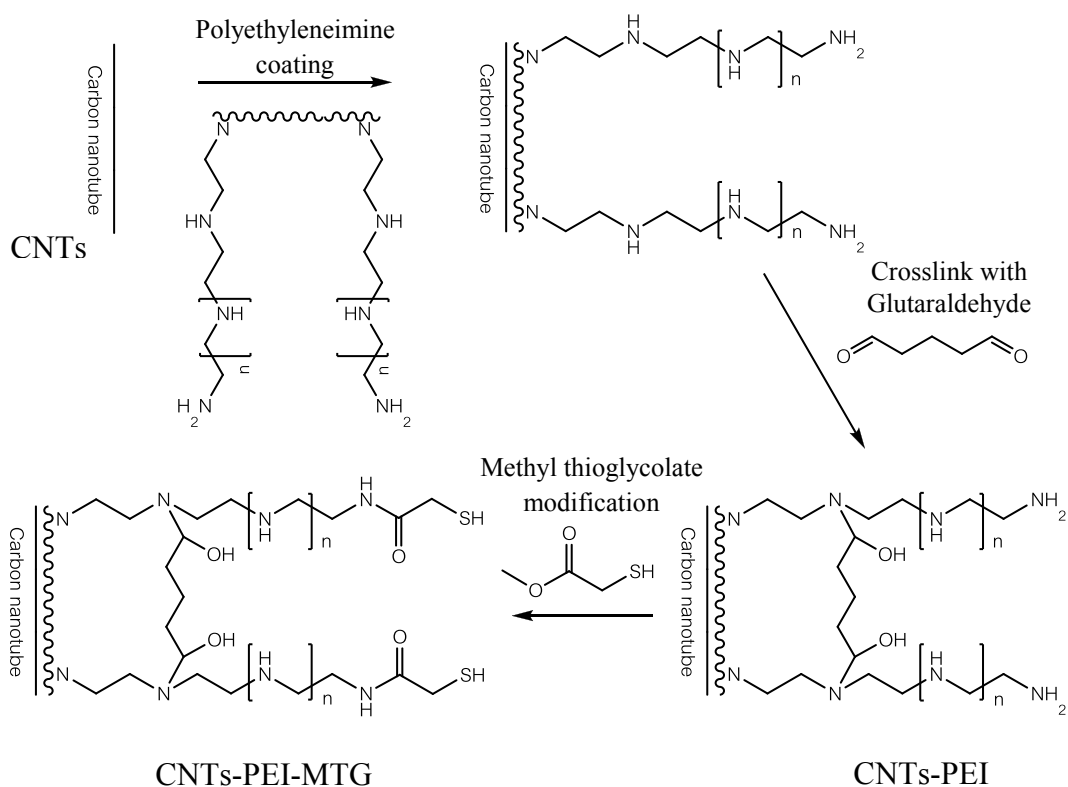


## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1 Preparation of Adsorbents

It is known that carbon nanotubes (CNTs) have great mechanical property suitable for various applications including as adsorbents. However, CNTs has low capability to adsorb Au(III) ions and the modification of this material is recommended to improve Au(III) adsorption efficiency.



**Scheme 4.1** The preparation steps of adsorbent

In this research, carbon nanotubes were coated with the amine-rich polymer, polyethyleneimine (PEI), via physical adsorption (Scheme 4.1). In order to prevent the leaching of polymer from CNTs surface due to the weak interaction between

polymer and CNTs, the PEI molecules were attached together by using glutaraldehyde as crosslinking agent. The amount of glutaraldehyde was varied based on the amount of the starting PEI by fixing a mole ratio to 2:1 PEI:glutaraldehyde. It resulted in certain number of free amine groups left on the surface for the further modification. These free amine groups could possibly form amide bond with ester functional group of methyl thioglycolate (MTG). The excessive amount of MTG was used to ensure that all of free amine groups will be reacted with MTG. In the assumption that MTG molecule will react with amine group with a mole ratio of 1:1, MTG was added ten times of free amine group content on PEI molecules. In summary, the ratio of MTG and the starting PEI was calculated to be  $8.92 \times 10^4:1$  by mole PEI. The modified adsorbent containing thiol group of MTG preferred to chelate with Au(III) ions and can be used for Au(III) adsorption.

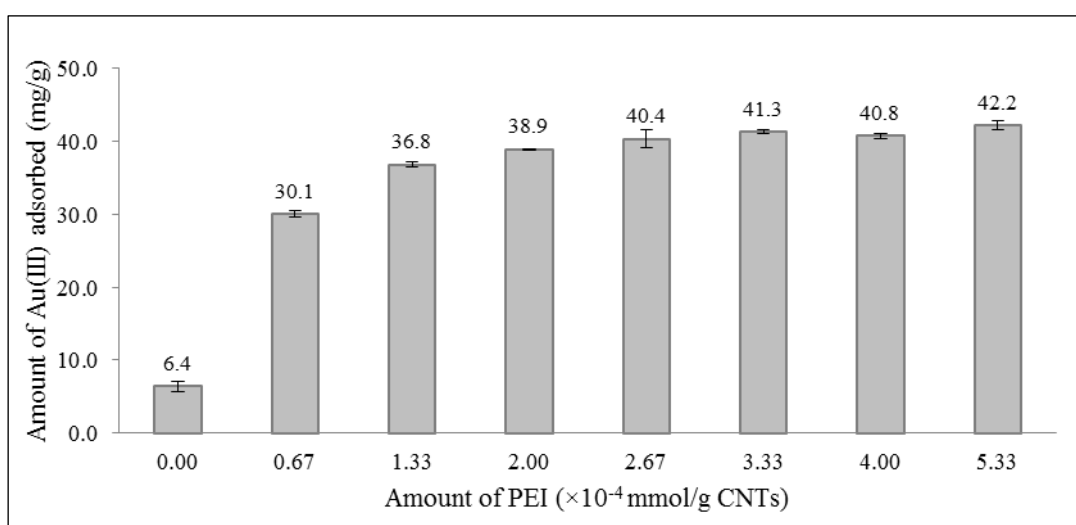
Certain parameters in CNTs modification were studied and optimized including the PEI and MTG amount. In an attempt to quantify the amount of PEI attached on CNTs surface, colorimetric and UV-vis method was performed to determine the amount of residual PEI in the coating solution. Unfortunately, the PEI solution after the coating contained a considerable amount of CNTs and could not be analyzed correctly by UV-Vis spectrometer. This is the same reason in MTG modification step. Thus, the effect of amount of PEI and MTG for the modification was determined indirectly by determining the efficiency in Au(III) adsorption by the adsorbents prepared by using different amount of PEI or MTG. The efficiency in Au(III) adsorption was presented in term of the amount of Au(III) adsorbed by adsorbent ( $q$ ), calculated from the given equation (4.1);

$$q = \frac{(C_i - C_f)V}{m} \quad (4.1)$$

where  $C_i$  and  $C_f$  are the initial and final concentration of Au(III) in solution (mg/L), respectively.  $V$  is the volume of Au(III) solution (L) and  $m$  is the weight of adsorbents (g). The results were demonstrated as follow.

#### 4.1.1 Optimized amount of PEI

CNTs-PEI adsorbents were prepared by varying the amount of PEI (MW 750,000) from  $0.67 \times 10^{-4}$  to  $5.33 \times 10^{-4}$  mmol in the coating of one gram CNTs. The crosslinking was performed immediately after PEI coating. The adsorption efficiencies of the obtained adsorbents are shown in Figure 4.1.



**Figure 4.1** Au(III) adsorption efficiency of CNTs-PEI prepared by using various PEI amounts; initial Au(III) concentration of 50 mg/L; 5 mg sorbent.

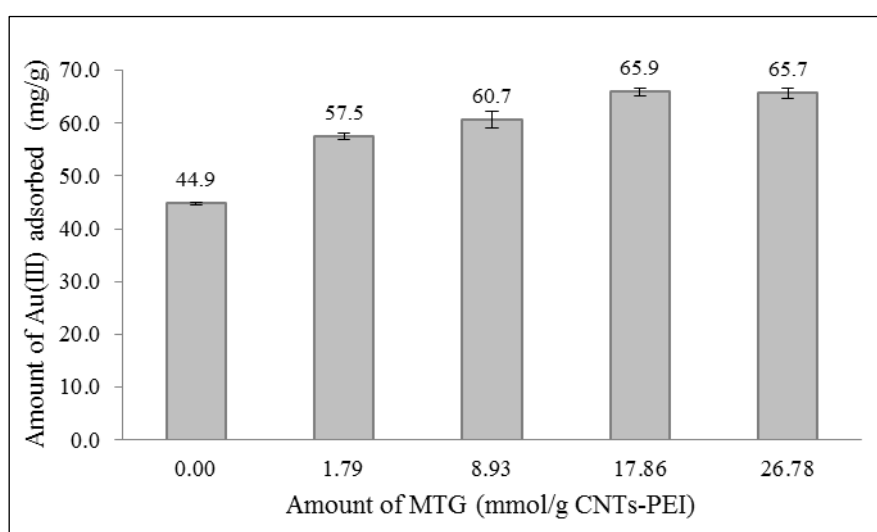
The efficiency in Au(III) adsorption on CNTs-PEI increased significantly, compared to bare CNTs and tended to constant value when PEI amount of higher than  $1.33 \times 10^{-4}$  mmol was used to coat one gram CNTs. Therefore, the PEI amount of  $2.00 \times 10^{-4}$  mmol/g CNTs was chosen for CNTs-PEI preparation.

The mechanism of Au(III) adsorption on both CNTs and CNTs-PEI is believed to occur via electrostatic interaction. The acid purification process caused defects and added more acid functional group to bare CNTs. This process also affected the point of zero charge (PZC) of CNTs which is defined as the pH at which the surface is electrostatically neutral in aqueous solutions [30]. At pH values below the PZC, the substrate becomes protonated and exhibits a positive net charge on the surface. In contrast, the net surface charge turns negative at pH values above the PZC. From literatures, the PZC of acid-treated carbon nanotubes is in the range of 1-3 [31-33], and the pH of Au(III) solution using in this experiment was below 1 that means the

CNTs surface became positive. In case of PEI-coated CNTs, the positively charged surface occurred by protonation of amine groups on PEI coating. This positively charged adsorbent surface can interact with negatively charged specie  $\text{AuCl}_4^-$ .

#### 4.1.2 Optimized amount of MTG

Once the optimized PEI amount was obtained, MTG was modified to the prepared CNTs-PEI by varied MTG amount from 1.79 to 26.78 mmol/g CNTs-PEI. The adsorption efficiency of CNTs-PEI-MTG adsorbents was evaluated and shown in Figure 4.2. Similarly to previous experiment, the more MTG amount used in the modification process, the higher efficiency in Au(III) adsorption was obtained. The optimum amount of MTG was found to be 17.86 mmol/g CNTs-PEI.



**Figure 4.2** Au(III) adsorption efficiency of CNTs-PEI-MTG obtained by using various MTG amounts in the modification; initial Au(III) concentration of 70 mg/L; 5 mg sorbent.

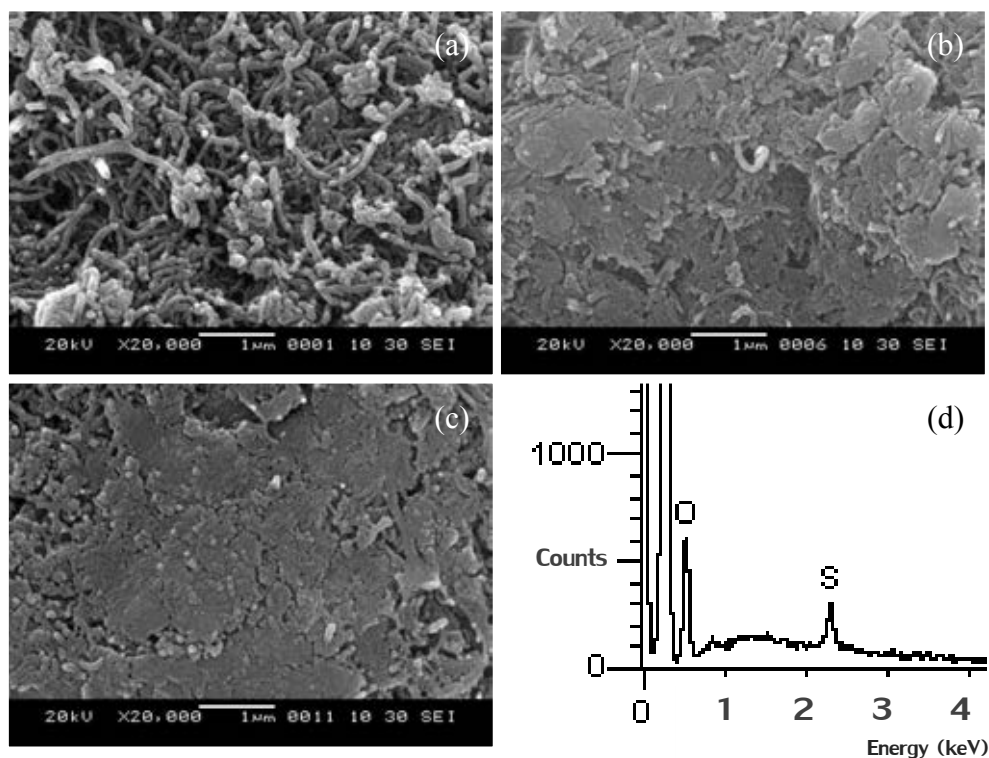
## 4.2 Characterization of adsorbents

The products obtained from each preparation step were characterized by scanning electron microscope equipped with energy dispersive X-ray analyzer (SEM-

EDX), thermal gravimetric analyzer (TGA), Fourier transforms infrared spectrometer (FT-IR), Fourier transforms Raman spectrometer (FT-Raman), and ninhydrin test. The results were shown and discussed in the following part.

#### 4.2.1 Characterization by scanning electron microscope with energy dispersive X-ray analyzer (SEM-EDX)

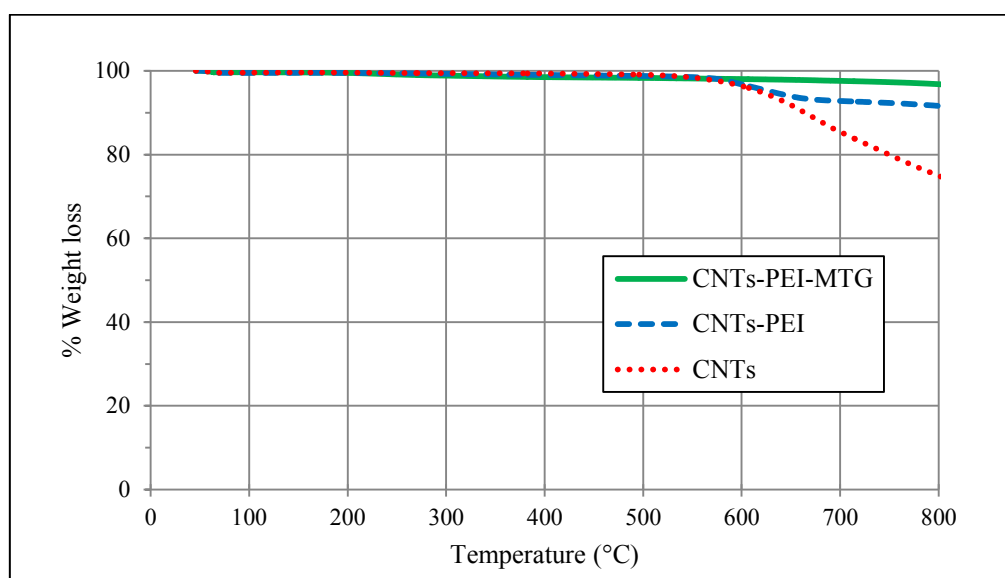
The adsorbents morphology was illustrated by SEM and the images are shown in Figure 4.3. The surface of CNTs-PEI is smoother than CNTs surface as a result of the polymer coating. The PEI molecules covered the whole bulk of entangled CNTs. CNTs-PEI-MTG has similar smooth surface as CNTs-PEI, and the EDX spectrum of CNTs-PEI-MTG surface shows small signal of sulfur atom indicating the existence of few MTG on the adsorbent surface.



**Figure 4.3** SEM images of CNTs (a), CNTs-PEI (b) and CNTs-PEI-MTG (c), and EDX spectra of CNTs-PEI-MTG (d).

#### 4.2.2 Characterization by thermal gravimetric analyzer (TGA)

From TGA curve of CNTs (Figure 4.4), there was no significant weight loss until temperature over 550°C indicating that bare CNTs had high thermal stability. However, weight loss of CNTs was observed and instantly increased at the temperature of 600°C and higher. The final weight loss at 800°C was approximately 25%. Upon PEI coating, the extent of weight loss at the temperature above 550°C was decreased, and in the presence of MTG, CNTs-PEI-MTG weight loss of only 3% was observed at 800°C.



**Figure 4.4** TGA curves of the adsorbents from each preparation step.

This phenomenon could be explained as follow. For CNTs-PEI adsorbent, PEI was coated as a layer on the surface of bulk CNTs as shown in SEM image. When the temperature increased to about 300-450°C which are the decomposition temperature of PEI [34, 35], the polymer began to decompose and become coke carbon that covered the bulk CNTs. Therefore, the oxygen cannot penetrate the coke to react with CNTs resulting in the absence of weight loss in this temperature range. Moreover, the rate of increasing temperature using in TGA program was 10°C/minute that was too fast for the decomposition of materials with low surface area. It was also observed by Yin *et al.* [6] as they found that high molecular weight PEI-impregnated activated

carbon had lower weight losses, compared to virgin activated carbon. The results of TGA and SEM indirectly indicate that PEI efficiently coated CNTs.

In case of MTG-modified adsorbent, MTG can be melted and decomposed in the range of 36-200°C [36]. The melted MTG was probably embedded in the cross-linked PEI network and decomposed along with PEI. This occurrence caused CNTs to contain higher amount of coke carbon coverage that prevented CNTs from thermal decomposition and resulted in less weight loss of adsorbent.

### 4.2.3 Results from ninhydrin test

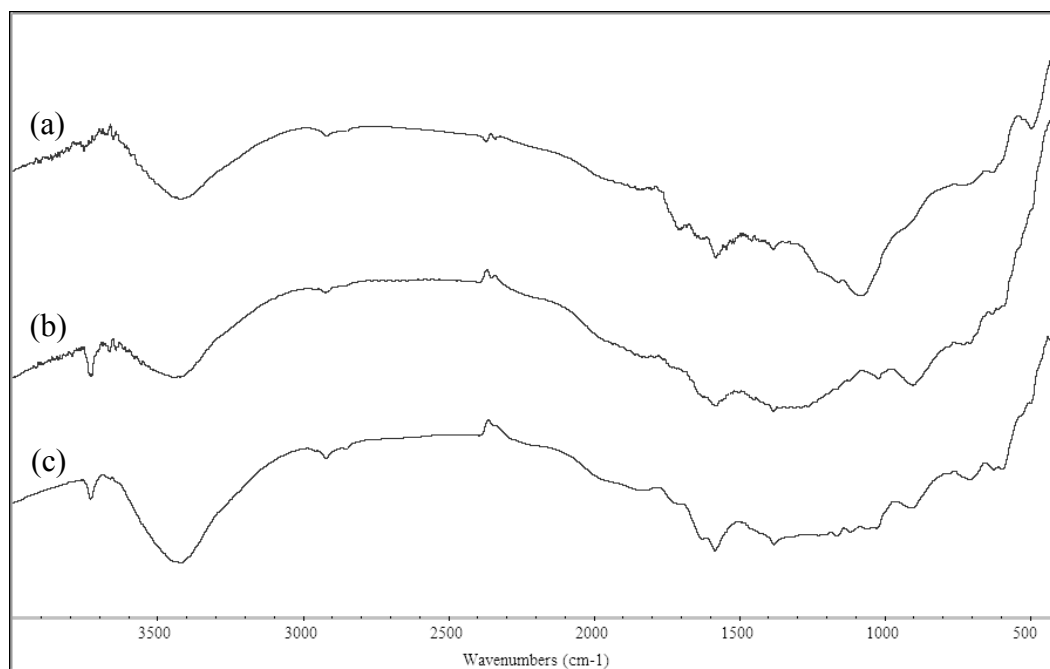
Results from ninhydrin test (Table 4.1), which the color of test solution turned from yellow to dark blue or purple when reacted with free amines such as primary and secondary amine group, confirmed that CNTs-PEI had free amines on the surface. In addition, ninhydrin test also showed positive result with CNTs-PEI-MTG indicating that the unmodified PEI amine groups still remained on adsorbent surface. MTG could not react with all free amine groups of PEI because of the steric effect between branched PEI molecules.

**Table 4.1** Results of ninhydrin test

<b>Samples</b>	<b>Color of solution</b>
Ninhydrin	Yellow
CNTs	Yellow
CNTs-PEI	Dark blue
CNTs-PEI-MTG	Dark blue

### 4.2.4 Characterization by Fourier transform infrared spectrometer (FT-IR)

FT-IR spectra of adsorbents were recorded using potassium bromide (KBr) technique. As shown in Figure 4.5, spectra of CNTs (a), CNTs-PEI (b), and CNTs-PEI-MTG (c) are very similar.



**Figure 4.5** FT-IR spectra of CNTs (a), CNTs-PEI (b) and CNTs-PEI-MTG (c).

Figure 4.5 (a) shows the FT-IR spectra of CNTs after purification. After acid treatment, carbon surface contained anchor groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (-C=O). The broad peak at  $3420\text{ cm}^{-1}$  corresponds to hydroxyl group whereas the peaks at the  $1750\text{--}1550\text{ cm}^{-1}$  range are normally assigned to the vibration of carboxylic groups [37-39]. In addition, the appearance of small peak around  $2900\text{ cm}^{-1}$  indicates the stretching of  $\text{CH}_2\text{--CH}_3$  groups, which indicates the rupture of the CNTs sidewalls by acid treatment [40].

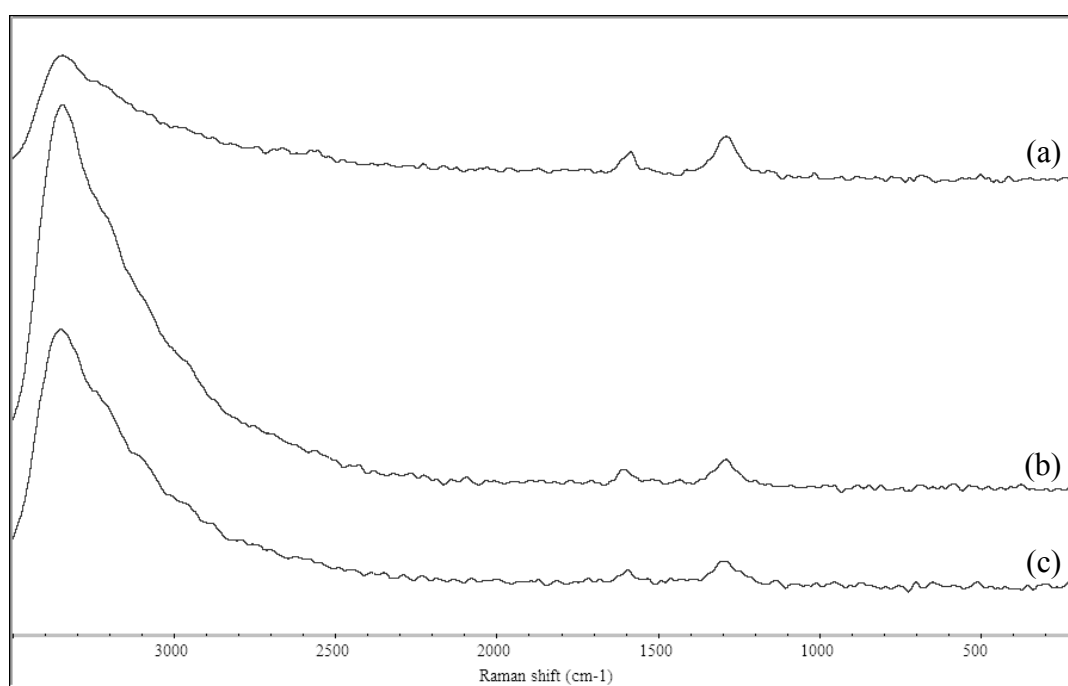
The FT-IR spectrum of the PEI-coated CNTs is displayed in Figure 4.5 (b). The broad peak assigned for N-H stretching would appear at the same place with O-H stretching signal ( $3500\text{--}3200\text{ cm}^{-1}$ ), whereas, the peak assigned for N-H bending would be at the same region with characteristic peaks of carboxylic groups ( $1700\text{--}1550\text{ cm}^{-1}$ ) [11]. Therefore, it cannot clearly confirm that PEI was attached on the CNTs surface by FT-IR spectrum. After MTG modification, FT-IR spectrum of CNTs-PEI-MTG in Figure 4.5 (c) has no differences from the previous spectra. The peaks assigned for amide bond ( $\text{--CO--NH--}$ ) at  $1650$  and  $1560\text{ cm}^{-1}$  [18] could not be clearly identified because they might overlap with the peaks of unreacted amine



groups from PEI and the carboxylic groups from CNTs. Moreover, the signal of  $\nu(\text{S-H})$  stretch that could appear in the range of  $2600\text{--}2550\text{ cm}^{-1}$  [41] was not found due to few amount of MTG on the surface as observed by SEM-EDX. Therefore, this FT-IR technique could not confirm that MTG was actually modified onto the adsorbent. Next, the adsorbents were characterized with FT-Raman spectroscopy.

#### 4.2.5 Characterization by Fourier Transform Raman Spectrometer (FT-Raman)

The FT-Raman spectra of CNTs (a), CNTs-PEI (b), and CNTs-PEI-MTG (c) are mostly similar (Figure 4.6). There are two characteristic peaks of carbon nanotubes at about  $1300$  and  $1600\text{ cm}^{-1}$  [42-44]. Moreover, the peak around  $3300\text{ cm}^{-1}$  of CNTs-PEI spectrum was higher than that of the spectrum of CNTs due to the overlap between the  $\nu(\text{O-H})$  stretching vibration from moisture and  $\nu(\text{N-H})$  stretching vibration of amine group of PEI. In addition, FT-Raman spectra of CNTs-PEI-MTG did not display characteristic peak of S-H stretching vibration from MTG at about  $2500\text{ cm}^{-1}$  because only few amount of MTG was attached on the adsorbent.



**Figure 4.6** FT-Raman spectra of CNTs (a), CNTs-PEI (b) and CNTs-PEI-MTG (c).

In conclusion, the results of characterization by FT-IR and FT-Raman could not confirm that MTG was actually modified onto the adsorbent. Even though, we believed that MTG-modified adsorbent was achieved due to the fact that the previous results of Au(III) adsorption showed significant differences of the adsorption efficiency between CNTs, CNTs-PEI and CNTs-PEI-MTG.

### 4.3 Au(III) adsorption study

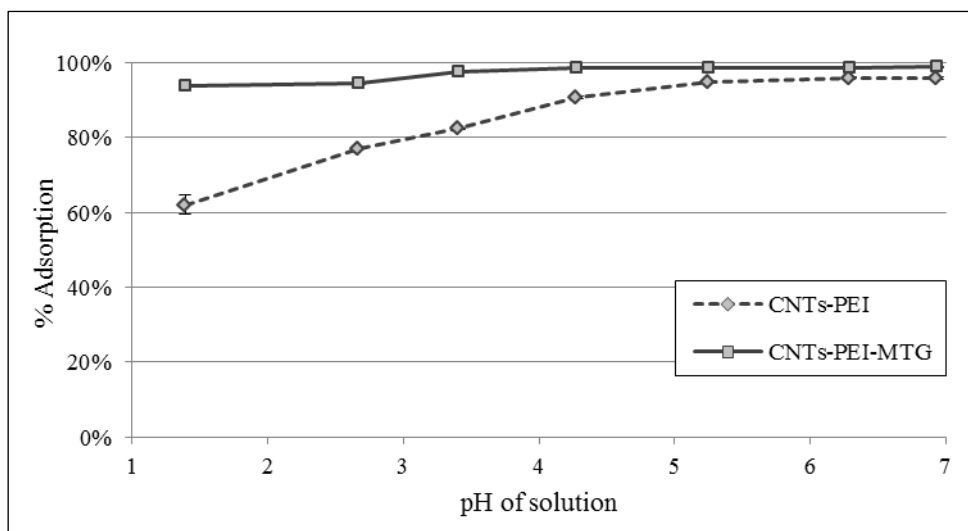
To obtain suitable conditions for applications in wastewater treatment, the effect of certain parameters such as the effect of pH, adsorption time and co-existing ions that may affect the adsorption of Au(III) on adsorbents was studied. The efficiency in Au(III) adsorption by the adsorbent was evaluated and presented in term of adsorption percentage (%adsorption) which obtained from following equation

$$\text{adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (4.2)$$

where  $C_i$  and  $C_f$  are the initial and final concentration of Au(III) in solution (mg/L), respectively. The adsorbent CNTs-PEI-MTG prepared from the optimized amount of PEI and MTG were used in this study.

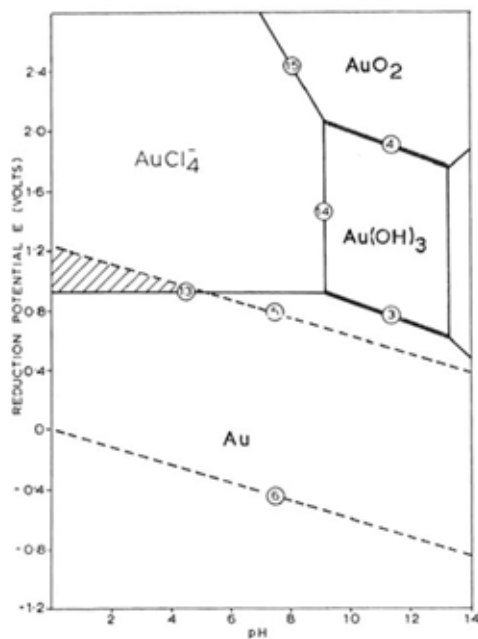
#### 4.3.1 Effect of pH

Au(III) would exist in various species form that have different behavior depending on the pH value of solution, and only the species that have good affinity with adsorbent functional groups will be adsorbed onto the adsorbent. Therefore, the first parameter in adsorption study to be investigated was the effect of pH. The adsorption percentage of MTG modified CNTs-PEI was evaluated and compared with PEI-coated CNTs by using working Au(III) solution (80 mg/L) in a pH range of 1-7 with adsorption time of 120 minutes. The adsorption results were displayed as function of pH value in Figure 4.7.



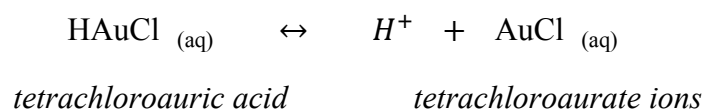
**Figure 4.7** Effect of pH on Au(III) adsorption on adsorbents; initial concentration 80 mg/L; adsorption time 120 minute; 5 mg sorbent.

In fact, amine groups on PEI were easily protonated because  $pK_a$  value of PEI is around 9-10 [11-13] resulting in positively charged CNTs-PEI adsorbent surface in solution at pH below 9. It can be seen in Figure 4.8 that the major species of Au(III) in this pH range is the negative tetrachloroaurate ion ( $AuCl_4^-$ ).



**Figure 4.8** Pourbaix diagram for the system gold-water- $Cl^-$  at 25°C [45].

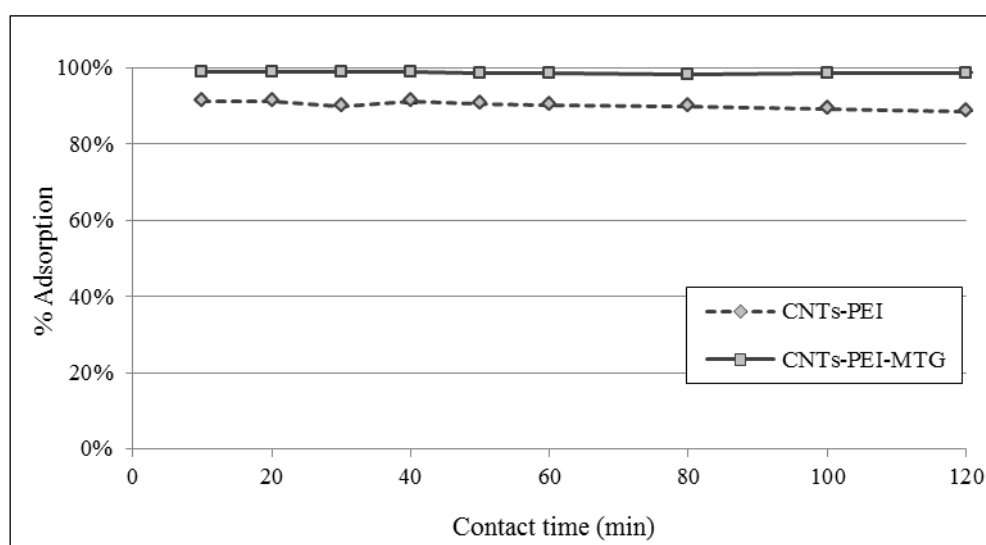
In case of PEI-coated CNTs, the adsorption probably occurred through electrostatic interaction between  $[\text{AuCl}_4]^-$  and the protonated amine of PEI on the surface. As a result, the efficiency in Au(III) adsorption by CNTs-PEI decreased by lowering the solution pH. This observation can be explained by the presence of different concentration of  $\text{AuCl}_4^-$  at different solution pH. In acidic solution, there are hydronium ions ( $\text{H}^+$ ) that can reversibly interact with  $\text{AuCl}_4^-$  yielding a higher amount of tetraaurochloric acid ( $\text{HAuCl}_4$ ) and less amount of negatively charged species  $\text{AuCl}_4^-$ . Therefore, the amount of Au(III) adsorbed decreased. On the other hand, increasing the pH value will result in higher adsorption efficiency. The equilibrium is shown below.



In case of MTG modified adsorbent, the Au(III) adsorption efficiency was enhanced by the presence of thiol groups of modified MTG. Au(III) ions were adsorbed onto adsorbent surface via chelation between thiol groups of MTG and Au(III) ions to form Au-SH complex [46]. It is observed that the solution pH did not affect the Au(III) adsorption on CNTs-PEI-MTG. It seems that MTG especially enhanced the adsorption efficiency at low pH range. The results indicate that the thiol groups of MTG have a good affinity toward  $\text{HAuCl}_4$  species present in strong acidic solution. When the adsorbents were used in solution having pH higher than 3, the efficiency in Au(III) adsorption did not change. In contrast, Andrea *et al.* observed a decrease in Au(III) adsorption on mercaptopropyl modified magnetic particles in solution having pH higher than 4 [47]. Regarding our adsorbent, it is believed that the presence of unmodified amine groups of CNTs-PEI compensated the low adsorption efficiency of thiol group toward Au(III) at higher pH. Therefore, in solution having pH value higher than 3, the adsorption of Au(III) might be contributed to the complexation of Au(III) species with thiol groups of MTG and the electrostatic interaction with protonated amine groups of PEI. In summary, this CNTs-PEI-MTG can be used in wide pH range. However, further adsorption study was performed in mild condition and pH 4 was selected.

### 4.3.2 Effect of adsorption time

The time to reach Au(III) adsorption equilibrium on adsorbent was investigated at optimum pH value by varying the adsorption time in time period of 10 to 120 minutes. Adsorption percentage of CNTs-PEI-MTG as function of time was compared to results of CNTs-PEI as shown in Figure 4.9.

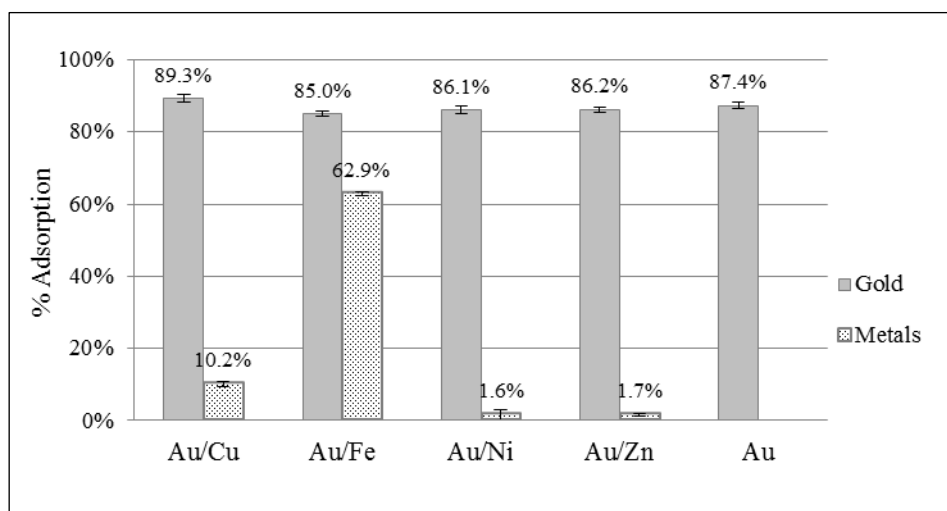


**Figure 4.9** Effect of adsorption time on Au(III) adsorption on adsorbents; initial concentration 80 mg/L; pH 4; 5 mg sorbent.

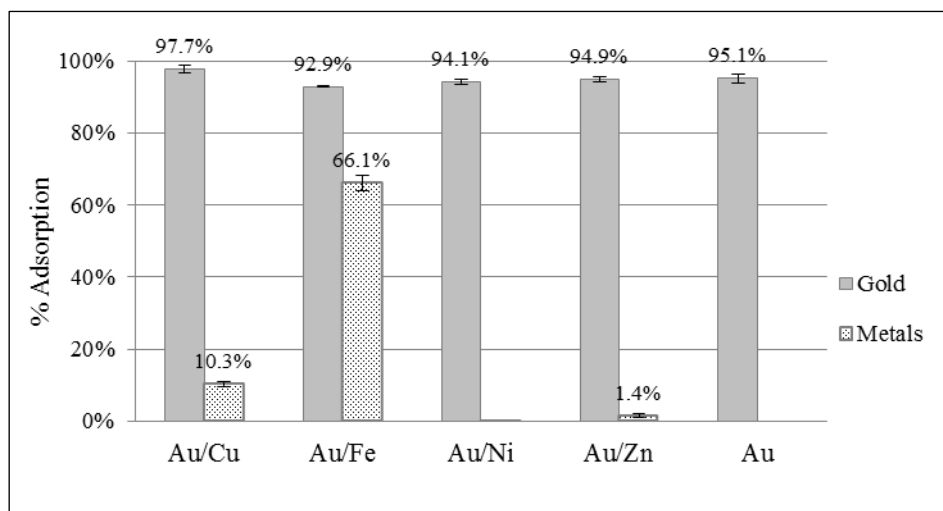
As the result, the adsorption equilibrium when using both CNTs-PEI and CNTs-PEI-MTG was reached rapidly within 10 minutes with approximately 90% and 99% of Au(III) adsorption, respectively. The adsorption percentage increased by 9% by using CNTs-PEI-MTG due to MTG modification. It seems that only 10 minutes of adsorption time should be enough to attain adsorption equilibrium, but in further experiments, especially in adsorption isotherm study, higher concentration of gold solution would be used and then the equilibrium would be reached in longer time. Therefore, the adsorption time of 60 minute was selected to ensure that the adsorption of Au(III) occurred and reached its equilibrium in every experiment.

### 4.3.3 Effect of co-existing ions

A good adsorbent should be selective toward the target analyte and should provide good efficiency when it is used in various samples. However in samples, there are other substances such as sodium salt and other metal ions that may interfere or compete with analyte in adsorption on adsorbent. This results in a decrease in adsorption efficiency. Thus, the effect of co-existing ions on the efficiency in Au(III) adsorption by the modified CNTs were studied. Working solution was prepared by mixing Au(III) ions with other metal ions i.e. Cu(II), Fe(III), Ni(II) or Zn(II). Concentration of each metal ions in solution was fixed at 80 mg/L with optimum pH value (pH 4). The experiment was carried out using 5 mg of adsorbent in these binary mixtures with 60 minute adsorption time. Au(III) adsorption percentages of CNTs-PEI and CNTs-PEI-MTG were compared to the percentages observed when the adsorption was performed in single Au(III) solution (Figure 4.10 and 4.11).



**Figure 4.10** Adsorption percentage of CNTs-PEI using Au(III)-metal solution compared with single Au(III) solution in optimum condition; initial concentration 80 mg/L; pH 4; adsorption time 60 minutes; 5 mg sorbent.

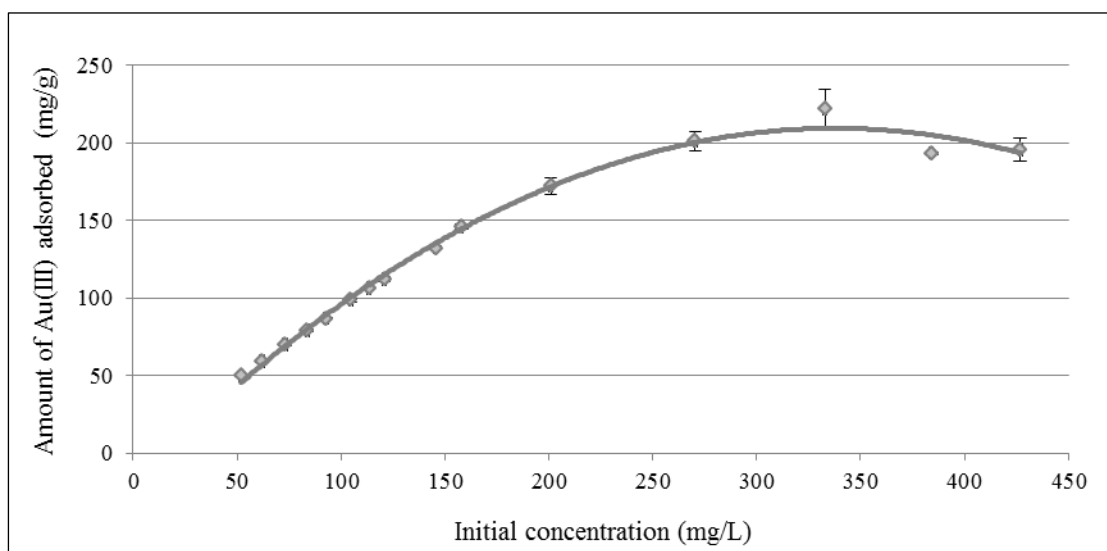


**Figure 4.11** Adsorption percentage of CNTs-PEI-MTG using Au(III)-metal ions binary solution compared to single Au(III) solution under optimum adsorption condition; initial metal ions concentration 80 mg/L; pH 4; adsorption time 60 minutes; 5 mg sorbent.

CNTs-PEI-MTG could adsorb in range of 93 to 98 % of Au(III) from Au(III) metal binary solutions and 95 % of Au(III) from pure Au(III) solutions and its efficiency was higher than that of CNTs-PEI (85-90%) when they were used in the same experimental condition. From T-test statistical method, Au(III) adsorbability of both CNTs-PEI and CNTs-PEI-MTG in single or binary metal solution are not significantly different. It was also found that both adsorbents could adsorb high amount of Fe(III) and a little amount of Cu(II) ions without losing efficiency in Au(III) adsorption. It is likely that some amine groups on CNTs-PEI and CNTs-PEI-MTG were not protonated at pH . They still acted as Lewis's base that would prefer to forming complexes with Fe(III) and Cu(II) cations. Therefore, if the adsorbent still had available active sites, Fe(III) and Cu(II) cations could be adsorbed onto surface. This phenomenon indicated that CNTs-PEI and CNTs-PEI-MTG probably have a lot of active sites. Moreover, the results indicate that the selectivity of CNTs-PEI-MTG toward Au(III) did not remarkably increase by the modification of methyl thioglycolate on adsorbent, compared to CNTs-PEI. It can be explained that only small amount of MTG was modified on the surface, hence, most of the active sites on CNTs-PEI-MTG were amine groups of PEI.

#### 4.3.4 Adsorption isotherm

The adsorption behavior of Au(III) on the adsorbent can be explained by the study of adsorption isotherms. By using fixed amount of CNTs-PEI-MTG (5 mg) with various concentration of Au(III) solution under the optimum extraction condition (solution pH 4; adsorption time 60 minutes) at  $25\pm 1^\circ\text{C}$ , then, the equilibrium adsorption data were obtained. Figure 4.12 displays the amount of Au(III) adsorbed by MTG-modified adsorbent after increasing the initial Au(III) concentration. The amount of Au(III) adsorbed on adsorbent increased linearly at low initial concentration and reached a constant value around 200 mg Au/g sorbent indicating the saturation of Au(III) on adsorbent surface.



**Figure 4.12** Adsorption efficiency of CNTs-PEI-MTG using various Au(III) concentration under optimum condition; pH 4; adsorption time 60 minutes; 5 mg sorbent.

The adsorption isotherm models used in this work are Langmuir, Freundlich and Elovich isotherms which are based on the different assumption. Langmuir isotherm explains the monolayer adsorption on homogeneous surface with limited number of active sites. Each site can adsorb only one target metal ion via chemisorption. Freundlich isotherm assumes that the adsorption occurs on surface bearing different active sites with different adsorption energy and these active sites can adsorb target metal ions as multilayer on surface of adsorbent. Elovich isotherm is commonly used



to describe the adsorption behaviour with a rapid equilibrium rate in the early period, while it slows down in later periods of the adsorption process [48].

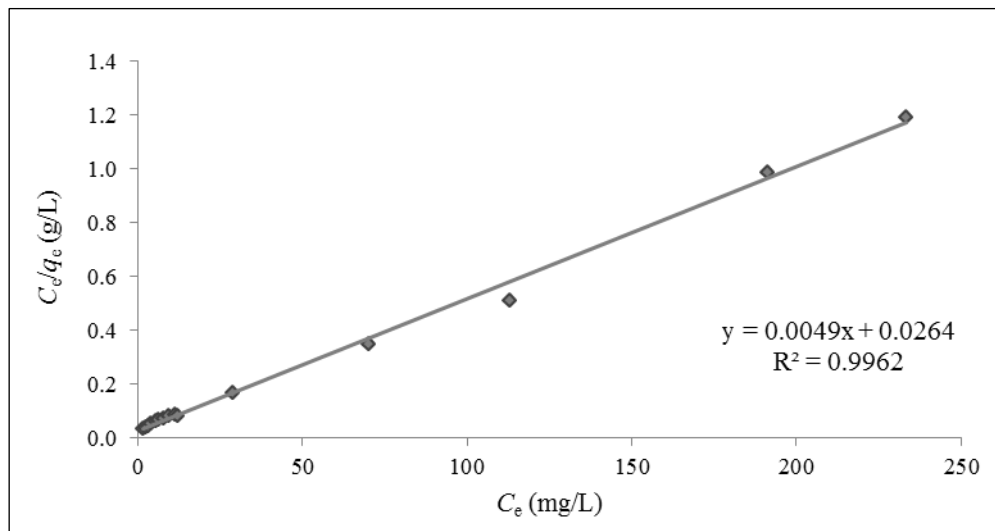
The best fit of the experimental data to the adsorption isotherm model was determined by correlation coefficient ( $R^2$ ) of linear plotting of the isotherm model equations using the same equilibrium adsorption data. Linearized equation of three isotherm models and their plots are shown below.

The Langmuir equation can be written in linear form in Equation 4.3

$$\frac{e}{q_e} = \frac{1}{q_m b} + \frac{e}{q_m} \quad (4.3)$$

where  $C_e$  and  $q_e$  are Au(III) concentration at equilibrium (mg/L) and amount of Au(III) adsorbed on adsorbent at equilibrium (mg/g), respectively.

The maximum adsorption capacity ( $q_m$ ) and Langmuir constant ( $b$ ) that are related to the energy of adsorption, can be calculated from slope and y-axis interception by plotting  $C_e/q_e$  versus  $C_e$  as shown in Figure 4.13.



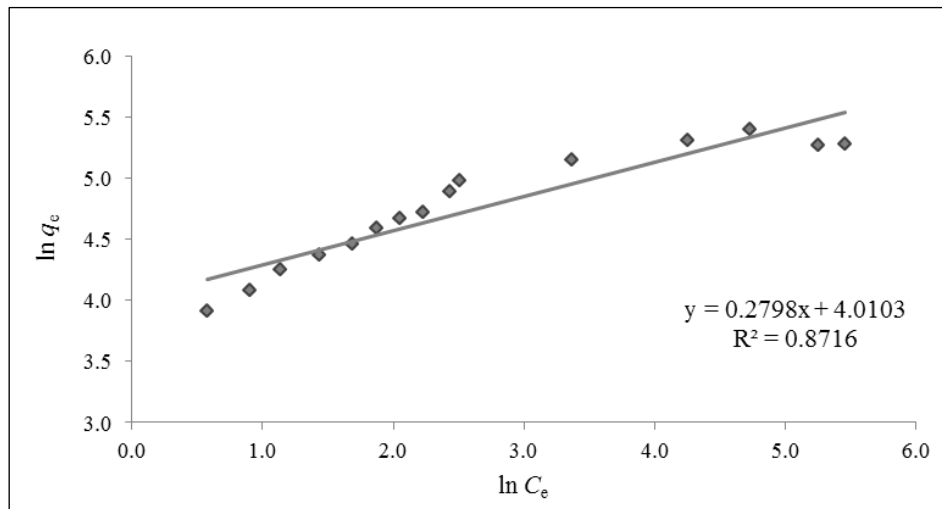
**Figure 4.13** Langmuir isotherm plot of Au(III) adsorption on CNTs-PEI-MTG.

Furthermore, the linearized Freundlich equation is shown in Equation 4.4

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4.4)$$

where  $K_F$  is a constant related to adsorption capacity of the adsorbent and  $n$  is Freundlich constant indicating the adsorption intensity.  $C_e$  and  $q_e$  are the same parameters as used in Langmuir equation, which are concentration (mg/L) and amount of Au(III) adsorbed (mg/g) at equilibrium, respectively.

The equilibrium adsorption data fitted to linear form of Freundlich equation by plotting  $\ln q_e$  versus  $\ln C_e$  is presented in Figure 4.14.



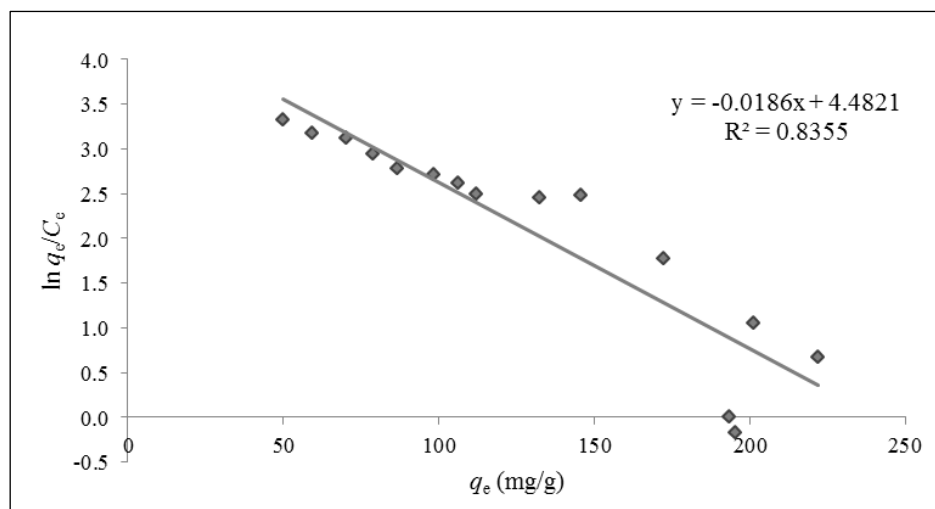
**Figure 4.14** Freundlich isotherm plot of Au(III) adsorption on CNTs-PEI-MTG.

And the linear form of Elovich equation is shown in Equation 4.5

$$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \quad (4.5)$$

where  $C_e$  and  $q_e$  are Au(III) concentration (mg/L) and adsorbed amount of Au(III) (mg/g) on sorbent at equilibrium, respectively.

Elovich maximum adsorption capacity ( $q_m$ ) and Elovich constant ( $K_E$ ) can be calculated from slope and y-axis interception of the plot of  $\ln (q_e/C_e)$  versus  $q_e$  displayed in Figure 4.15.



**Figure 4.15** Elovich isotherm plot of Au(III) adsorption on CNTs-PEI-MTG.

From correlation coefficient ( $R^2$ ) in Figure 4.12, 4.13 and 4.14, the experimental data of Au(III) adsorption fit to Langmuir model better than Freundlich and Elovich model. It reveals that Au(III) adsorption on the MTG-modified adsorbent follows Langmuir isotherm assumption that is Au(III) ions were adsorbed as a monolayer on the surface via chemical adsorption. Although the adsorption of Au(III) on CNTs-PEI-MTG occurred via two possible mechanisms that are electrostatic interaction with protonated amine groups from PEI and complexation with thiol groups from MTG, but the number of amine groups active sites seems to be much greater than the number of thiol groups active sites and be the majority of active sites on surface. Therefore, the adsorption of Au(III) was likely to occur on homogeneous surface as mentioned in Langmuir isotherm assumption. The maximum adsorption capacity ( $q_m$ ) and Langmuir constant ( $b$ ) were calculated to be 203.7 mg/g and  $3.66 \times 10^4$  L/mol, respectively. The high value of Langmuir constant is related to high energy of adsorption, which significantly proves that the adsorption mechanism was chemisorption.

#### 4.4 Au(III) desorption study

Desorption study lets us know how to recover adsorbed Au(III) back from CNTs-PEI-MTG adsorbents for recycling in many proposes. In this part, type and the suitable amount of desorbing solution were investigated. The results are presented in term of desorption percentage (%elution) calculated from equation as follow;

$$\text{elution} = \frac{m_d}{m_a} \times 100 \quad (4.6)$$

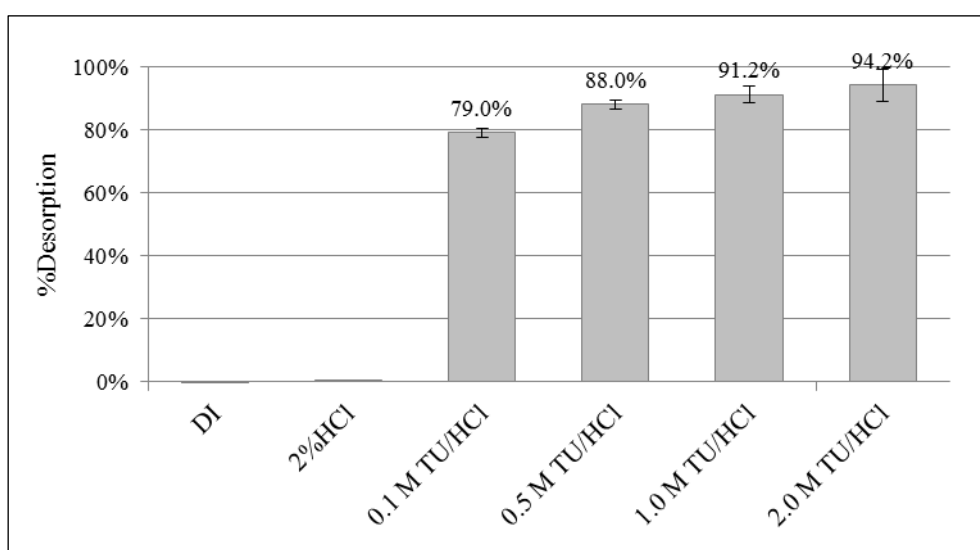
where  $m_d$  is amount of Au(III) desorbed from adsorbents (mg) and  $m_a$  is amount of Au(III) adsorbed onto adsorbents (mg).

##### 4.4.1 Type of desorbing solution

The results from adsorption showed that the possible interactions between Au(III) ions and CNTs-PEI-MTG were electrostatic interaction (with protonated amine groups of PEI) and chelation (with thiol groups of MTG). Then, eluent that was used for desorption must has stronger interaction with Au(III) ions than the active sites on adsorbents. Many researchers have used various reagents as desorbing solutions [49-55] including acidic thiourea solution (was the suggested one). Thiourea (TU) is a complexing agent that can form complex with many heavy metals ions including Au(III) ions with high stability constant [56], so, thiourea was chosen as desorbing solution for this study.

Before regeneration, the adsorbent was used to adsorb Au(III) ions by using 5 mg of CNTs-PEI-MTG with 65 mg/L of Au(III) solution under the optimum extraction condition (solution pH 4; adsorption time 60 minutes). After separated adsorbent from the solution, the desorption of Au(III) ions remained on the adsorbent was performed using 5.0 mL of different eluent types and concentrations, i.e. DI water, 2% (v/v) HCl, 0.1 M, 0.5 M, 1.0 M and 2.0 M thiourea in 2%(v/v) HCl solution with 60 minutes of desorption time. The results are displayed in Figure 4.16.

As zero percent elution observed, DI water and acid solution (2% HCl) could not elute the adsorbed Au(III) ions from CNTs-PEI-MTG. In contrast, Au(III) ions could be easily desorbed by acidic thiourea. The desorption percentage rises up to 80% when using only 0.1 M thiourea and the higher concentration of thiourea, the higher percent elution was achieved. However, thiourea will crystallize due to saturation state in solution ( $>1.87$  M at  $25^{\circ}\text{C}$  [57]), therefore, 0.5 M thiourea in 2%(v/v) HCl solution which gave 90% elution was chosen as desorbing solution in the next desorption experiments.



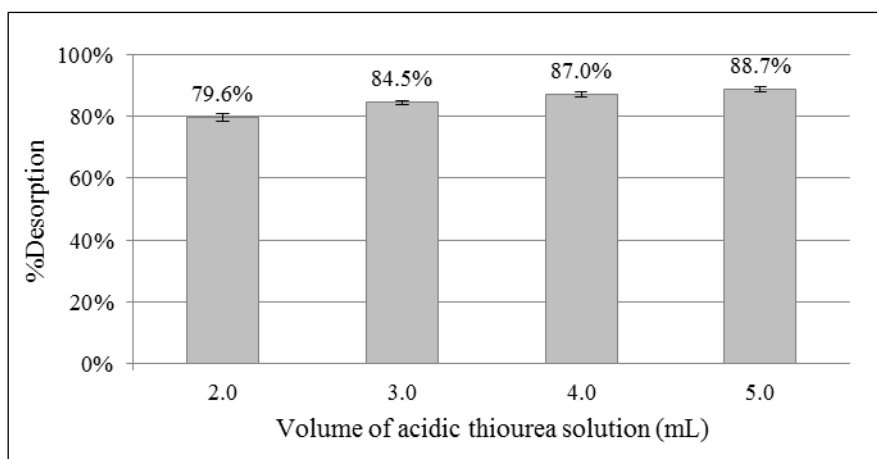
**Figure 4.16** Desorption percentage of Au(III) ions when using different type that are DI water, hydrochloric acid (HCl) and acidic thiourea solution (TU/HCl), and their concentration; desorption time 60 minutes; 5 mg sorbent.

#### 4.4.2 Volume of desorbing solution

For economical reason, Au(III) desorbing solution should be used as less as possible. The eluent (0.5 M thiourea in 2%(v/v) HCl) volume was varied in a range of 2–5 mL for the recovery of Au(III) from 5 mg of used adsorbent with 60 minute desorption time. The results are shown in Figure 4.17.

From result, higher amount of acidic thiourea used gave higher desorption percentage of Au(III). Compromising between the eluent volume and the desorption

percentage gained, it seems that using only 2.0 mL of eluent could be enough. It provided the recovery of Au(III) as high as 79.6%. In the other hand, the percentage increases only 9% when using 2.5 times higher eluent volume (5.0 mL). The Au(III) solution recovered by using small eluent volume, will has high concentration that is suitable for the storage and further uses. Moreover, in large scale work, the less consumption of eluent will highly reduce the production and waste treatment cost.



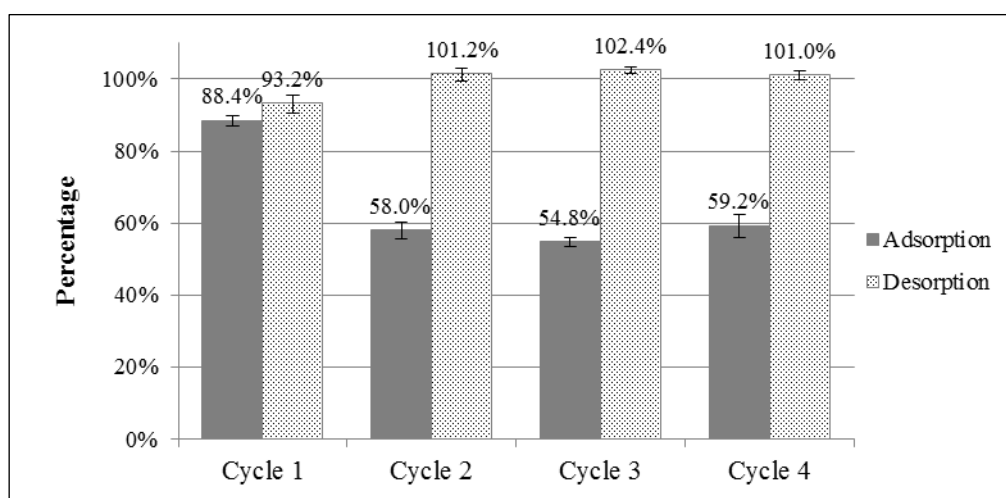
**Figure 4.17** Desorption percentage of Au(III) ions using different volume of 0.5 M thiourea in 2%(v/v) HCl; desorption time 60 minutes; 5 mg sorbent.

Furthermore, this research do not study the suitable desorption time because thiourea can form complex with Au(III) rapidly, then the desorption time should be fast. This is an advantage for the large scale application, less time used means less production cost even though it did not have much impact in laboratory scale. However, the next experiment in this research is to study reusability of the adsorbent. Au(III) ions should be completely eluted from adsorbent in every cycle of uses, and longer desorption time used will result in higher desorption efficiency. Thus, an hour of desorption time was selected.

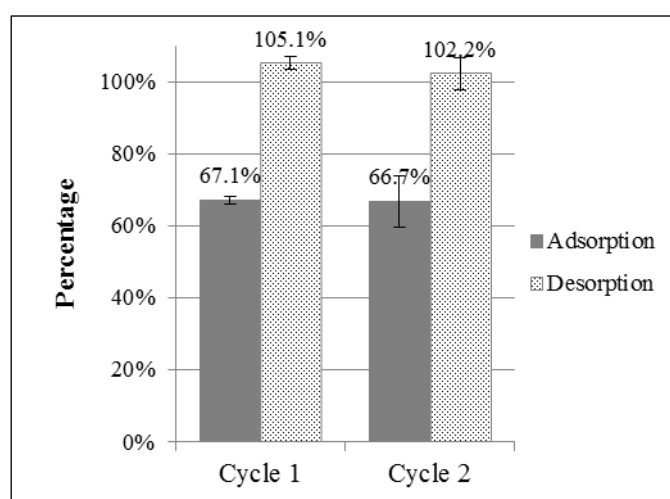
#### 4.5 Reusability of the adsorbent

The reusability of this adsorbent was investigated in order to know how many times CNTs-PEI-MTG could be reused in Au(III) adsorption. Due to their high

Au(III) adsorption capacity, this study required high amount of gold to interact with all active sites of adsorbent. To ensure that the adsorbent will adsorb gold at full of its capacity, the initial concentration of Au(III) solution used was 200 mg/L. After gold adsorption, Au(III) ions were desorbed from CNTs-PEI-MTG using 0.5 M thiourea in 2% hydrochloric acid. Results of CNTs-PEI-MTG reusability are displayed in term of adsorption and desorption percentage calculated from Equation 4.2 and 4.6, respectively (Figure 4.18, 4.19).



**Figure 4.18** Au(III) adsorption and desorption percentage of CNTs-PEI-MTG in sequential uses.



**Figure 4.19** Au(III) adsorption and desorption percentage of CNTs-PEI in sequential uses.

In the first time of use, percentage of Au(III) adsorption on CNTs-PEI-MTG was 88.4%. However, when the adsorbent was regenerated by acidic thiourea solution and used in Au(III) extraction for the second time, adsorption percentage decreased significantly to around 60% and remained constant in the third and fourth cycle of adsorption-desorption. Comparing with the adsorption percentage of CNTs-PEI, this adsorbent adsorbed Au(III) ions only 67.1% at the first cycle. After regenerated by acidic thiourea, the adsorption percentage of CNTs-PEI did not change significantly (66.7%) from the first adsorption.

Considering Au(III) desorption percentage, it is found that acidic thiourea solution cannot completely elute Au(III) ions from CNTs-PEI-MTG at the first desorption (93.2% elution). But the desorption percentage of the second, third and fourth cycle are over 100% and the same results were observed in both cycles of CNTs-PEI. This error might be caused by eluent dilution process during Au(III) determination by flame atomic absorption spectrometer. However, it can be assumed that acidic thiourea solution can elute Au(III) ions from the adsorbent completely except for the desorption of CNTs-PEI-MTG at the first cycle.

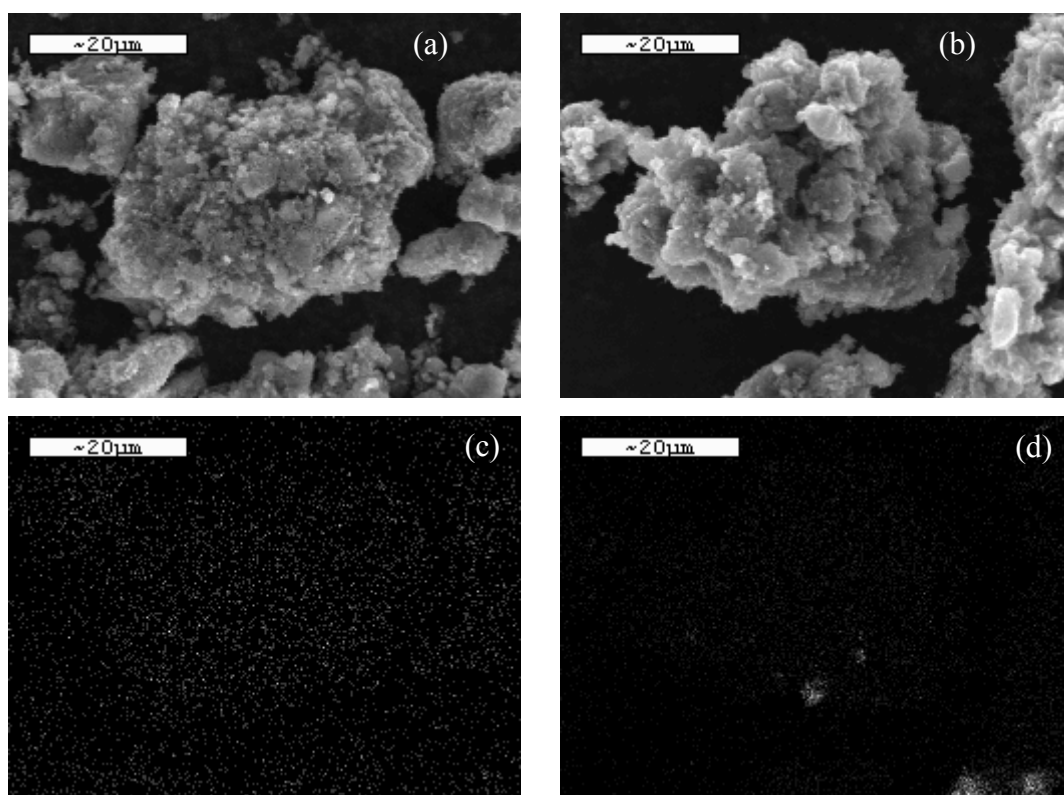
Few assumptions on adsorption efficiency loss are proposed. Firstly, losing in adsorption efficiency after first cycle of CNTs-PEI-MTG use may be the result of a loss of some active sites after being used in the first time. During adsorption processes, the bulk of entangled CNTs could be cracked by stir force. Some PEI molecules probably lose out from the surface leading to a loss of MTG modified on that PEI and a decrease in Au(III) adsorption efficiency when used in the second time. However, if the adsorption efficiency was decreased by losing in PEI and MTG each time of use, a gradual decrease in adsorption efficiency would be observed in the third and fourth cycle of CNTs-PEI-MTG use or both cycle of CNTs-PEI use. But this occurrence could not be found, therefore, this assumption is not valid in this case.

Secondly, it could be explained that some Au(III) ions were probably stuck in CNTs-PEI-MTG due to the strong chelation between Au(III) ions and thiol groups of MTG. The acidic thiourea solution could elute only Au(III) ions interacted with the protonated amine of PEI because of their weaker interaction (electrostatic interaction).

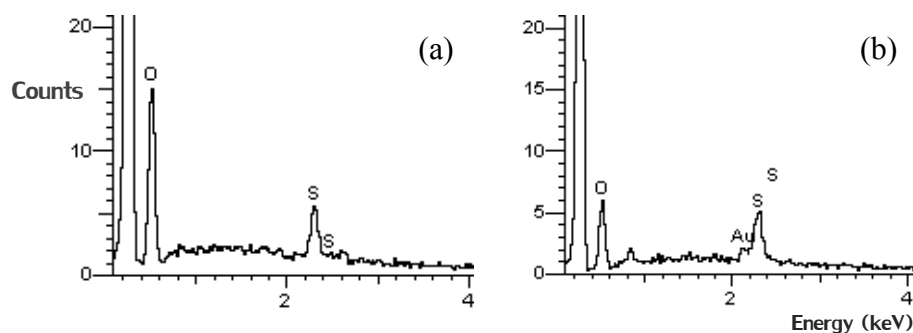


It related to the result that CNTs-PEI-MTG had desorption percentage at the first cycle lower than 100%.

In order to prove above assumptions, used CNTs-PEI-MTG adsorbent was characterized by SEM after the use in the first cycle and sulfur atom distribution on adsorbent surface was illustrated through X-ray mapping using SEM-EDX compared with CNTs-PEI (Figure 4.20). White spots in pictures represent sulfur atoms that referred to the presence of MTG on the adsorbent surface. It can be seen that white spots spread all over the bulk of adsorbent revealing a good distribution of MTG on CNTs-PEI-MTG surface. When CNTs-PEI-MTG was used and regenerated with the acidic thiourea, this adsorbent still has a good MTG distribution on its surface but the sulfur atom signal intensity was diminished as shown as faded spots in Figure 4.20 (d). Furthermore, EDX spectra of CNTs-PEI-MTG after being used in the first cycle (Figure 4.21) show a small peak of gold revealing that little amount of gold (III) could not be eluted by the acidic thiourea and still remained on adsorbent surface.



**Figure 4.20** SEM images and sulfur atom distribution (white spots) of CNTs-PEI-MTG before (a, c) and after (b, d) use at the first cycle.



**Figure 4.21** EDX spectra of CNTs-PEI-MTG before (a) and after (b) use at the first cycle.

In conclusion, CNTs-PEI-MTG was an efficient adsorbent with high Au(III) adsorption capacity. After the first adsorption, some of Au(III) ions still remained on adsorbent surface and resulted to losing of active sites. Thus, CNTs-PEI-MTG will be less effective when used repeatedly.

#### 4.6 Real Sample

To confirm that CNTs-PEI-MTG will suit the actual use, adsorbent was used to adsorb Au(III) ions in wastewater from analytical lab from the Gem and Jewelry Institute of Thailand (Public Organization). The pH value of wastewater was measured to be 1. Then, the wastewater was diluted and analyzed by flame atomic adsorption spectrometer (FAAS) and inductively couple plasma-optical emission spectrometer (ICP-OES). The content of Au(III) and other metals ions are shown in Table 4.2.

**Table 4.2** Metal ions content in wastewater

Metal	Content ( $\mu\text{g/L}$ )
Gold (III)	384,400 <sup>a</sup>
Copper (II)	157 <sup>b</sup>
Iron (III)	169 <sup>b</sup>
Zinc (II)	140 <sup>b</sup>

<sup>a</sup> measured by FAAS

<sup>b</sup> measured by ICP-OES

The wastewater was diluted tenfold with DI water before use and pH of diluted wastewater was measured to be 2. The adsorption experiment was performed by using 5 mg of CNTs-PEI-MTG to extract Au(III) in 5 mL of diluted wastewater with 60 minutes adsorption time. After extraction, Au(III) amount remained in solution was determined by FAAS. The efficiency of Au(III) adsorption by CNTs-PEI-MTG was compared with CNTs-PEI and shown in Table 4.3.

**Table 4.3** The percentage in adsorption of Au(III) from wastewater by CNTs-PEI and CNTs-PEI-MTG

<b>Adsorbent</b>	<b>% Au(III) adsorption</b>
CNTs-PEI	83.0 ± 1.4%
CNTs-PEI-MTG	97.6 ± 0.1%

The initial gold ions concentration in diluted wastewater was 38.6 mg/L. Under this condition, CNTs-PEI-MTG showed higher capability in Au(III) adsorption from real wastewater than CNTs-PEI and similar trend was observed in the study of the pH effect. CNTs-PEI-MTG can extract 97.6% of Au(III) in wastewater which was a better performance than CNTs-PEI (83.0%). The effect of interference of the other metal ions was not pronounced due to very low concentration of them in diluted wastewater. It is demonstrated that CNTs-PEI-MTG can be used in real applications.

## CHAPTER V

### CONCLUSION

A new adsorbent (CNTs-PEI-MTG) was prepared by coating of the polyethyleneimine on the carbon nanotubes surface, followed by modification with methyl thioglycolate. The modified adsorbents in each step were characterized by Scanning electron microscope (SEM-EDX), Fourier transforms infrared spectrometer (FT-IR), Fourier transforms Raman spectrometer (FT-Raman), thermogravimetric analysis (TGA) and ninhydrin test. The results from these characterization techniques and the increased efficiency in Au(III) adsorption can prove that CNTs-PEI-MTG was successfully prepared.

The CNTs-PEI-MTG was applied to extract gold(III) ion in aqueous solution using batch method before its determination by flame atomic absorption spectrophotometry (FAAS). The effects of pH of Au(III) solution and extraction time as well as the adsorption isotherms were investigated. The adsorption behavior and suitable conditions of using CNTs-PEI-MTG in extraction of Au(III) ion are summarized in Table 5.1

**Table 5.1** The adsorption behavior and suitable conditions of the extraction of Au(III) ion

Parameters	Adsorption behavior
Solution pH	no effect
Adsorption time to reach equilibrium	Very rapid, within 10 minutes
Co-existing ions effect	Fe(III) and Cu(II) ion are the potential interfering ions
Adsorption isotherm	Langmuir isotherm
Maximum adsorption capacity (mg/g)	203.7 mg/g

The adsorption of gold(III) onto CNTs-PEI-MTG is believed to occur mainly via (i) the electrostatic interaction between positively charged protonated amine group of PEI and negative charge of gold(III) anion species ( $\text{AuCl}_4^-$ ) and (ii) the complexation between gold and  $-\text{SH}$  groups from MTG. The CNTs-PEI-MTG showed higher efficiency in gold adsorption than the starting CNTs material.

Lastly, the recovery of Au(III) from used adsorbents was studied. Acidic thiourea solution was used for elution of Au(III) ions with a high desorption efficiency. It was found that only 2 mL of 0.5 M thiourea in 2% hydrochloric acid is enough to elute Au(III) from 5 mg adsorbent with desorption percentage up to 80%. Unfortunately, the efficiency in Au(III) adsorption decreased at the second time of use but stable afterward. The adsorbents were successfully applied to extract Au(III) in wastewater.

#### **Suggestion of future work**

- This adsorbent should be applied for large scale adsorption including large scale wastewater treatment.
- The reusability of this adsorbent should be improved by using other type of desorbing reagents that can form complex with Au(III) ions such as the solution of  $\text{I}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$  and  $\text{SCN}^-$ .

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