การสกัด โกลด์(III) โดยใช้คาร์บอนกัมมันต์ดัดแปร

นาย จักรพันธ์ สุวรรณวิจิตร

EXTRACTION OF GOLD (III) USING MODIFIED ACTIVATED CARBON

Mr Jakraphan Suwanvijit

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2009

Thesis Title   EXTRACTION OF GOLD(III) USING MODIFIED ACTIVATED CARBON

By   Mr Jakraphan Suwanvijit

Field of Study   Chemistry

Thesis Advisor   Assistant Professor Narong Praphairaksit, Ph.D.

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

………………………………… Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat)

THESIS COMMITTEE

………………………………… Chairman

(Associate Professor Sirirat Kokpol, Ph.D.)

…………………………………Thesis Advisor

(Assistant Professor Narong Praphairaksit, Ph.D.)

………………………………… Examiner

(Assistant Professor Apichat Imyim, Ph.D.)

………………………………… External Examiner

(Assistant Professor Nitinat Suppakarn, Ph.D.)

จักรพันธ์ สุวรรณวิจิตร :   การสกัดโกลด์(III)โดยใช้คาร์บอนกัมมันต์ดัดแปร. (EXTRACTION OF GOLD(III) USING MODIFIED ACTIVATED CARBON) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. ณรงค์ ประไพรักษ์สิทธิ์, 74 หน้า.

ทำการปรับปรุงคุณภาพถ่านกัมมันต์ด้วยสารเคมีที่มีศักยภาพในการเกิดอันตรกิริยาได้ดีกับทองคำโดยใช้เทคนิค impregnation และทดสอบประสิทธิภาพการแยกสกัดทองคำจากสารละลาย ซึ่งพบว่า Tetrabutyl ammonium iodide (TBA) สามารถให้ผลที่ดีที่สุดทั้งในแง่ของประสิทธิภาพและความรวดเร็วในการแยกสกัด และได้ทำการศึกษาปัจจัยต่างๆ เพื่อหาสภาวะที่เหมาะสมในการเตรียมและการใช้ถ่านกัมมันต์ที่ปรับปรุงคุณภาพด้วย TBA นี้ทั้งในระบบ Batch และในระบบของ Column รวมทั้งผลการรบกวนของโลหะไอออนต่างๆ ที่พบได้ทั่วไปในน้ำทิ้งจากอุตสาหกรรมเครื่องประดับ โดยพบว่าโลหะเหล่านั้นไม่มีผลต่อประสิทธิภาพของการแยกสกัดทองคำ จากนั้นได้ทำการศึกษา Adsorption isotherm ของถ่านดังกล่าว ตลอดจนทำการเปรียบเทียบประสิทธิภาพการสกัดและความจุของการดูดซับทองระหว่างถ่านกัมมันต์ที่ผ่านการปรับปรุงคุณภาพด้วย TBA กับถ่านกัมมันต์ที่มีจำหน่ายเชิงพาณิชย์ทั่วไป ซึ่งพบว่าถ่านกัมมันต์ที่ผ่านการปรับปรุงคุณภาพด้วย TBA ให้ค่าความจุของการดูดซับที่ 90.62 mg/g ในขณะที่ถ่านกัมมันต์ทั่วไปมีความจุเพียง 18.00 mg/g นอกจากนี้ ยังได้นำถ่านกัมมันต์ที่ผ่านการปรับปรุงคุณภาพดังกล่าวไปใช้ในการสกัดแยกทองคำออกจากน้ำทิ้งจากโรงงานอุตสาหกรรมเครื่องประดับได้อย่างมีประสิทธิภาพอีกด้วย

ภาควิชา............เคมี............ลายมือชื่อนิสิต...

สาขาวิชา............เคมี............ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.......................

ปีการศึกษา............2552............

4972243023 : MAJOR CHEMISTRY

KEYWORDS : GOLD / ACTIVATED CARBON / EXTRACTION / TETRABUTYL AMMONIUM IODIDE

JAKRAPHAN SUWANVIJIT: EXTRACTION OF GOLD(III) USING MODIFIED ACTIVATED CARBON. THESIS ADVISOR: ASST.PROF. NARONG PRAPHAIRAKSIT, Ph.D., 74 pp.
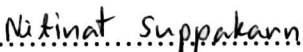
The activated carbons were modified with various potentially gold binding reagents by impregnation technique and their extraction efficiencies toward gold were evaluated. Tetrabutyl ammonium iodide (TBA) was found to be the most effective modifying agent for gold in terms of both extraction efficiency and speed. Various parameters were optimized around the preparation and utilization of this modified carbon in both batch and column methods. Several interfering ions commonly found in gold waste samples were found to have absolutely no effects to the extraction of gold. The adsorption isotherm was studied but no definite relation to any model was established. The breakthrough curve was used to demonstrate the improvement in gold extraction of the TBA-impregnated carbon over a commercial activated carbon and determine the adsorption capacity. The breakthrough capacity of the TBA-carbon and the commercial carbon were 90.62 and 18.00 mg/g respectively. The TBA-carbon was successfully applied to the recovery of gold from a real industrial waste sample.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Department :	Chemistry	Student's Signature
Field of Study :	Chemistry	Advisor's Signature
Academic Year :	2009	

ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure   **Page**

LIST OF ABBREVIATIONS

AC	Activated carbon
ATS	Ammonium thiosulfate
ATU	Ammonium thiourea
CTAB	Cetyltrimethyl ammonium bromide
°C	Degree celsius
DI H_2O	Deionized water
g	Grams
g dm^{-3}	Grams per cubic decimetre
g mol^{-1}	Grams per mole
hr	Hours
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LOD	Limit of detection
LLE	Liquid liquid extraction
mg L^{-1}	Milligrams per litre
mol dm^{-3}	Moles per cubic decimetre
μg L^{-1}	Micrograms per litre
mL	Millilitres
μm	Microns
min	Minutes
NDF	N,N-dimethylformamide
ppb	Part per billion
ppm	Part per million
%	Percent
SEM	Scanning electron microscope
SDS	Sodium dodecyl sulfate
SPE	Solid phase extraction
TBAI	Tetrabutyl ammonium iodide
TMAC	Tetrabutyl ammonium chloride
TOAB	Tetraoctyl ammonium bromide
TGA	Thermogravimetric analysis

w/v   Weight by volume

CHAPTER I

INTRODUCTION

1.1   Statement of the problem

Gold is a precious metal with certain distinct characteristics and values. It has been extensively used not only as jewelry but also as raw materials in various industries i.e. electronic, fuel cell, catalyst, biochemical industries and dentistry, and thus its demand is ever growing nowadays. The increases in jewelry industrial as well as electrical industrial demands for gold contribute to the increase of wastes. As the natural resource of gold is rapidly depleted, a great deal of attention has been turned toward the recovery of gold discharged from industries.

The manufacturing and processing of gold in the mentioned industries generate a large quantity of waste, usually as gold-containing sludge or gold solution. Several methods have been widely used to retrieve the noble metal in these wastes, namely precipitation and electrolysis [1]. However, both methods are relatively expensive and complicated in practice and its efficiency is still far less than perfect. Recently, adsorption technique has become a decent alternative for the gold recovery process largely due to its simplicity and economical standpoint. The adsorption of gold onto activated carbons (AC) has been discussed on numerous reviews due to the fact that AC is less expensive than other methods. Moreover, the activated carbon is highly porous materials, which provide high surface area and high degree of surface reactivity.

Activated carbon is a crude from graphite with a random and amorphous structure, which is highly porous. These materials are cheap, rugged and reliable adsorbent and thus is a leading candidate for the process. Carbons are widely used for the retention of organic and inorganic compounds water due to such factors as low cost, high surface area, micro-porous structure and also a high degree of surface reactivity. However, the problem of using activated carbon for gold adsorption does exist in which it has limited sorption capacity, time consuming and incomplete extraction. Thus, the modification of activated carbon is the main interest in this work in order to enhance the adsorption efficiency as well as selectivity of gold. In this

research, the carbon was initially modified by impregnation with modifying reagents that can potentially interact with gold. These modified carbons were assessed for its extraction efficiency of Au(III) in aqua regia compared with a commercial activated carbon. Various parameters affecting Au adsorption efficiency, were investigated in both batch and column methods along with its adsorption isotherm. The application of this modified carbon in jewelry waste is also described.

1.2 Research objectives

1. To modify the activated carbon with certain gold sorption enhancing reagents by impregnation technique.
2. To study factors and conditions affecting gold extraction using the modified activated carbon.
3. To study the adsorption isotherm and gold sorption capacity of the modified activated carbon.
4. To evaluate the application of modified activated carbon for the gold recovery of jewelry wastes.

1.3 The benefits of this research

Modified activated carbons which provide a great improvement in gold extraction from jewelry industrial waste as well as in the gold mining process.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1   Gold

Gold is element which has an atomic number of 79. It has been a highly sought-after precious metal for jewelry and other arts for centuries. The metal occurs as nuggets or grains in rocks, in veins and in alluvial deposits. In general, gold is dense, soft, shiny and the most malleable and ductile pure metal. Pure gold has traditionally revealed both bright yellow color and luster as it is naturally protected from being oxidized in air or water.

2.1.1 General properties

Some general properties of gold are presented in Table 2.1.

Table 2.1 General properties of gold [2]

Physical properties	
Atomic mass	196.966 amu
Melting point	1064.43 °C
Boiling point	2807 °C
Density	19.32 g cm^{-3}
Mohs hardness	2

Gold is a soft metal typically found in an oxidation state from -1 to +5. The main forms of gold ions are aurous (Au^{1+}) and auric (Au^{3+}). The coordination number of aurous ion is 2 and the geometry of this ion is a linear. In the case of auric ion, the common coordination number of 4 and a square planar geometry are usually found [3].

Gold is a transition metal which forms as either trivalent or univalent cations in solutions. Pure gold revealed lesser reactivity when compared with other metals. Nevertheless, it can be attacked by a mixture of nitric acid and hydrochloric acid, called aqua regia. Gold can be formed as chloroauric acid ($HAuCl_4$), which not only form in individual acids but also in alkaline solutions of cyanide. Gold dissolves in mercury, forming as amalgam alloy, but does not react with it. Gold is insoluble in nitric acid, conversely with silver and other base metals which show greater solubility in this acid.

Gold is attacked by and dissolved in alkaline solutions of potassium or sodium cyanide, and gold cyanide is the electrolyte used in commercial electroplating of gold onto base metals and electroforming. Gold chloride (chloroauric acid) solutions are used to make colloidal gold by reduction with citrate or ascorbate ions. Gold chloride and gold oxide are used to make highly valued cranberry or red-colored glass, which, like colloidal gold suspensions, contains evenly sized spherical gold nanoparticles [4].

2.1.2 Gold production

The growing consumption of gold has led to a significant increase in the gold production over the last decades. Figure 2.1 schematically illustrates common processes involved in a gold mining production.
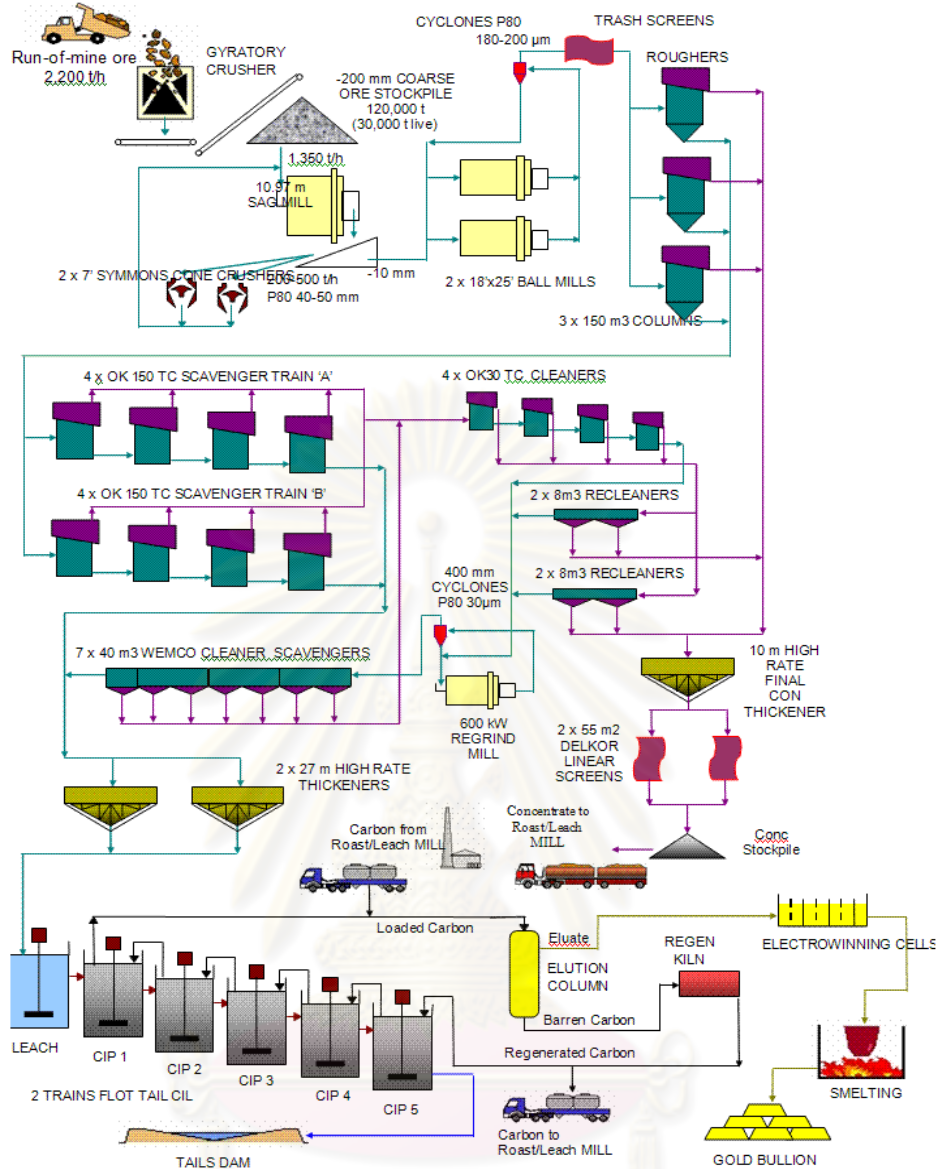
Figure 2.1 Gold mining processes [5].

2.1.2.1 Mining

Gold mining involved an exploration, drilling, geological assessment, financing, development, extraction, initial refinement, and delivery of gold bars to a bullion refiner.

After the exploration and assessment, the gold ores are crushed and ground. The higher energy consumption is required in order to grind an ore in this process. A different concentration of minerals in the earth's crust is needed to evaluate in mining process, such as iron content (average 5.8%) in the earth's crust needed to concentrate

for 5 times. A lower grade of gold ore is containing 5 grams of Au per ton (5 parts per million). Thus, Au ore is necessary to concentrate about 1,000 times for gold mining [6].

2.1.2.2 Leaching and extraction

The most common extraction processes of metal ores, especially of gold, are gravity concentration, amalgamation, floatation, pyrometallurgy, hydrometallurgy, and combination methods. At a mining company, about 30 percent of gold is discovered in gravity traps. On the other hand, the floatation of gold is effective in the 300 to 1,000 μm particle size range and treated by conventional smelting and refining or subjected to cyanidation process to recover the value metals. Gold cyanidation is typically employed to recover gold at very low concentration in ores with less than 10 g of Au per ton of ore. In cyanidation process, metallic gold is oxidized and dissolved in an alkaline cyanide solution. The oxidant employed is atmospheric oxygen, which in the presence of an aqueous solution of sodium cyanide, cause the dissolution of gold and the formation of sodium cyanoaurite ($NaAu(CN)_2$). When dissolution of gold is complete, the gold-bearing solution is separated from the residues and adsorbed onto the activated carbon. After elution from the activated carbon, the gold is further concentrated by precipitation or electrodeposition. In some cases, regrinding and roasting (preferably to limestone) prior to cyanidation results in higher recoveries. Floatation is effective in the treatment of gold ores containing carbonaceous materials. Alternate methods for refractory gold ores include pressure leaching in autoclave prior to acid neutralization followed by cyanidation or bio-oxidation prior to cyanidation. However, gold extraction using cyanidation is significantly concerned due to highly poisonous nature of cyanide. Therefore, the recovery processes have continued to play an increasingly important role since such processes are more efficient, lower operating costs, are less energy consuming, and are environmentally more attractive [2].

2.1.2.3 Carbon adsorption in gold mining

Gold solutions are commonly recovered by conventional precipitation with zinc dust. Ion-exchange and solvent extraction are also used in recent years. The alternate scheme of Au adsorption on activated carbon are preferred over the last decade due to more effective recovery of precious metal and low operating cost. The modifications of carbon adsorption systems are Carbon-in-Pulp (CIP), Carbon-in-Leach (CIL), and Carbon-in-Column (CIC).

1. Carbon-In-Pulp (CIP) is a variation of the conventional cyanidation process. Ore is crushed, finely ground, and cyanide leached in a series of agitated tanks to solubilize the gold values. Instead of separating solids from the pregnant solution, as in the traditional cyanidation process, granular activated carbon is added to the leached slurry.

The carbon adsorbs the gold from the slurry solution and is removed from the slurry by coarse screening. In practice, this is accomplished by a series of five or six agitated tanks where carbon and ore slurry are contacted in a staged countercurrent manner.

This greatly increases the possible gold loading onto the carbon while maintaining a high recovery percentage. Carbon is retained within the individual CIP tanks by CIP tank screens. The opening size of the CIP tank screens is such that the finely ground ore particles will pass through the screens, but the coarse carbon will not. Almost every imaginable type of screen has been tried for this application, with some types being much more successful than the rest.

2. Carbon-In-Leach (CIL) process is an integrated leaching and carbon-in-pulp into a single unit process operation. Leach tanks are fitted with carbon retention screens and the CIP tanks are eliminated. Carbon is added in leach so that the gold is adsorbed onto carbon almost as soon as it is dissolved by the cyanide solution. The CIL process is frequently used when native carbon is present in the gold ore. This native carbon will adsorb the leached gold and prevent its recovery. This

phenomenon is referred to commonly as "preg-robbing". The carbon added in CIL is more active than native carbon, so the gold will be preferentially adsorbed by carbon that can be recovered for stripping. The CIL process will frequently be used in small cyanide mills to reduce the complexity and cost of the circuit [6].

3. Carbon-In-Column (CIC) is the carbon-in-column operation. The solution flows through a series of fluidized bed columns in an up-flow direction. Columns are most frequently open topped, but closed top pressurized columns are occasionally used.

Carbon columns are most commonly used to recover gold and silver from heap leach solutions. The major advantage of fluidized bed carbon columns is their ability to process solutions that contain as much as 2 to 3 wt% solids. Heap leach solutions are frequently high in solids due to fine particle washing from heaps. Down flow carbon columns are rarely used for gold recovery, because they act like sand filters and are subsequently subject to frequent plugging.

2.1.2.4 Purification and refining

The residual gold from mining process is recovered by carbon adsorption. The final product of gold containing impurities such as copper, zinc, iron, lead, selenium and tellurium is generally refined and purified depend on the ratio of gold to silver. If the proportion of gold is over 30 percent, the Miller process (or Chlorination) is used which the chlorine gas is passed into the molten to collect the impurities as chlorides in the flux which is skimmed off and the Au recovered as a 996.0 fine product. If further purification is required, the last product is further treated by electrochemical method called the Wohlwill electrolytic process. Conversely, if the gold to silver ratio is less than 30 percent, electrolytic and chemical refining method is utilized. The electrolysis is carried out to obtain high purity (999.9 fine) gold [2]. Moreover, the Aqua regia method is another process which can provide high purity (999.9 fine) of Au within one step. This process is to dissolve Au in aqua regia solution (HCl and HNO_3 solution), and then results of purified Au are obtained from precipitation process [7-8]. The final product is called gold bar which can be classified into two

types, namely casted and minted, respectively. Casted bars are made by pouring molten gold into an ingot mold to shape the gold product. Meanwhile, minted bars are made from gold blanks that have been cut to a flat piece of gold.

2.1.2.4.1 Eletrowining (Wohlwill Electrolysis)

The recovery of metal ions from solution by the application of direct current is known as electrowinning. Recovery of gold from elutes of carbon-adsorption process is usually accomplished by electrowinning with specially designed packed-bed electrodes. Nowadays, new eletrowinning cells have been developed and designed. Direct electrowining of Au from aurocyanide leach solution has been given little commercial attention, and research in this area has been limited. The development of direct electrowinning process was investigated due to the use of small current densities as well as the use of very low current efficiencies provided low concentration recovery of Au. Recently, the extended study of modification and improvement of cell design was evaluated in cell hydrodynamics. Extended surface area cathodes have been studied using conductive materials in the form of packed-fibers, rotating tubular bed and fluidized particle beds. The Bureau of Mines is developing an electrowinning cell (IMT) having improved mass-transfer characteristics. Recovery of Au from low grade cyanide heap-leaching solution by the IMT cell yields 96% gold recovery but very low current efficiency. Therefore, direct electrowinning of Au from dilute heap-leach cyanide solution has not been practiced to any extent and further development is necessary required [2].

2.1.2.4.2 Chlorination

Chlorination was used before the use of cyanidation. Chlorine was first used to recover gold from residues from amalgamation. Thereafter, it was used in big operations in gold fields. At the present time, chlorination for gold recovery is used on extremely small scale where gold is a minor constituent with other precious metals. The most important example is the treatment of matte leach residues to recover the platinum group metals where gold is a by-product. Gold dissolves in aqueous chloride solution to form Au^+ and Au^{3+} chloride complexes[9].

$Au + 2Cl^- = AuCl_2^- + e$

$Au + 4Cl^- = AuCl_4^- + 3e$
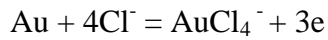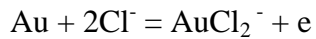
In the chlorination process, gold is dissolved as gold chloride, $AuCl_4^-$ and $AuCl_2^-$. The methods of recovering gold from chloride solution include adsorption by activated carbon. Thermodynamically, gold chlorides can be reduced to metallic gold by activated carbon as it is adsorbed from a chloride solution.

$AuCl_4^- + 3C + 6H_2O = 4Au + 16Cl^- + 12H^+ + 3CO_2$

$AuCl_2^- + C + H_2O = 4Au + 8Cl^- + 4H^+ + CO_2$

The gold chlorides can be easily reduced to metallic gold by activated carbon. As in other heterogeneous reactions between solids and fluids, the process of gold chlorides adsorption on activated carbon includes the following step: first $AuCl_4^-$ and $AuCl_2^-$ diffuse through the liquid film surrounding the carbon particle and then the gold chloride are reduced to metallic gold on the carbon surface.

2.1.2.4.3 Aqua regia method

Aqua regia is the mixture of one part of nitric acid and three parts of hydrochloric. It is typically used for dissolving gold becoming the chloroaurate anion complex or chloroauric acid. This dissolution method can be used in the refining of gold in which gold of lower purity are dissolved in aqua regia and the solution is then precipitated using sodiumbisulfite. The solution is filtered through filter paper and the filtrate is cleaned before subjected to fusion process.

2.1.3 Applications

With its beauty, permanence and rarity gold is still the material of choice for the fabrication of religious artefacts, decorative articles and jewellery However, the

unique chemical and physical properties offered by this precious metal are increasingly being sought for use in a growing number of industrial and medical applications. Normally, the refining of gold with the purification of 99.5 – 99.999% have been transformed to the gold bar and it was then applied to various industries. Gold is currently used in a large number of jewelry and other applications including uses within the fields of nanotechnology, medicine and electronics for products such as smart-cards, automotive, electronics, sensors, medical implants and drug delivery systems[10].

2.1.3.1 Jewelry

Gold jewelry has existed for thousands of years. In fact, the precious mineral used to create such items has been valued by humans since before recorded history. In earlier times, the material was hard to come by. In addition, much skill was required to work the metal into desirable designs. Nowadays, many different aspects of fashion options which make them appealing are available *i.e.* gold rings, gold earrings, gold bracelets and gold necklaces, etc.

Because of the softness of pure gold (24k), it is usually alloyed with base metals for use in jewelry, altering its hardness and ductility, melting point, color and other properties. Alloys with lower caratage, typically 22k, 18k, 14k, 10k and 8k contain higher percentages of copper, or other base metals or silver or palladium in the alloy. Copper is the most commonly used base metal, yielding a redder color. Eighteen carat gold containing 25% copper is found in antique and Russian jewelry. It has a distinct, though not dominant, copper cast, creating rose gold. Blue gold can be made by alloying with iron and purple gold can be made by alloying with aluminium, although rarely done except in specialized jewelry. Blue gold is more breakable and therefore more difficult to work with when making jewelry. Fourteen and eighteen carat gold alloys with silver alone appear greenish-yellow and are referred to as green gold. White gold alloys can be made with palladium or nickel. White 18 carat gold containing 17.3% nickel, 5.5% zinc and 2.2% copper is silver in appearance. Nickel is toxic, however, and its release from nickel white gold is controlled by legislation in Europe. Alternatively, the white gold alloys are available based on palladium and silver but the palladium alloys are more expensive than those using nickel. High-carat

white gold alloys are far more resistant to corrosion than are either pure silver or sterling silver.

2.1.3.2 Electronics

Gold is highly conductive to electricity, and has been used for electrical wiring in some high-energy applications as well as the use of silver, but gold has the advantage of corrosion resistance. Thus, one area that has seen significant growth is the use of gold in electronics, particularly within telecommunications, information technology and safety critical applications. Within computers there are usually gold-plated edge connectors. Gold bonding wires are used extensively within semiconductor packages, gold thick film inks are applied in the fabrication of hybrid circuits and gold's excellent solder wetting properties are used to form a very thin protective layer on copper laminate printed circuit boards prior to storage. Also, some DVDs and recordable CD-Rs have thin gold metallisations . Besides sliding electrical contacts, gold is also used in electrical contacts because of its resistance to corrosion, electrical conductivity, ductility and lack of toxicity [10].

2.1.3.3 Dentistry

Several dental historians have referred to the discovery of two molar teeth held together by a gold wire. Another evidence exists at present is insertion of a substitute tooth by replacing the gold wire by gold bands in front of and behind the incisor teeth on each side of the gap, drilling a hole through both bands and the new teeth, and inserting a gold wire as a rivet. In some case, the artificial tooth is the lost tooth with its root cut off. In a few instances, an artificial tooth has been fashioned from gold[11-12].

2.1.3.4 Medical devices

Currently, there are a number of direct applications of gold in medical devices. As with dental applications, these are related to the excellent biocompatibility of gold as a material. Applications include wires for pacemakers and gold-plated stents used to inflate and support arteries in the treatment of heart disease

as gold is highly opaque to X-rays aiding positioning of the stent. Gold possesses a high degree of resistance to bacterial colonisation and because of this it is the material of choice for implants that are at risk of infection, such as the inner ear. For example, gold-plated myringotomy tubes are used for implantation in the tympanic membrane to drain and temporarily aerate the tympanic cavity [10].

2.1.3.5 Drug delivery microchips

Another interesting application of gold in medicine is the concept of drug delivery microchips. These products contain drug-filled reservoirs covered, sealed and protected by thin gold membranes. For drug delivery applications, the microchips are implanted, swallowed, or integrated into an intravenous delivery system. A dose of the drug is administered to the patient by applying a small electric voltage to the gold reservoir cap, causing it to dissolve and allowing the drug to release from the reservoir. The timing of each dose can be controlled by the doctor or the patient through the use of microprocessors or remote control or biosensors. Originally conceived during research at MIT in the USA, MicroCHIPS has now begun to commercially exploit this technology.

2.1.3.6 Catalyst

Of all the new uses of gold, perhaps the most interesting development is based on its use as a catalyst in chemical processing, pollution control and fuel cell applications. The platinum group metals have long been known as important industrial catalysts. However, most researchers had overlooked gold as a possible catalyst until very recently, as its use requires careful and unconventional preparation centred on achieving a very small particle size (less than 5nm).

One of the most exciting aspects about catalysis by gold is the 'light off' temperature (the temperature at which the catalyst becomes functional) that can be achieved. Potentially, gold catalysts operate effectively at temperatures as low as −700°C. Other precious metal catalysts tend to have optimum performance in the range of 130°C-530°C. This offers the opportunity for gold to catalyse new reactions and in some cases offer alternative cost effective solutions to the platinum group metals.

Gold is already being used at a new British Petroleum (BP) Chemicals plant for the production of vinyl acetate monomer, which uses a gold-palladium alloy catalyst to excellent effect. Odour reduction applications are possible, as well as the potential to remove nitrogen oxides from diesel engine exhaust gases [10].

2.2 Activated carbon

Activated carbon is an excellent adsorbent due to its high contact efficiency, flexibility, and high capacity [13]. It is a crude from graphite with random amorphous structure which is highly porous. Activated carbon adsorptive properties are due to such factors as surface area, a micro-porous structure, a high degree of surface reactivity[14]. The starting materials and the activation method used for carbon production determine surface functional groups.

2.2.1 Preparation of activated carbon

Traditionally, activated carbons are derived from low-cost materials such as coconut shells, wood, char, lignin, petroleum coke, bone char, sawdust, carbon black, rice husks, etc., as well as virtually any materials comprising of cellulose[14]. common steps used in the preparation of activated carbon are displayed in figure 2.2

Raw materials

⬇

Grinding

⬇

Carbonization

⬇

Activation

⬇

Drying

⬇

Sieve

⬇
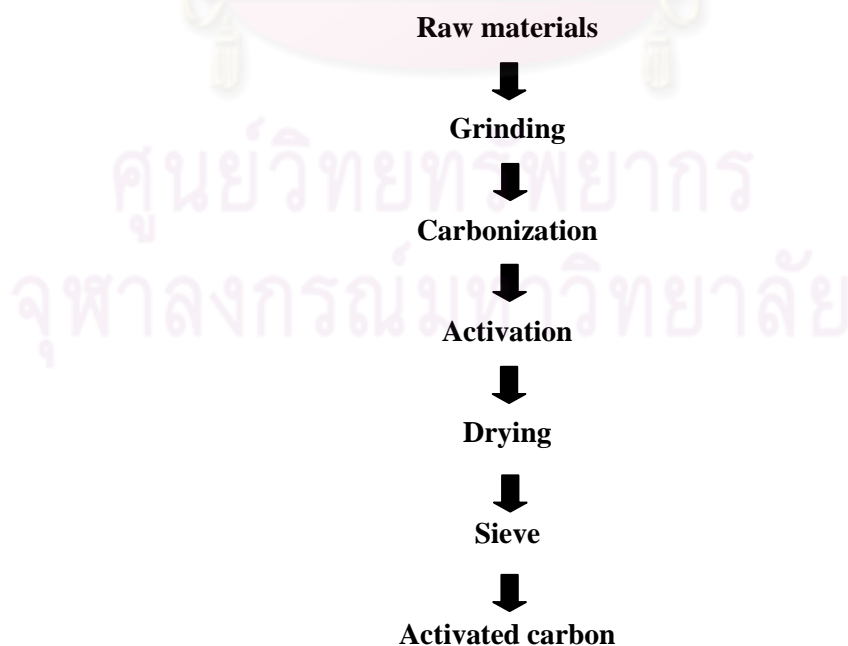
Activated carbon

Figure 2.2 Schematic representation of the preparation of activated carbon

2.2.1.1 Carbonization

After cleaning and grinding, the raw materials are subjected to carbonization in which the materials are heated to approximately 200-500°C for several hours under controlled atmosphere. Carbonization is a complex reaction involving elimination of volatile products and structural re-organizations within the remaining solid phase [15]. The elimination of water molecules favors the formation of dehydrocellulose, the main source of solid residue. The heating rate during carbonization noticeably affects the composition of the volatiles and the char properties [16]. Char from carbonization at high heating rates yielded higher reactivity than those subjected to slow heating rates and also yielded a slightly increase surface area of activated carbon.

2.2.1.2 Activation

The activation process of AC can be classified into two types, physical activation and chemical activation, of which is used to impart a porous structure within carbon [14]. During the activation process, the spaces between the elementary crystallites are cleared by the removal of loosely bound with carbonaceous materials. The resulting channels through the graphite regions, the spaces between the elementary crystallites, together with cleaves within and parallel to the graphite planes constitute the porous structure with a large surface area [17].

2.2.1.2.1 Physical activation

The precursor is developed into activated carbons using gases. This is generally done by a combination of the following processes [14].

Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600-900 °C, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)

Activation/Oxidation: Raw material or carbonised material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600-1200 °C [15].

2.2.1.2.2 Chemical activation

Prior to carbonization, the raw material is impregnated with certain chemicals. The chemicals are typically an acid, strong base, or a salt (phosphoric acid, potassium or sodium hydroxide, hydroxide and zinc chloride, respectively). Then, the raw material is carbonized at lower temperatures (450-900 °C). It is believed that the carbonization/activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases, because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

2.2.2 Classifications

Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics in to 3 types as followed.

2.2.2.1 Powdered activated carbon (PAC)

Powder activated carbons are normally made in particular form as powders or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 mm [2], thus they present a large surface to volume ratio with a small diffusion distance. PAC is not commonly used in a dedicated vessel, owing to the high

headloss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

2.2.2.2 Granular activated carbon (GAC)

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapours as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodourisation and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8x20, 20x40, or 8x30 for liquid phase applications and 4x6, 4x8 or 4x10 for vapour phase applications. A 20x40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as 85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as 95% retained). The most popular aqueous phase carbons are the 12x40 and 8x30 sizes because they have a good balance of size, surface area, and headloss characteristics.

2.2.2.3 Extruded activated carbon (EAC)

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

2.2.3 Applications

Activated carbon is used in gas purification, gold adsorption, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and filter masks, filters in compressed air and many other applications. One major industrial application involves the use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level.

2.2.4 Modification of activated carbon

It is known that activated carbon is relatively less effective in removing metal species from aqueous solution. The reason for this can be attributed to the relatively non-polar characteristic of AC which inhibits attraction between charged metal species and its surface. In addition, one significant drawback of AC is less adsorption selectivity [18]. Thus, the carbon surface chemistry has been studied extensively [19] in order to enhance the selectivity of AC to certain metal species. Modification of activated carbon are categorized into three types, namely, chemical modification, physical modification and biological modification.

2.2.4.1 Chemical modification

Due to the fact that the activated carbon surface area can display acidic, basic and/or neutral characteristics depending on the presence of surface functional groups [20]. It has been widely reported that chemical species can be removed by AC due to the surface complex formation between the chemical species and the surface

functional groups of AC. Thus, the chemical modification is taken to treat the carbon surfaces.

Predominant types of surface functional groups on AC are oxygen complexes such as carbonyl group. The surface oxygen complexes of AC can be created *via* two major oxidation methods, namely, dry and wet methods [21]. Dry method is involves the reactions with gas phase, such as CO_2, steam at high temperature ($> 700°C$) while wet method involves reactions between AC surfaces and oxidizing solutions (such as HNO_3, H_2O_2, NaOCl) under mild conditions ($20 - 100°C$). The chemical modification can be classified into 3 types, namely, acidic treatment, basic treatment and impregnation method.

2.2.4.1.1 Acidic treatment

Many investigations are directed towards modifying carbon surface to increase their acidic surface functional groups, which are types of oxygen complexes [22]. Examples of theses acidic functional groups are carboxyl, quinine, carbonyl, lactone, hydroxyl and carboxylic anhydride. These specific functional groups are essential for the adsorption of heavy metals due to chelating attribute of these groups where alkaline-earth metal cations can be integrated with the groups to from complexes as following equation;

$$M^{n+} + n(\text{-COOH}) \longleftrightarrow (\text{-COO})_n M + nH^+$$
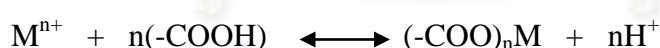
The reaction above is due to cation exchange mechanism where the metal cation exchanges site with the hydrogen ion previously attached as a whole carboxylic group. In general, acidic reactions with AC have been associated with oxide structures, which are part of the chemisorbed oxygen found on all carbon surfaces, which have been exposed to air or other oxidizing media [23]. Moreover, the use of strong acid oxidizing agents such as nitric acid or hydrogen peroxide is also used to increase acidic functional groups although exhibiting a lesser effect [24].

The conventional treatments using oxidizing agents in carrier medium can reduce the AC surface area. The oxygen plasma is another method treatment which is capable of modifying the external surface of AC with the formation of acidic functional groups, while the internal surface was practically unaffected. Generally, there is a hypothesis that plasma species do not penetrate into the internal structure of the carbon because of high reactivity of mono-oxygen radicals, etching the surface without affecting microporosity.

2.2.4.1.2 Basic treatment

There were studies achieved to determine the effect of basic treatment of AC on metal adsorption capacity. The adsorption of Cr(VI) reduced by using NaOH-treated AC was investigated [25]. This reduction is due to the decrease of specific surface area or micropore volume. Under basic environment, it is expected that OH^- ion will react with surface functional groups of AC [26]. This finding was verified in the study of AC treated with NaOH which showed major increase in the concentration of phenolic functional groups on the surface [27]. The basic treatment is beneficial in enhancing uptake of organic-based substances from aqueous solution. In the study of the influence of AC treatment with gaseous ammonia from 400°C to 800°C on adsorption toward phenol from aqueous solution, it was found that the optimum temperature for treatment condition was 700°C. Another method is to investigate the modification of AC surface with ammonia thermal treatment to achieve higher adsorption capacity for perchlorate from aqueous solution. In addition, the most favorable improvement occurred between 650°C to 700°C for perchlorate adsorption.

2.2.4.1.3 Impregnation method

It is generally accepted that the adsorption capacity of activated carbon to remove hazardous substances can be strongly supported by the impregnation with appropriated chemicals [28]. The three main specification for impregnating AC are to optimize the existing properties of AC *via* enhancement of its in-built catalytic oxidation capability, promote synergism between AC and impregnating agent to increase adsorption capacity as well as to raise the capacity of AC as inert porous carrier [29].The impregnated AC is particularly significant as impregnated materials can be distributed on large internal surface area, making them accessible to incoming reactants. They further elucidated processing method to manufacture industrial-grade impregnated AC in which the AC are sprayed with impregnation materials in a rotary or fluidized-bed. In some applications, the impregnating materials are present in the form of hydroxides, carbonates, chromates or nitrates by which the impregnated AC are subjected to thermal after treatment at various temperature (150-200°C) to decompose the anions.

2.2.4.2 Physical modification

Activated carbon modification techniques sometimes constitute minor changes in its physical characteristics. However, there are researches specifically aimed to modify the physical characteristics such as BET surface area and pore volume. Therefore, the increase of these characteristics can be enhanced by contaminant removal, especially in the case of organic adsorptions [30]. The majority of thermal treatment studied as a sole technique to achieve the required physical characteristic enhancements.

A significant drawback of thermal treatment of AC is that oxygen surface functional groups, which are thermally unstable, can be destroyed at high temperature [31]. As such, destruction of these groups may indicate lesser capacity to form cheaters with metal species, and thus reduces their uptake onto the modified AC. However, carbons are generally required a basic characteristics after high temperature (above 700 °C) heat treatment in an inert atmosphere [32]. Hence, it can be argued that heat-treated AC is generally favorable for enhancing adsorption of organic

compounds from aqueous solution since basic characteristic of the AC is amplified at high temperature conditions.

2.2.4.3 Biological modification

Additionally, the removal of organics from industrial wastewater was also an application of modified AC in removing agricultural-based herbicides as well as fungicides from aqueous solutions. Both natural and residual waters containing microorganisms that can be adsorbed on AC during water treatment due to its rough and fissured surface which microorganisms can settle and colonize easily [33]. Adsorption of microorganisms onto AC has been the subject of researches for the past several decades. Most researches on bioadsorption on AC is directed at the removal of readily biodegradable compounds that have low molecular weight such as phenol [34]. Bioadsorption can give rise to the formation of bacteria colonies onto the AC [35] due to (1) the adsorption properties of AC, which produce an increase in the series of nutrients and oxygen concentrations as well as the removal of disinfection compounds; (2) the porous structure of the carbon particles, which provides the bacteria with the protective environment; (3) the presence of a large variety of functional groups on the surface of the carbon, which enhances the adhesion of the microorganism. However, adsorption of these microorganisms onto AC can be beneficial in several ways. One of such benefits is that in biological AC process, carbon-bed life can be prolonged by converting a portion of recalcitrant organics to biodegradable organics by preozonizing. The attached microorganisms then convert the biodegradable portion to biomass, carbon dioxide and waste products before this material can occupy adsorption site onto AC [36]. Moreover, the biofilm formed on AC can change the surface charge density of the AC, mainly increase its negative value, which could enhance its adsorption capacity against some positively charged pollutant species, such as most of the heavy metals [37].

2.3   Sorption

To understand any of the extraction techniques, it is necessary to understand the physical and chemical processes of sorption. Absorption, referred to as a

partitioning, occurs when analytes pass into the bulk of the extracting phase and are retained. Adsorption is attraction of an analyte to a solid that results in accumulation of analyte's concentration at porous surface of the solid. Absorption results from stronger interactive forces than that of adsorption. Because adsorption and/or absorption process are sometimes difficult to distinguish experimentally and often occurs simultaneously. Generally, the term sorption will be used when referring to these processes. The term of sorbent will refer to solid extracting phase, including certain solid-supported liquid phase. Prediction and optimization are important for the analyst to be aware of the nature of the sorbent used.

Solid phase extraction (SPE) is an interestingly useful sample preparation as well as extraction method used to isolate analyte from a solution. SPE is not only used often to prepare liquid samples and extract semi-volatile or non-volatile analytes, but also can be used with solids that are pre-extracted into solvent.

2.3.1 Solid phase extraction

Solid-phase extraction (SPE) is an approach of sample preparation technique that offers a number of important benefits for isolating analytes from a gaseous or liquid phase by transferring onto the solid surface. SPE is similar to Liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, the SPE method is more efficient than liquid–liquid extraction (LLE) with several advantages such as quantitative extractions, enrichment of analytes, ease of operation operate, automation and reduction of lab times.

SPE method consists of four main steps, i.e. conditioning, loading, washing and elution as schematically illustrated in Figure 2.3. [38]
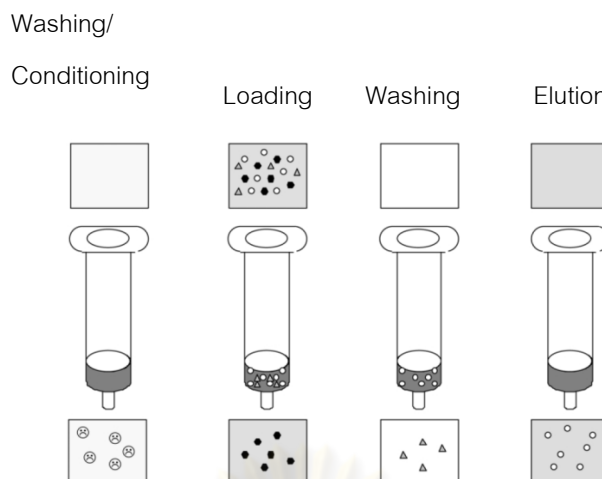
☹ impurity, • partitioning component, Δ interfering component and ○ analyte

Figure 2.3 The operating procedures of SPE.

In the first step, an appropriate solvent is used to condition the solid sorbent, and to remove the initial impurities on the sorbent surface or the packing material. The sample is then spread throughout onto the solid sorbent. During this step, the analytes are accumulated on the sorbent surface. The solid sorbent (that is saturated with the analytes) is washed with an appropriate solvent in the third step. The appropriate solvent used for washing should be of lower elution strength and able to eliminate matrix components on the surface of sorbent. The final step is elution. The analytes sorbed on solid sorbent are eluted by an appropriate eluent, without eluting of matrix components.

Although different processes may dominate in different situation, it can be assumed that multiple steps occur during sorption of a compound from liquids "into" or "onto" solid phase. A rate-limiting process will occur in any steps in controlling sorption of an analyte. It may interact with a solid-phase sorbent in at least four ways;

1. Through absorption, the analyte may interact with the sorbent by penetrating its three-dimension structure, similarly to water adsorbed by sponge. Three dimensional penetrations into the sorbent is particularly predominating process for solid-supported liquid phase. In the absorption process, analyts do not compete for sites; thus, absorbents provide a high capacity for analyte.

2. The analyte may interact two-dimensionally with the sorbent surface through adsorption due to the intermolecular forces such as *Van der Waals* force or dipole-dipole interaction. Surface interaction may result in displacement of water or other solvent molecules by the analyte. In the adsorption process, analytes may

compete for sites; thus, limitation capacity of adsorbents occurs. There are three steps occur during the adsorption process on porous sorbents *i.e.* film diffusion, pore diffusion and adsorptive reaction.

    3. If the compound is ionogenic (or ionizable) in aqueous solution, the electrostatic interaction between the analyte and charge site on the sorbent surface may occur. Sorbents specifically designed to exploit these types of ionic interactions are referred as ion-exchange sorbents.

    4. The analyte and the sorbent may chemically react toward each other such that the analyte becomes covalently bonded to the solid-phase sorbent. This type of sorption is generally detrimental to analytical recovery and may lead to slow or reduced recovery. All of these interactions have potentially operated during sorption simultaneously.

2.4   Adsorption isotherm

    The equilibrium adsorption models are used to describe adsorption processes. There are several equilibrium adsorption models such as Brunauer, Emmett, Teller (BET), Langmuir and Freundlich adsorption isotherm. The mentioned models explain different types of adsorption processes. However, these isotherms are simply relationships between the models of residual dissolved metal ion in solution at equilibrium (at a constant temperature) and a mass of sorbent. Experimental determination of an isotherm is usually achieved by mixing a known amount of sorbent with the given volume of metal ion solutions of which the initial concentration is known. The system is allowed to come to equilibrium at a selected temperature. Then, the residual dissolved metal concentration is measured. The concentration change is then subjected to calculate the moles of dissolved metal adsorbed.

(2.1)

$$x = (C_i - C)V$$

Where x = mole of metal adsorbed

      C_i = initial molar concentration of dissolved metal

      C = equilibrium molar concentration of dissolved metal

      V = liquid volume

Moles adsorbed are then divided by the mass of sorbent m ($x/m = N_f$) and the result is plotted against the equilibrium constant C.

Most equilibrium data can be fitted into one of two types of mentioned model *i.e.* Langmuir or Freundlich. Langmuir isotherm is based on theoretical developments and assumes that only a single (mono) layer can be adsorbed, while the Freundlich isotherm is an empirical relationship.

2.4.1 Langmuir adsorption isotherm

Langmuir adsorption isotherm results from assumption that adsorption is reversible and this model is used to predict the analytes in an aqueous phase accumulated onto sorbent surface in a monolayer adsorption above the sorbent surface. The Langmuir equation is shown in equation 2.2 [39].

$$\frac{C}{N_f} = \frac{1}{bN^s_f} + \frac{C}{N^s_f} \tag{2.2}$$

where
C = the residual concentration (mol dm^{-3})

N_f = the mole of analyte per gram of sorbent (mol g^{-1})

N^s_f = the maximum sorption capacity of the sorbent (mol g^{-1})

b = Langmuir constant to energy of adsorption (L mol^{-1})

Data are plotted either as shown in Figure 2.4 or one of the two alternate linear forms as shown in Figure 2.5.
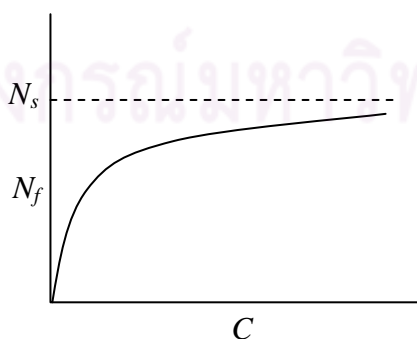
Figure 2.4 Plot of Langmuir adsorption isotherm

Approximately, the linear form is not necessary for the Langmuir isotherm, and first plot of satisfied data will demonstrate whether or not the model is applicable and also will allow determination of the coefficients. In many cases, a single model will not be satisfactory for a wide range of concentrations but will serve in narrow regions.
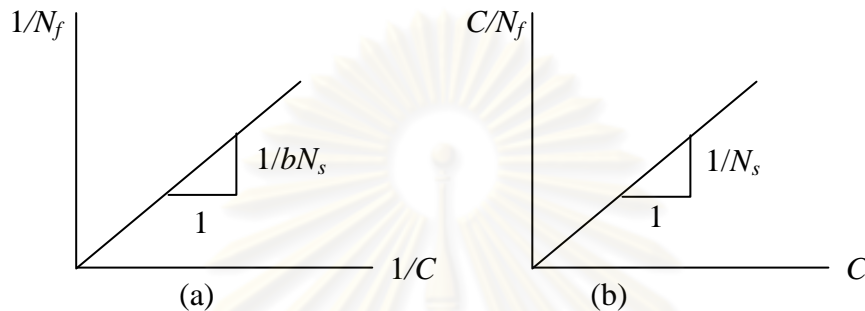
Figure 2.5 (a) Conventional linear form of Langmuir adsorption isotherm (b) Modified form of Langmuir adsorption isotherm emphasizing higher concentration data.

2.4.2 Freundlich adsorption isotherm

This isotherm, developed by Freundlich, describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The Freundlich isotherm is an exponential model and commonly used as adsorption expression, the model is described by equation 2.3

$$\log N_f = \log K_f + \frac{1}{n} \log C_e \tag{2.3}$$

where N_f is the amount of solute adsorbed per unit weight of sorbent (mg/g), C_e the saturation concentration of solute in the solution (mg/L), K_f is the Freundlichadsortion (mg/g). A plot of N_f versus C_e result in a curve of the form shown in Figure (a). Generally, the Freundlich adsorption isotherm is plotted on log-log paper (Figure (b)) to facilitate determination of the model's validity and the values of the coefficients K_f and n.
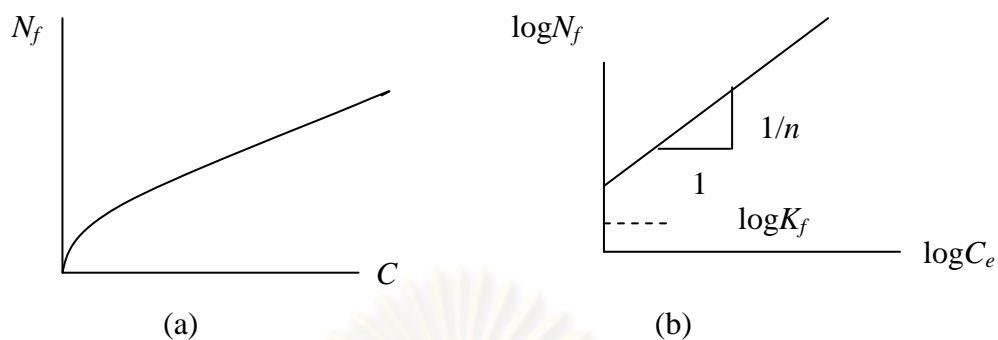
Figure 2.6 (a) Freundlich adsorption isotherm (b) Linear from of Freundlich adsorption isotherm

2.5 Analytical techniques

2.5.1 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)
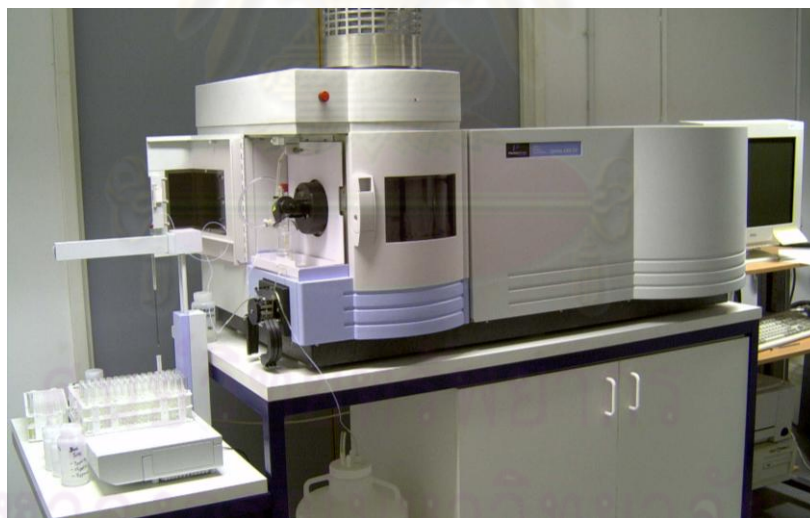
Figure 2.7 Inductively coupled plasma-optical emission spectrometer

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is one of several techniques available in analytical atomic spectroscopy. ICP-OES utilizes a plasma as the atomization and excitation source. Analytical plasmas are partially ionized gas which typically range in temperature from 6,000 to 8,000 K. ICP-OES is a technique used to perform qualitative and quantitative analysis of elements.

Typically, the solution sample is nebulized into the hot plasma where the desolvation, vaporization, atomization, ionization and excitation take place as shown in Figure 2.8. The excited atoms or ions are unstable and emit radiation of characteristic wavelength. This emitted radiation is then focused into a spectrometer where the light is dispersed and detected as schematically represented in Figure 2.9.

1. Sample Preparation: Some samples require special preparation steps incuding treatment with acids and heating digestion.

2. Nebulization: Liquid converted to aerosol.

3. Desolvation/Volatization: Water is driven off, and remaining solid and liquid portions are converted to gases.

4. Atomization: Gas phase bonds are broken , and only atoms are present. Plasma temperature and inert chemical environment are important at this stage

5. Excitation/Emission: Atoms gain energy from collisions and emit light of a characteristic Wavelength.
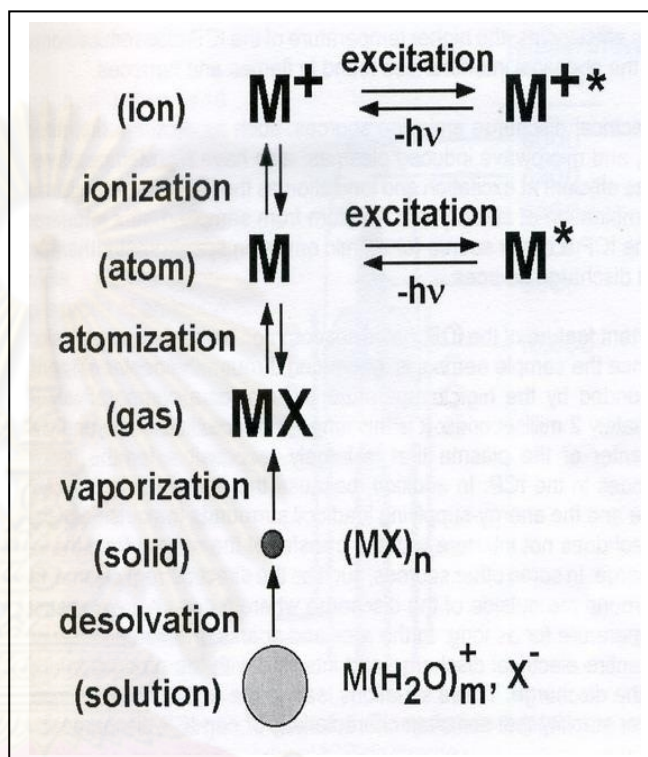
Figure 2.8 Process that take place when a sample droplet is introduced into an ICP discharge.
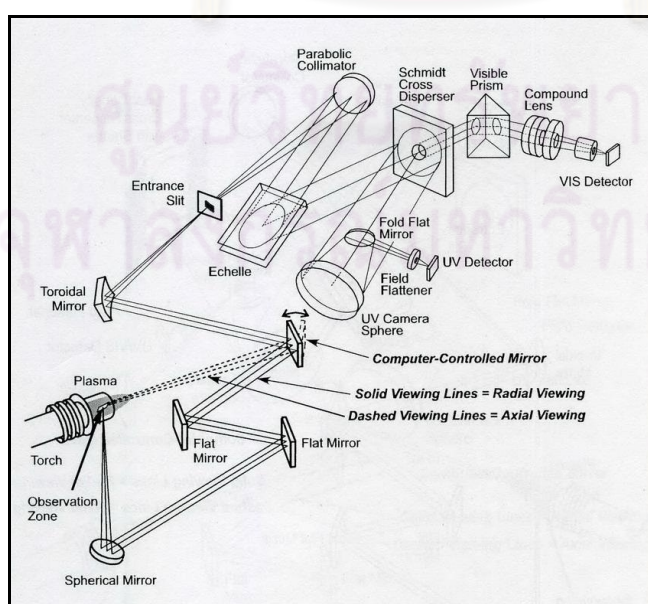
Figure 2.9 Schematic representation of ICP-OES instrument.

ICP-OES is a very useful analytical technique for elemental analysis capable of detecting over 70 elements in the part per billion (ppb) level. Some of the elements which can be measured together with its characteristic wavelength and typical detection limit achieved with ICP-OES are listed in Table 2.2.

Table 2.2 Characteristic wavelength and typical detection limit of selected elements by ICP-OES.

Element	Wavelength	Limit of detection (mg L^{-1})
Al	396.15	0.0280
Ag	328.06	0.0070
	243.77	0.1200
Au	242.79	0.0170
	208.20	0.0420
Cu	324.75	0.0054
	224.70	0.0077
Fe	238.20	0.0046
Pt	265.94	0.0810
	214.42	0.0300
Ni	232.00	0.0150
	221.64	0.0100
Zn	213.85	0.0018
	202.54	0.0040
Rh	343.48	0.0600
	233.47	0.0440

2.5.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements which consist of weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.
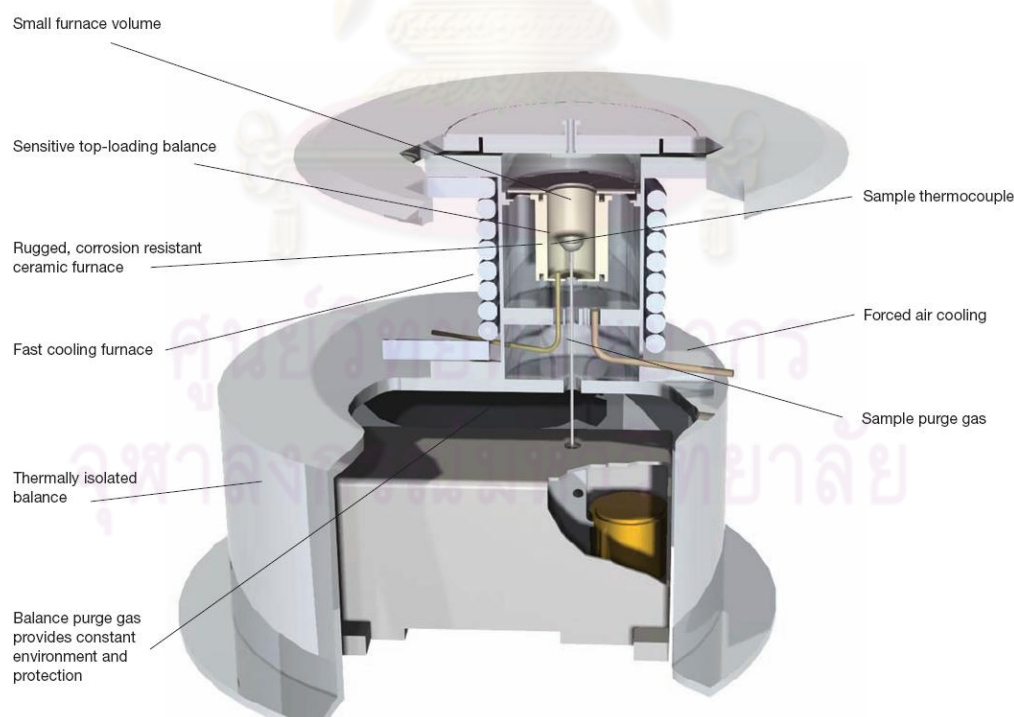
Figure2.10 Thermal gravimetric analyzer**.**

Simultaneous TGA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).
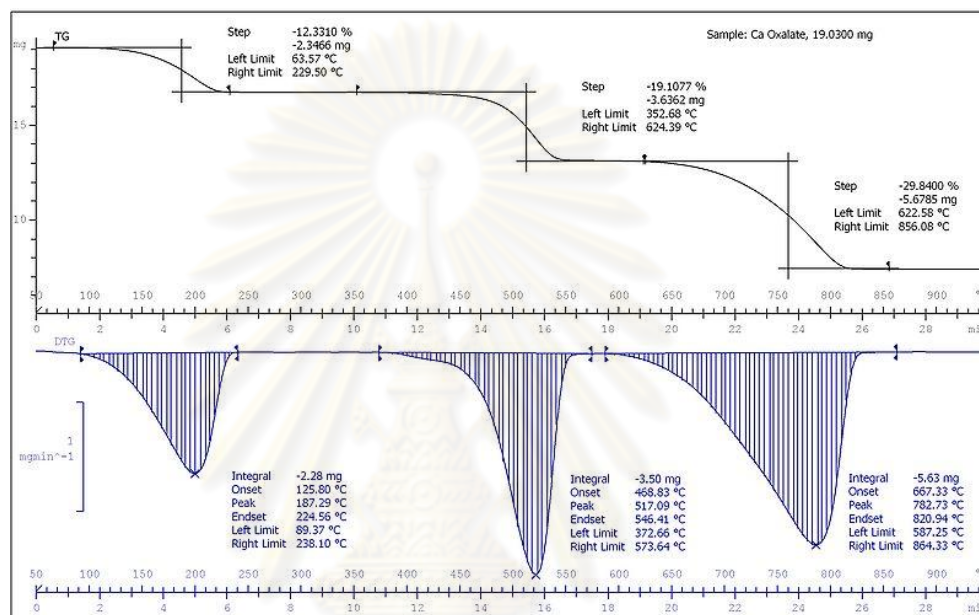
Figure 2.11 A typical TGA thermogram.

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection.

A method known as hi-resolution TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified. Several modern TGA devices can vent burn off to an infrared spectrophotometer to analyze composition.

2.5.3 Scanning electron microscopy (SEM)

The scanning electron microscope has unique capabilities for analyzing surface and morphology of materials. This technique is to reflect light microscope as well as different radiation sources served to produce the required illumination. The reflected light from sample surface provides an image, whereas the SEM uses electrons for image formation. The different wavelength of these radiation sources result in different resolution levels which generally provided much shorter wavelength than light photons, the shorter wavelength is capable of generating the higher resolution information. The resolution was enhanced without loss of any details. If the magnified level is over 2,000 times, the magnification is empty or does not provided additional information. Meanwhile the upper magnification limit is 2000 Å which equal to the theoretical maximum resolution of conventional light microscope. Normally, the wavelength of electron is less than 0.5 Å. Therefore, theoretically the maximum magnification of electron beam instrument is over 800,000 times. The SEM consists basically of 4 systems *i.e.* the illuminating/imaging system which produces the electron beam and directs it onto the sample, the information system includes the data released by the sample during electron bombardment and detectors which discriminate among these analytic information signals, the display system consists of one or two cathode-ray tubes for observing and photographing the interested surface and the vacuum system which used to removes gas from the micropore column which increases the free path of electron, hence the better image quality.
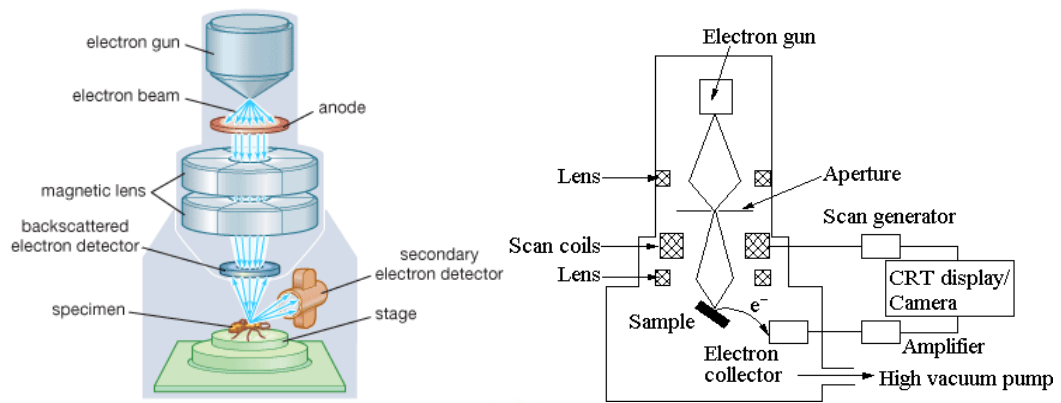
Figure2.12 Schematic representation of the scanning electron microscope (SEM)

2.6   Literature review

Activated carbon is one of adsorbents which is widely used for adsorption process and established as effective adsorbents for the removal of a wide variety of pollutants and others. Heavy metals have been one of the main targets under study for their removal using activated carbon. Zhaoa et al. [40] studied the adsorption of chromium on activated carbon adsorbents that had undergone surface modification with various chemicals *i.e.* HNO_3, H_2O_2, and $Fe(NO_3)_3$. These modified carbons were able to enhance the capacity of chromium adsorption over 10 mg/g. In addition, Gomez-Serrano et al. [41] investigated the adsorption of mercury, cadmium and lead by evaluating the carbon surface chemistry upon thermal activation and hydrogen sulfide modification. The results showed that mercury was attained the best adsorption capacity (1.5 mmol/g) among the metals investigated. Recently, Daorattanachai et al. [42] studied the adsorption of heavy metals *i.e.* copper, cadmium, nickel and zinc on activated carbon that had undergone surface modification with ammonium pyrrolidine dithiocarbamate (APDC) using impregnation technique. It was found that the activated carbon impregnated with APDC provided remarkably improved extraction efficiency for all metals investigated.

There were a few exists of articles that have appeared on gold adsorption using activated carbon. Aworn et al. [43] investigated the use of wood shaving fly ash, which is one of the residues generated in the combustion of coal, to extract gold from water/wastewater. The adsorption of gold obtained by this material was only roughly 8 mg/g. A relatively limited number of studies have been conducted to investigate the improvement of gold adsorption using the modifying agents and/or the activated carbon. Narita et al. [44] evaluated the use of *N,N*-di-*n*-octylacetamide (DOAA) and *N,N*-di-*n*-octyllauramide (DOLA) on the extraction of Au(III) containing different interfering ions *i.e.* Pd(II), Pt(IV), Rh(III), Fe(III), Ni(II), Cu(II) and Zn(II) using liquid-liquid extraction method. It was found that a near complete extraction of Au(III) was readily achieved with the DOAA. Ubaldini et al. [45] studied the gold removal from ores using activated carbon adsorbents and Thiourea (TU) which forms a relatively stable gold complex, $[Au(TU)_2]^+$, in solution. The results showed high yield, over 80%, of recovered gold with thiourea. On the other

hand, Monser et al. [46] used the activated carbon impregnated with Tetrabutyl ammonium iodide (TBAI) to extract CN^- from solution and obtain a much improved sorption capacity. It was concluded that the strong affinity of TBAI toward CN^- was attributed to the ion paring effect between the ammonium ion and the cyanide ion. Although not particularly related, we believe that this reagent might be useful in the extraction of gold as Au(III) are normally present in the form of chloroaurate ion ($AuCl_4^-$) in acidic solution and could possibly behave like CN^-. Xiangjum et al. [47] studied solvent extraction of Au (I) from auro-cyanide solution with column – shaped extraction equipment, using tri-n – butylphosphate as extractant with the addition of cetyltrimethylammonium bromide (CTAB). The column – shaped extraction equipment was suitable for Au (I) extraction from low content of auro-cyanide solution at high level of aqueous/organic phase ratio, with more than 97% of Au (I). Navarro et al. [48] studied the adsorption of gold on activated carbon in ammoniacal thiosulfate solution. The adsorption of gold was investigated by adding individually those anions into the gold solution as the corresponding thiosulfate. Tagashira et al. [49] employed an anionic surfactant solution of sodium dodecylsulfate (SDS) to successfully extract gold in the form of thiourea complex, $[Au(TU)_n]^{3+}$, into the SDS phase of a liquid–liquid extraction systems.

Therefore, in this study, we aim to improve the effectiveness of gold extraction by activated carbon. The improvement was directed to the modification of activated carbon in order to enhance its adsorption capacity as well as selectivity for gold(III). Several reagents that reportedly have gold-binding potential or believed to be so, for example, tetraalkyl ammonium halide (eg, TBAI, CTAB), *N,N*-dimethylformamide**,** ammonium thiosulfate and sodium dodecylsulfate, were impregnated into the carbon and its gold extraction efficiency were evaluated.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals were of analytical grade and listed in Table 3.1.

Table 3.1 Chemicals list

Chemicals	Supplier
Ammonium thiosulfate	MERCK
Cetyltrimethyl ammonium bromide	MERCK
Coconut shell-activated carbon	T.M.D.Co.,LTD
Copper standard solution	MERCK
Gold standard solution	SCP SCIENCE
Hydrochloric acid 65 %	MERCK
Iron standard solution	SCP SCIENCE
N,N-dimethylformamide	MERCK
Nickel standard solution	SCP SCIENCE
Nitric acid 35 %	MERCK
Platinum standard solution	SCP SCIENCE
Rhodium standard solution	ACROS
Sodium dodecyl sulfate	SIGMA ALDRICH
Tetrabutyl ammonium iodide	ACROS
Tetramethyl ammonium chloride	Fluka
Tetraoctyl ammonium bromide	MERCK
Zinc standard solution	MERCK

3.2   Instruments

1. Indutively couple plasma optical Emission Spectrometer (ICP-OES), 4300 DV, Perkin Elmer, USA

2.Scanning electron microscope, JSM-6400, JEOL, Japan

3.Thermal gravimetric analyzer, SFA409, Netzsch, Germany

4. Multi-position hot plate Stirrer, RT-5, IKA, China

5. Balance, AX105, Mettler Toledo, Switzerland

6. Peristaltic pump, ISM827B, ISMATEC, Switzerland

7. Oven, UNB 400, Memmert, Germany

3.3   Preparation and modification of activated carbon

3.3.1 Preparation of chemicals and modifying reagents

Standard solutions of Au(III), Cu(II), Zn(II), Ni(II), Rh(II), Pt(II) and Fe(II) were prepared by stepwise dilution of 1000 mgL^{-1} stock standard solution to the desired concentrations.

To obtain the modifying reagent solution with the concentration of 1.0 %(w/v), N,N-dimethylformamide (1g), Ammonium thiosulfate (1g), Cetyltrimethyl ammonium bromide (1g),Sodium dodecyl sulfate (1g), Tetrabutyl ammonium iodide(1g), Tetrametyl ammonium chloride (1g), Tetraoctyl ammonium bromide(1g), were dissolved in DI water using a 100 mL volumetric flask. Other concentrations of these reagents were prepared by appropriate dilution.

3.3.2 Modification of activated carbon

A commercial coconut shell- activated carbon (Filtra sorb 300, T.M.D. Co., LTD) were ground and sieved through a No.48 and No.32 mesh to obtain granular activated carbon (GAC) with particle size in the range of 300-500µm. The carbon was then washed and dried in an oven (60 °C) for 4 hours and kept in a desiccator until further use.

The carbon surface was modified using impregnation technique in order to improve its gold extraction efficiency. The modifying reagents used were Tetrabutyl ammonium halide, N,N-dimethylformamide, Cetyltrimethyl ammonium bromide, Ammonium thiosulfate, Sodium dodecyl sulfate. In the impregnation process, approximately 1.0 g of carbon was weighed and immersed into 100 mL aqueous solution of 1% (w/v) of the reagents. The mixture was gently stirred at room temperature for 24 hours.The impregnated carbon was then filtered through a paper filter, The filtrate of impregnated carbon was dried in an oven (60 °C) for 4 hours and kept in a descicator until further use.

3.4   Batch extraction

3.4.1 Gold extraction efficiency of the modified activated carbons

The commercial activated carbon and each of the impregnated − activated carbons were weighed nearest to 0.02g and placed in 100 mL of 20 ppm Au solution. The mixture was gently stirred at room temperature. The sampling was carried out at the intervals of 0, 5, 10, 20, 30, 60, 120 and 180 minutes, in which the stirrer was stopped prior to sampling and 5 mL of the supernatant was removed and transferred to a vial. Each aliquot was then subject to the determination of residual gold content using ICP-OES. The initial and residual Au concentrations at each interval were used to calculate the Au extraction efficiency according to the following equation 3.1.

% Au Extraction = ((C_i-C_f)/C_i)x100   (3.1)

C_i = Initial Au concentration (ppm)

C_f = Residual Au concentration at each sampling time (ppm)

3.4.2 Effect of alkyl chain length

As it was suggested in the previous experiment that tetrabutyl ammonium ions play a key role in the extraction of gold, therefore in this section, the effect of various alkyl chain length of the modifying agent was investigated. Tetramethyl ammonium (C1), Tetrabutyl ammonium (C4) and Tetraoctyl ammonium (C8) with the

concentration of 1% (w/v) were chosen to evaluate such effect toward extraction efficiency.

Portions of approximately 1.0 g of activated carbon were individually impregnated with 100 mL of 1% (w/v) TMAC, 1% (w/v) TBAI and 1% (w/v) TOAB. The mixtures were gently stirred at room temperature for 24 hours prior to filtering through a paper filter. The filtrate was then dried in an oven (60°C) for 4 hours and kept in a desiccator. The incorporation of these modifying reagents into the activated carbon were evaluated utilizing thermal gravimetric analysis.

Afterward, these modified materials were each weighed nearest to 0.02 g and placed in 100 mL of 20 ppm gold solution. The mixtures were gently stirred at room temperature. The residual gold content was monitored after 0, 10, 20, 30, 40, 50, 60, 80, 120 and 180 min using ICP-OES. The initial and residual Au concentrations at each interval were used to calculate the Au extraction efficiency.

3.4.3 Effect of concentration of the modifying reagent

The effect of loading amount of TBA was studied in order to determine the optimum TBA concentration for impregnation of activated carbon. In this experiment, TBA concentrations were varied from 0.001 to 1%(w/v).

Portions of approximately 1.0 g. of activated carbon were each impregnated with 100 mL of 0.01, 0.05, 0.1, 0.5 and 1%(w/v) TBA at room temperature for 24 hours. Each of the modified carbon (0.02 g.) was allowed to adsorb gold in 100 mL of 20 ppm Au solution with gentle stirring at room temperature. The residual Au contents were determined after 0, 10, 20, 30, 40, 50, 60, 80, 120 and 180 min by ICP-OES. The initial and residual Au concentrations at each interval were used to calculate the Au extraction efficiency. Thermal gravimetric analysis (TGA) was also performed on the modified carbons to evaluate the loading efficiency of the modifying reagent.

3.4.4 Effect of impregnation time

Portions of approximately 1.0 g. of activated carbon were each placed in with100 mL of 1% (w/v) TBAI and stirred at room temperature for 2, 4, 8 and 24 hours. These modified materials were each weighed to 0.02 g and allowed to adsorb

gold in 100 mL of 20 ppm Au solution. The mixture was gently stirred at room temperature for 180 min. The residual Au concentrations were determined after 0, 10, 20, 30, 40, 50, 60, 80, 120 and 180 min by ICP-OES and the Au extraction efficiencies were calculated.

3.4.5 Interference study

The effect of potentially interfering metals on Au extraction efficiency was studied. In this experiment, a number of metals commonly found in wastewaters from gold or jewelry related industries were chosen for the investigation using different metal solutions *i.e.* Au, Pt, Cu, Zn, Rh, Fe and Ni with various concentrations from 10 to 50 ppm of each kind.

The 1.0 g activated carbon portions were impregnated with 100 mL of 1% (w/v) TBA-impregnated carbon at room temperature and were gently stirred at room temperature for 24 hours and filtered through a paper filter. Thereafter, the filtrate was dried in an oven at 60°C for 4 hours immersed in solutions of mixed metals (Au, Pt, Cu, Zn, Rh, Fe and Ni) with the concentration of 10, 20, 30, 40 and 50 ppm. The residual concentrations of these elements were determined after 60 min by ICP-OES and their extraction efficiencies were calculated.

3.4.6 Adsorption isotherm

Under the optimum condition for TBA-carbon (1%(w/v)), the adsorption isotherm was studied. The TBA-carbon was weighed to 0.006 g and allowed to adsorb gold in 10 mL of 10, 20, 40, 60, 80, 100, 200, 300, 400 and 500 ppm for 120 min. Thereafter, the residual Au concentration was determined by ICP-OES. The results were treated with both Langmuir adsorption isotherm and Freundlich adsorption isotherm to describe the mechanism at the solid-liquid interface.

3.5 Column extraction

3.5.1 Effect of flow rate

A homemade mini-column (shown in figure 3.1) was prepared by a polyethylene rubber tube with 6.0 mm i.d. and 3.0 cm in length. The column was packed with 0.04 g of TBA-carbon, prepared under the optimized conditions from the previous studies. Cottons were placed at both ends of the mini-column to prevent the sorbent losses. The flow rates of the solutions were controlled by a peristaltic pump. Initially, deionized water was used to rinse the column and calibrate the flow rate in the range of 1 to 10 mL min^{-1}. Thereafter, 20 mL of 20 ppm Au solution was passed through the TBA-carbon loaded column at selected flow rates, namely 1, 2, 4, 7, 10 mL min^{-1}. The elutes were then collected and its remaining gold contents were determined by ICP-OES.

Figure 3.1 A photograph of the homemade mini-column.

3.5.2 Breakthrough curve and sorption capacity

In This section, a commercial activated carbon (CAC) was compared with the activated carbon impregnated with 1%(w/v) TBA (at room temperature for 24 hours) for its sorption capacity by means of a breakthrough curve.

A mini-column loaded with 0.06 g TBA-carbon was prepared according to the previous section. The TBA-carbon column was conditioned by DI water at flow rate of 1 mL min^{-1}. A solution of 20 ppm Au was then passed through the column at 1 mL

min^{-1}. The effluents were collected portionwise after certain volumes had passed through and their remaining gold concentrations were determined. The process was continued until the column substantially failed to retain gold (over 95% Au passed through). The same procedures were repeated with another column loaded with 0.08 g of commercial activated carbon and 10 ppm Au solution for comparison.

3.6   Gold extraction from waste water

The waste sample employed in this work was obtained from The Gem and Jewelry Institute of Thailand (GIT). This waste was a mixture of discharged materials from jewelry related sectors, consisting mainly of trace gold and varying amounts of their common base metals. Before the experiment, the Au concentration of this waste was determined by ICP-OES. The experiments were carried out in both batch and column methods utilizing the activated carbon impregnated with 1%(w/v) TBAI at room temperature for 24 hours. The commercial activated carbon was also investigated for comparison purpose.

3.6.1 Batch extraction

To study the waste extraction by batch method, the TBA-carbons were weighed between 0.01-0.3 g with variable increments and suspended in 100 mL of the waste. The mixtures were gently stirred at room temperature for 60 min. The Au concentrations were then determined and the Au extraction efficiencies were calculated. The experiments were repeated using the commercial activated carbon.

3.6.2 Column extraction

The column was prepared according to the method described in section 3.5.1. A 100 mL of the waste was passed through the TBA-carbon (0.02 g) loaded column. The flow rate of this column was maintained at 1 mL min^{-1}. The residual Au concentration was determined by ICP-OES and calculated to obtain the Au extraction efficiency. The experiment procedures were repeated with a commercial activated carbon loaded column.

3.7 Scanning electron microscopy (SEM) analysis

Approximately 1.0 g of the commercial and the TBA-impregnated activated carbons were separately added into beakers containing 100 mL of 1000 ppm Au solution. The mixtures were gently stirred at room temperature for 1 hour. The carbons were then filtered, dried, and their surface characterization were investigated by SEM analysis.

3.8 Gold recovery (Desorption study)

The desorption of Au from TBA-carbon was evaluated by using various eluents *i.e.* aqua regia, 1%(w/v) and 5%(w/v) ammonium thiosulfate and ammonium thiourea solutions. TBA-carbon was weighed to 0.02 g and placed in 50 mL of 20 ppm Au solution. The mixture was gently stirred at room temperature for 2 hours. Thereafter, the mixture was filtered to remove the TBA-carbon. The residual Au concentration in the solution after the filtration was determined by ICP-OES.

A 10 mL of 1%(w/v) and 5%(w/v) ammonium thiosulfate solution were added into a dried filtrate, and stirred at room temperature for 2 hours. Thereafter, all mixtures were filtered to remove the TBA-carbon. The solution was then made up to volume with DI water using a 10 mL volumetric flask. The Au concentration in the solution was determined by ICP-OES. The experimental procedures were repeated using 1%(w/v) and 5%(w/v) ammonium thiourea solution and aqua regia (50mL). Each of the eluent was investigated at both room temperature and 60 ºC for 2 hours. The gold recovery percentages were calculated according to the following equation 3.2.

$$\% \text{ Au recovery} = \frac{Au_{(Recovered)}}{Au_{(Adsorbed)}} \text{ x } 100 \qquad (3.2)$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Modification of activated carbon

The commercial coconut shell-activated carbons used for the modification are shown in Figure 4.1(a). The materials comprise mainly of carbon pellets with diameter in the range of 2-4 millimeters. After the carbons were ground, sieved and impregnated with the modifying reagents (*i.e.* Tetrabutyl ammonium halide, N,N-dimethylformamide, Cetyltrimethyl ammonium bromide, Ammonium thiosulfate and Sodium dodecyl sulfate), the carbons appear as granular activated carbon (Figure 4.1(b)).

(a)   (b)

Figure 4.1 A photograph of (a) the commercial activated carbons and (b) the modified activated carbons

4.2 Batch extraction

4.2.1 Gold extraction efficiency of the modified activated carbons

The activated carbons impregnated with Tetrabutyl ammonium halide, N,N-dimethylformamide, Cetyltrimethyl ammonium bromide, Ammonium thiosulfate and Sodium dodecyl sulfate, namely TBA-carbon, NDF-carbon, CTA-carbon, ATS-carbon and SDS-carbon were assessed for their gold extraction efficiencies by suspending in 100 mL of 20 ppm Au solution. The commercial activated carbon

(CAC) was used for comparison. The initial and residual Au concentrations were used to calculate the Au extraction efficiency. The remaining concentrations of gold in the solutions at various time after the extraction are presented in Table 4.1.

Table 4.1 The residual Au concentrations after the extraction by the modified carbons

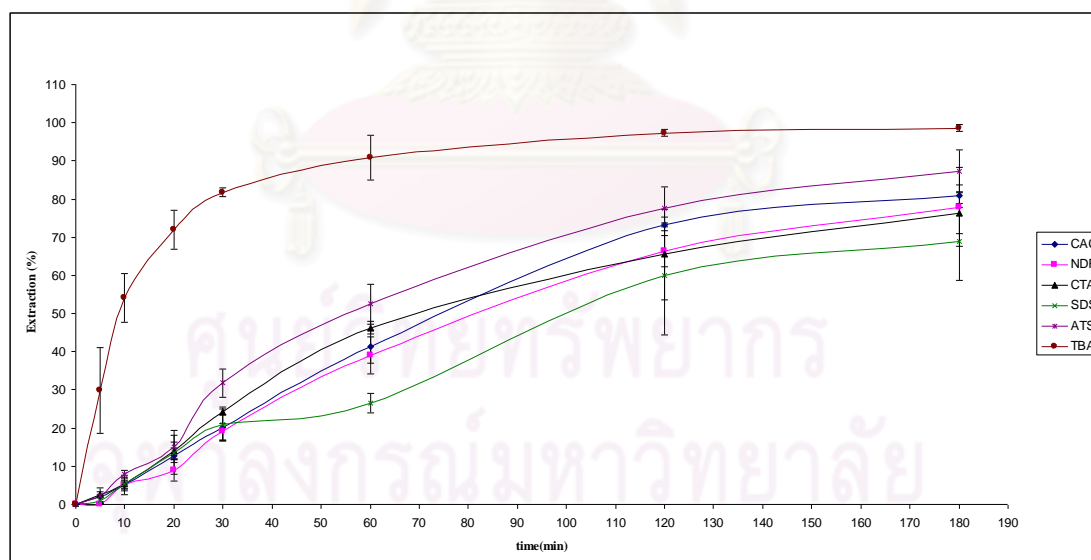| Time(min)	Residual Au concentration (ppm)					
	CAC	NDF	CTA	SDS	ATS	TBA
0	20.00	20.00	20.00	20.00	20.00	20.00
5	19.59	19.99	19.51	19.80	19.54	14.02
10	18.98	18.98	18.93	18.95	18.40	9.17
20	17.43	18.20	17.19	17.27	17.00	5.60
30	15.96	16.19	15.15	15.80	13.64	3.65
60	11.71	12.21	10.76	14.67	9.51	1.83
120	5.34	6.73	6.90	8.03	4.50	0.53
180	3.84	4.43	4.72	6.24	2.54	0.28

Figure 4.2 Au extraction profiles of the commercial and modified activated carbons (n=3)

The Au extraction profiles of the commercial activated carbon (CAC) along with those of the modified carbons are shown in Figure 4.2. All carbons similarly demonstrated increasing adsorption for gold as time proceed, nevertheless, it was

clearly shown that the extraction efficiency of the TBA-impregnated carbon distinctly stood out. With this TBA-carbon, over 50% extraction of gold was quickly attained in less than 10 minutes and 80% within 30 minutes. The adsorption apparently reached its equilibrium, presumably the completion of the process (> 90% extraction), roughly within 1 hour. Meanwhile, far less significant adsorption of gold were obtained with the commercial activated carbon for the same intervals. An unprecedented enhancement of roughly 50-60% extraction was observed with the TBA-carbon over its commercial counterpart earlier in the process and slightly less so afterward. This remarkable improvement was believed to be due to the favorable ion pairing of the quaternary ammonium ion (Bu_4N^+) toward the chloroaurate anion ($AuCl_4^-$) which were the dominant species of gold in acidic medium. A similar behavior was previously reported for the binding of a different anion complex (CN^-) to the TBA-carbon [46].

While the TBA-carbon demonstrated such an outstanding extraction characteristic, the other modified carbons remained somewhat comparable to those of the commercial one and thus their investigations were discontinued. With its potential as an extraordinary gold sorbent, the TBA-carbon was chosen as a model for subsequent studies.

4.2.2 Effect of alkyl chain length

It was believed that the hydrophobic parts of the TBA may have played a major role in adhering to the carbon surface, presumably via van der Walls interaction. Therefore, the influence of alkyl chain length of the modifying agent on the gold extraction was investigated. Tetrametyl ammonium (TMA), Tetrabutyl ammonium (TBA) and Tetraoctyl ammonium (TOA) were chosen to represent short, medium and long chain length, respectively. These modified carbons were assessed for its extraction efficiency toward gold. The Au concentrations were observed at the intervals of 5, 10, 20, 30, 60, 120 and 180 min using ICP-OES. The Au extraction efficiency and extraction profiles of modified carbons were illustrated in Table 4.2 and Figure 4.3.

Table 4.2 The residual Au concentrations after the extraction by the activated carbon modified with tetraalkyl ammonium ions of various chain length.

Time(min)	Residual Au concentration (ppm)			
	CAC	TMA	TOA	TBA
0	20.00	20.00	20.00	20.00
5	18.95	18.90	18.20	13.31
10	18.06	18.09	17.83	8.61
20	15.86	16.86	15.45	5.53
30	14.04	14.84	13.12	3.68
60	9.99	9.97	8.21	1.87
120	5.38	5.38	4.39	0.64
180	3.63	2.83	1.56	0.33
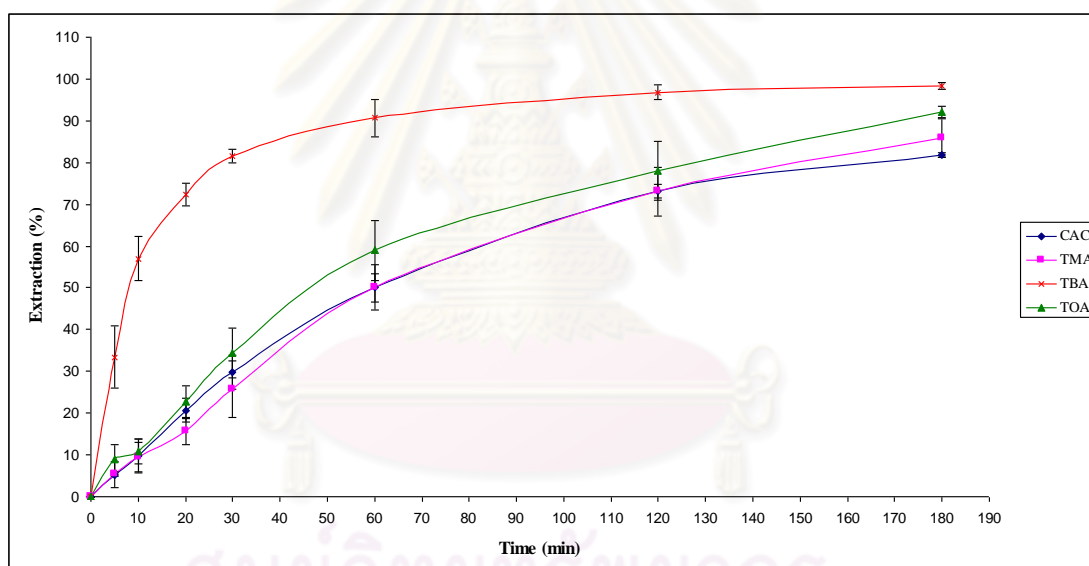
Figure 4.3 Au extraction profiles of TMA-, TBA-, TOA-carbons and the commercial activated carbon

Unlike what was seen with the TBA, the TMA-carbon produced nearly identical extraction pattern as that of the commercial activated carbon. This observation may have been attributed to the insignificant interaction of short methyl chain to the carbon and hence could be leached out easily. On the other hand, with its longer alkyl chain length the TOA-carbon resulted in a slightly better extraction profile than that of the commercial one but still inferior to that of the TBA-carbon. The adsorption of TOA onto the carbon may have been favored by its long alkyl chain, however, the steric effect created by this long side chain might have

deteriorated the accessibility as well as the ion pairing of the gold ion complex. These findings were further supported by the results from thermogravimetric analysis. The TGA thermograms of the commercial activated carbon and those impregnated with 1% w/v of TMA, TBA and TOA are illustrated in Figure 4.4 (a)-(d).
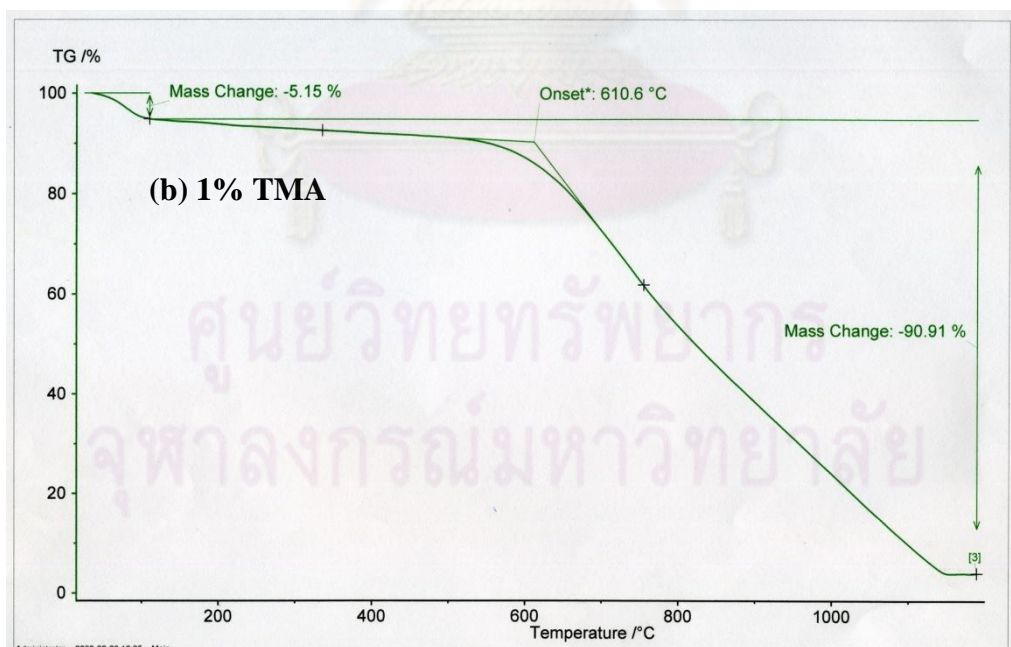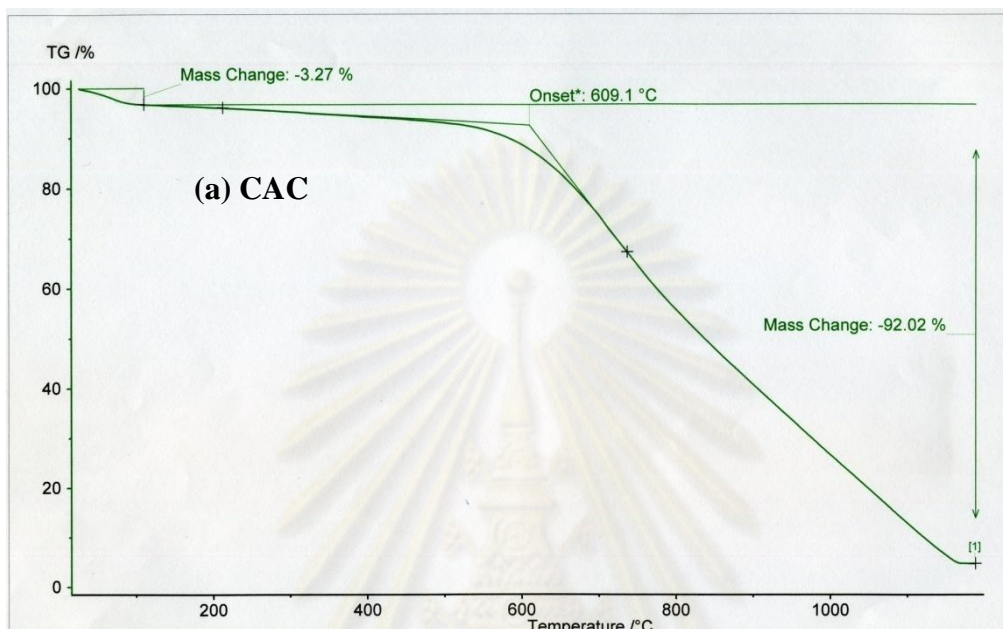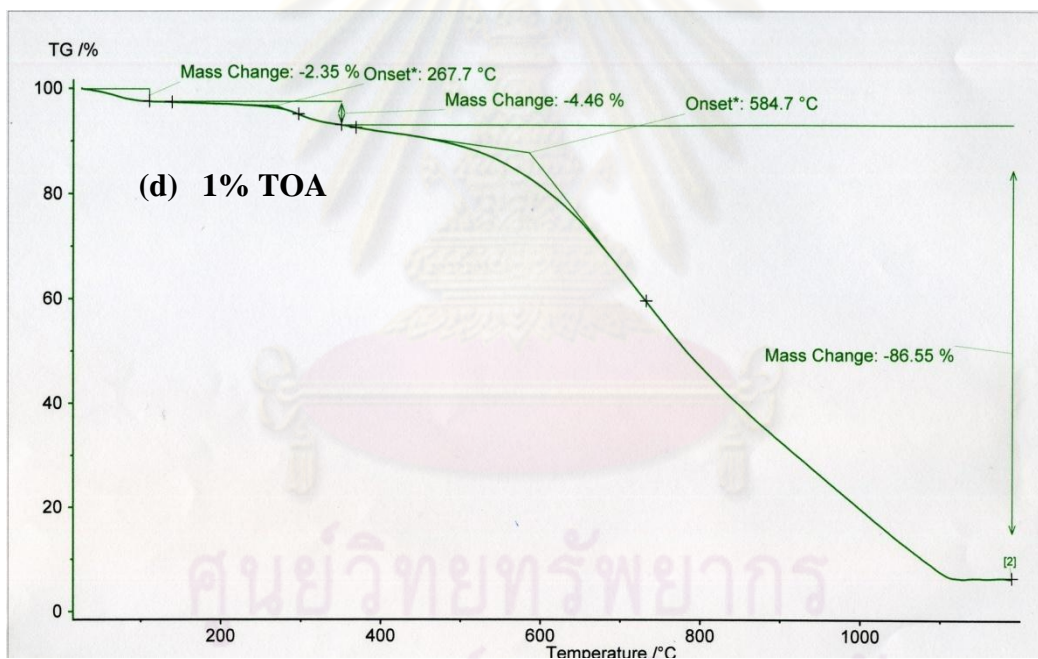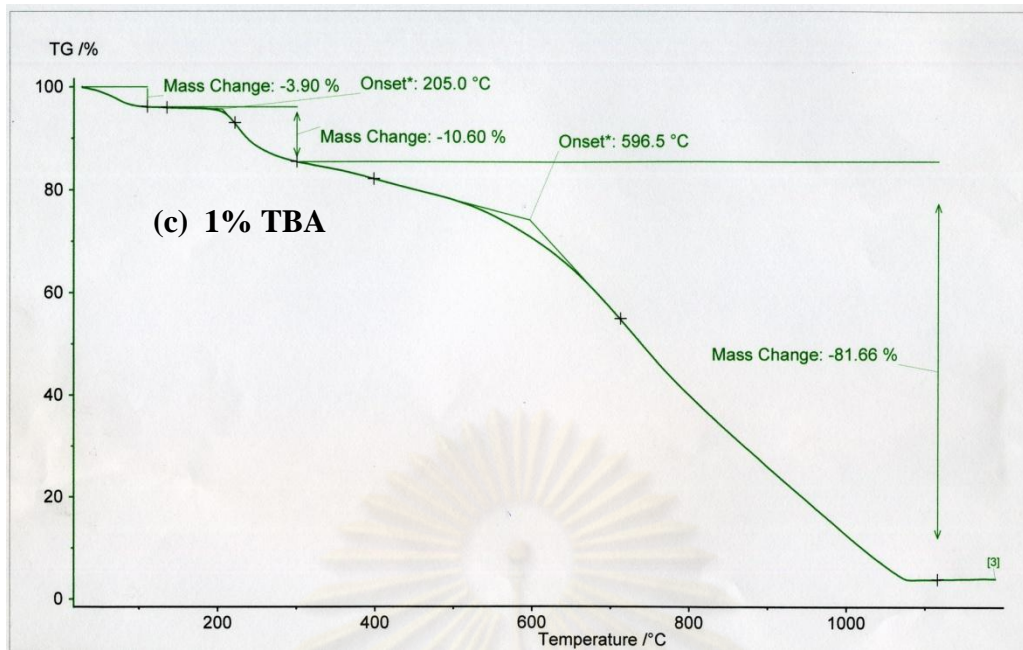
Figure 4.4 TGA curves of the commercial activated carbon (a) and the carbons impregnated with 1% TMA (b), 1% TBA (c) and 1% TOA (d)

The TGA curve of the commercial activated carbon (Figure 4.4 (a)) showed two stages of heat loss, one roughly around 100 °C and the other above 600 °C apparently due to the vaporization of trapped moisture and the decomposition of the carbon material respectively. An almost identical pattern was exhibited by the carbon

impregnated with 1% (w/v) TMA indicating that the incorporation of TMA into the carbon was truly insignificant, concurring with the gold sorption efficiency observed earlier. An additional intermediate stage of heat loss was seen in the temperature range of 200 – 400 °C for both TBA- and TOA-impregnated carbons. These mass losses can indeed be attributed to the decomposition of the modifying agents. A mass loss of 10.60% was seen for the TBA-carbon and 4.46% for the TOA-carbon indicating that both materials had been successfully integrated into the carbon framework and became the major contributing factor for the gold sorption enhancement.

Overall, it was technically reiterated by these experiments that the best extraction efficiency of gold was achieved with the TBA-impregnated carbon.

4.2.3 Effect of the concentration of modifying reagent

Based on earlier findings, TBA was chosen as a model modifying agent for further optimization. The loading amount of TBA onto the activated carbon was thought to be a contributing factor and thus was investigated in this section. The AC was impregnated with varying amount of TBA and its adsorption efficiency toward gold was evaluated. The results were displayed in the Table 4.3 and Figure 4.5.

Table 4.3 The residual Au concentrations after the extraction by the modified carbons with various TBA loadings.

Time(min)	Residual Au concentration (ppm)				
	0.01%TBA	0.05%TBA	0.1%TBA	0.5%TBA	1.0%TBA
0	20.00	20.00	20.00	20.00	20.00
5	18.38	17.02	16.88	15.77	13.17
10	16.94	16.33	14.86	12.01	7.98
20	15.38	14.97	13.11	9.72	5.54
30	14.05	13.08	8.76	6.59	3.97
60	7.90	5.37	5.01	3.05	1.37
120	5.08	3.17	2.42	1.89	0.68
180	2.23	0.89	0.96	0.78	0.42
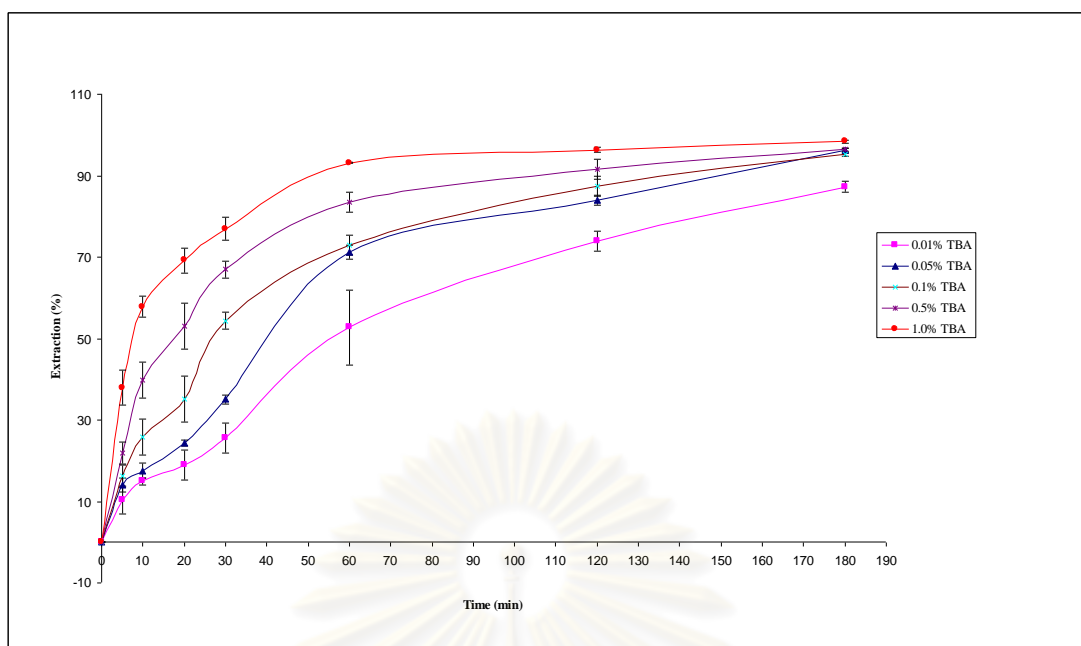
Figure 4.5 Au extraction profiles of the modified carbons with various TBA loadings.

Figure 4.5 demonstrated the TBA-carbon behavior on the extraction of gold as a function of time at room temperature. It was clearly seen that a growing trend in % extraction of gold was established as the quantity of TBA increased at all intervals. The maximum extraction was obtained with 1% (w/v) TBA impregnating solution in which a virtually complete extraction of gold was achieved within an hour. The Au extraction efficiency of carbons impregnated with TBA of lower doses decreased proportionally to its concentration, *i.e.* the extraction for 0.01, 0.05, 0.1 and 0.5% (w/v) TBA, were 60.50, 73.15, 74.95 and 84.75 % respectively for the same period.

These findings were further supported by the results from thermogravimetric analysis. The TGA curves of the AC impregnated with 0.01% TBA, 0.1% TBA and 1.0 % TBA are illustrated in Figure 4.6 (a)-(c).
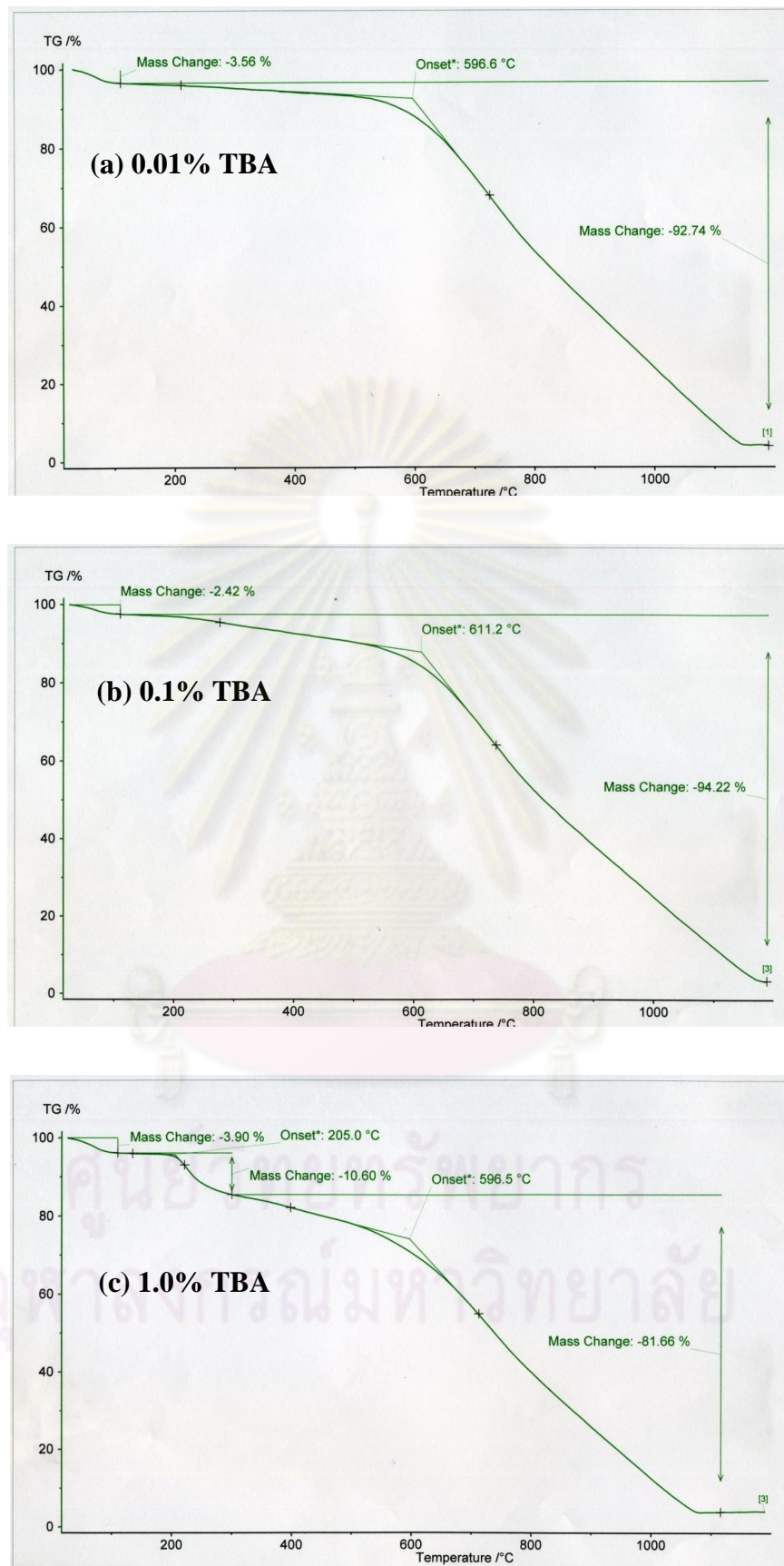
Figure 4.6 TGA curves of the activated carbon impregnated with 0.01% TBA (a), 0.1% TBA (b) and 1.0% TBA (c)

The thermograms obtained all have similar heat loss pattern with the only difference being the magnitude of the mass loss in the second step (due to the decomposition of the impregnating agent) which became larger as the loading increased. The mass loss of 0.01% TBA was absolutely negligible suggesting that there was no TBA present in the carbon. The mass loss became noticeable for 0.1% TBA and totaling up to 10.60% of mass loss with 1.0% TBA. These results are in good agreement with the gold extraction study in which a slight improvement was seen with the carbon impregnated with 0.1% TBA and a drastic enhancement with 1.0% TBA. Based on this observation, higher TBA concentrations (i.e. higher TBA loading) would be expected to yield better Au extraction. Unfortunately, the TBA became insoluble beyond this concentration.

4.2.4 Effect of impregnation time

The activated carbon was impregnated with 1% (w/v) TBA for 2, 4, 8 and 24 hours to evaluate the effect of impregnation time on the Au sorption. The extraction efficiency towards gold of these materials was monitored at various times. Table 4.4 shows the residual Au concentration for these modified carbons along with those of CAC at each interval, which the Au concentration was exhibited in Figure 4.7.

Table 4.4 The residual Au concentrations after the extraction with TBA-carbon prepared under various impregnation time

Time(min)	Residual Au concentration (ppm)			
	2hrs	4hrs	8hrs	24hrs
0	20.00	20.00	20.00	20.00
5	16.67	12.20	13.37	10.49
10	12.75	8.53	8.55	7.78
20	10.55	6.55	6.60	5.53
30	7.18	4.68	4.63	4.05
60	4.64	2.68	2.82	1.43
120	2.50	1.09	0.86	0.30
180	1.05	0.63	0.48	0.25
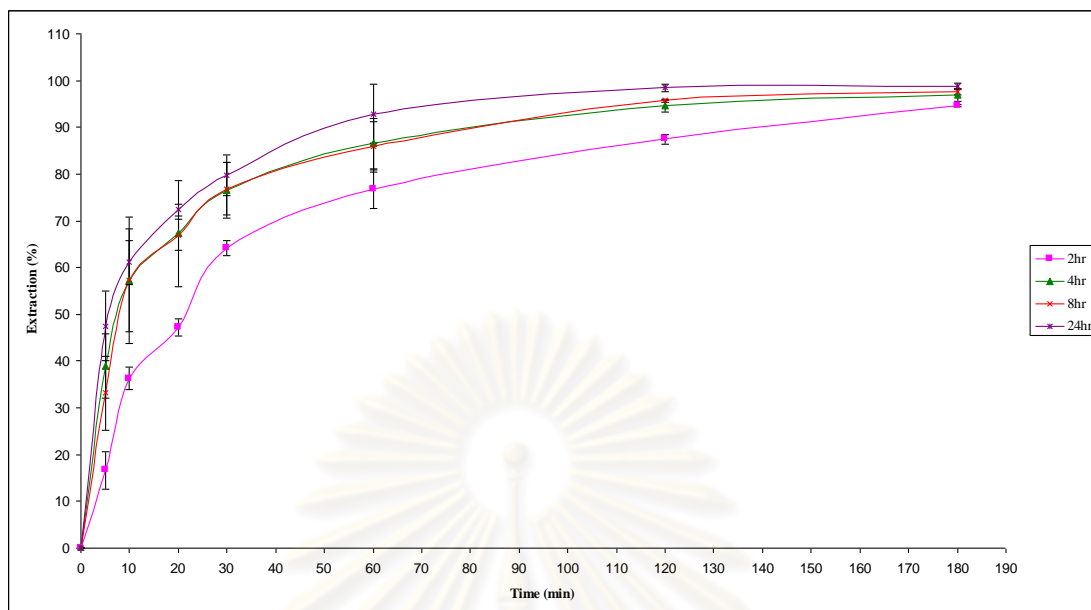
Figure 4.7 Au extraction profiles of the TBA-modified carbons prepared under different impregnation time

The results showed that the Au extraction efficiency of the modified AC was directly affected by its impregnation time. The carbon impregnated for 24 hours bearing the best performance provided roughly 93 % extraction of gold after 1 hour while those impregnated for 4 and 8 hours both produced slightly less Au adsorption (86%) and approximately 77% extraction for the 2 hour impregnation batch. These similar trends were established throughout the whole observation period. The result was of no w/v as longer contact time may allow for TBA to be incorporated into the carbon and enhance its gold sorption efficiency and thus the impregnation time of 24 hours was chosen for further experiments.

4.2.5 Interference study

As gold recovery from the jewelry-related industrial waste was one of the main interests in this work, it is inevitable that the success of this study must be challenged by the presence of other base metals. Therefore, an investigation to

determine potential interferences of these metals was conducted. A number of metal ions *i.e.* Cu, Zn, Fe, Ni, Rh, Pt, which were commonly found in gold waste solution, were chosen as interfering ions in this experiment. The extraction of Au and these co-existing metals at various concentrations were determined and the results were shown in Figure 4.8.
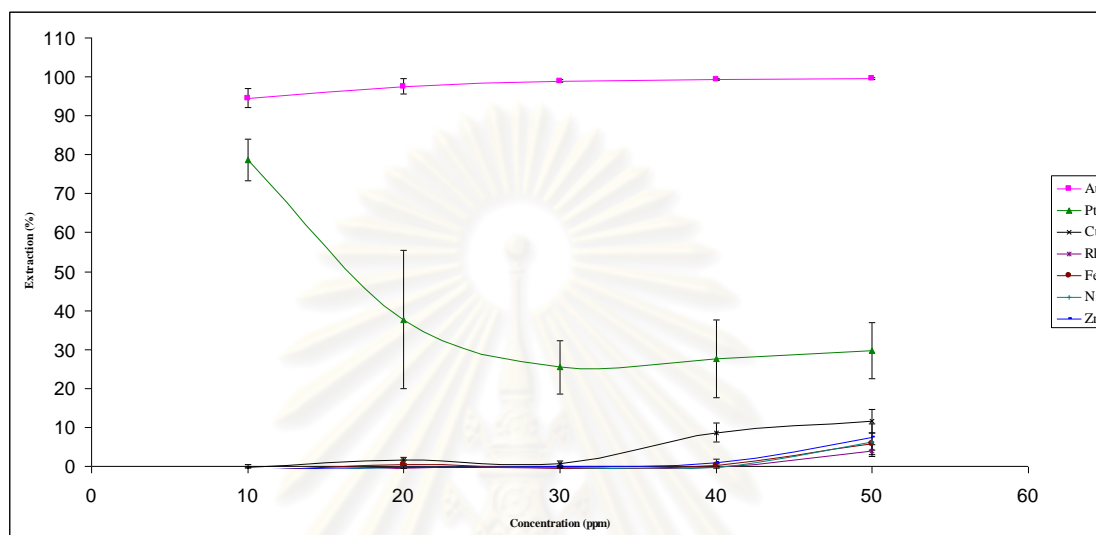
Figure 4.8 The extraction profiles of various metal ions obtained with the TBA-carbon

As can clearly be seen from the figure, the presence of common interfering metals hardly affected the gold extraction efficiency of the modified carbon. The near complete extraction of gold was maintained throughout the whole concentration range studied. The adsorption of common base metals (Cu, Rh, Fe, Ni and Zn) was almost negligible for the concentration up to 40 ppm and merely noticed at 50 ppm. However, an interesting behavior was observed with Pt, another precious metal commonly found in the gold refining process. Nearly 80% extraction of Pt was attained with 10 ppm solution but then declined onwards as the concentration increased. The high extraction efficiency of Pt at lower concentration may be due to the fact that, in acidic medium, Pt is normally present as $PtCl_4^-$ which would then be favorable to bind with the TBA in the same fashion as $AuCl_4^-$. However, at higher concentrations, both ions may have competed for the adsorption site with the gold being preferred and hence the extraction of Pt became less significant.

Therefore, it can undoubtedly be concluded that the TBA-modified carbon not only shows a remarkable improvement in the gold extraction but also possesses an excellent selectivity toward gold.

4.2.6 Adsorption isotherm

The adsorption isotherm is a tool used to describe the adsorption equilibrium between metal ions in solution and the sorbents. Langmuir and Freundlich relations are the two models commonly used in the study of adsorption behavior. The Langmuir sorption isotherm is used to describe monolayer sorption in which the adsorption capacity of the adsorbent is limited while the Freundlich isotherm is an empirical model based on sorption on heterogeneous surface sites of various affinities.   In this experiment, a fixed quantity of TBA-carbon was allowed to adsorb variable amount of gold under the optimum condition. After the equilibrium was reached, the remaining gold concentrations were determined. A plot of adsorption isotherm of the TBA-carbon is shown in Figure 4.9.
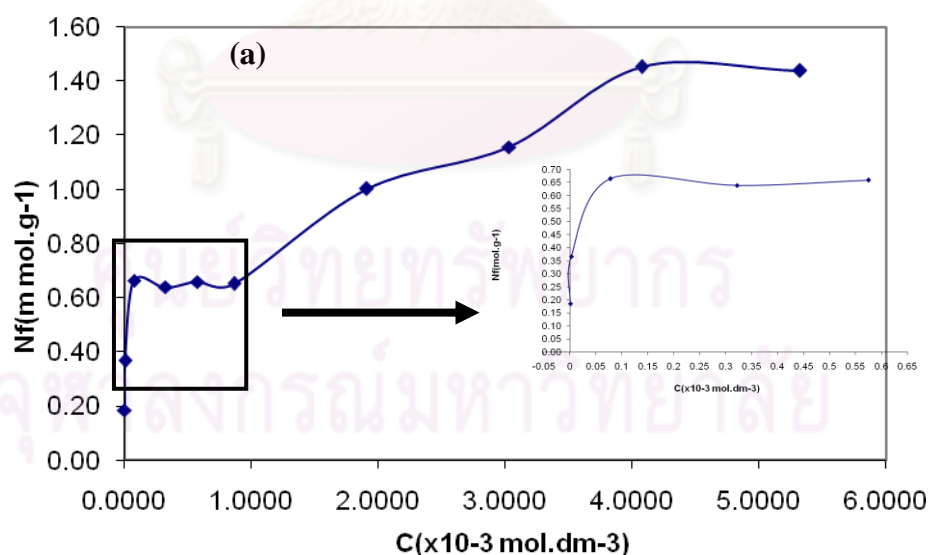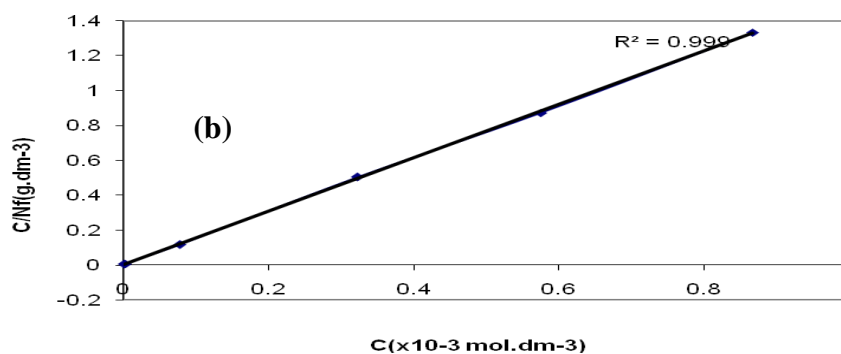
Figure 4.9 Adsorption isotherm of gold on the TBA-impregnated carbon (a) and its Langmuir isotherm fitting (b)

The adsorption data were treated for both Langmuir and Freundlich models. As seen in the inset of the figure, the TBA-carbon demonstrated an apparent Langmuir relation early in the process with a near perfect correlation coefficient (R^2) of 0.999. However, after a seemingly equilibrium plateau was reached, the adsorption continued to grow further at higher concentrations. The overall profile was fit to Freundlich model but no satisfactory correlation was found. This behavior suggests that the adsorption isotherm of gold on the TBA-carbon may result from a combination of both types of isotherm with a monolayer coverage built up in the early stage and additional layers accumulated on the heterogeneous sites later on.

4.3 Column extraction

Column extraction is the most widely used method in the gold mining industry as well as the extraction of other interested species from industrial wastes. Hence, a mini-column filled with TBA-impregnated AC was fabricated and assessed for its efficiency towards gold extraction from a continuous feed.

4.3.1 Effect of flow rate

It was shown previously that one of the key advantages of the TBA-carbon over its unmodified counterpart was its speed in the enhancement of gold adsorption. This could prove valuable in the column extraction process since the contact time is very limited. In this experiment, the influence of flow rate of the Au feed solution through the column was investigated. Two columns were used, one filled with TBA-carbon prepared under the optimum conditions from previous experiments and the other with commercial activated carbon for comparison. Twenty millilitres of 20 ppm Au solution was passed through the column by means of a pre-calibrated peristaltic pump at different flow rates. The elutes were then collected and its remaining Au concentrations were determined by ICP-OES. The procedures were repeated with 100 ppm Au solution. As usual, all experiments were performed in 3 replicates and averaged and the results were shown in Figure 4.10.
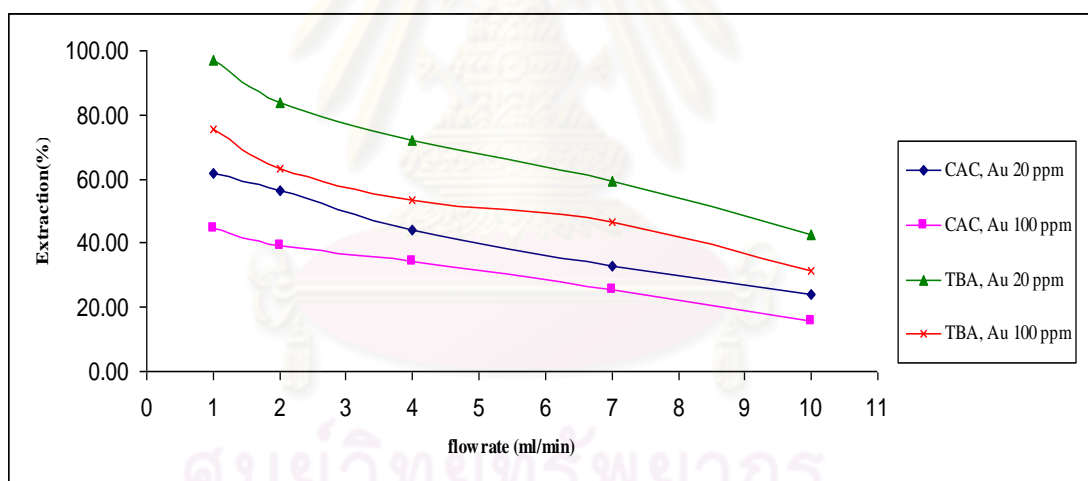
Figure 4.10 Au extraction profiles of the commercial and TBA-carbon as a function of flow rate

The results indicated that the adsorption of Au onto the column were strongly influenced by the flow rate. A relatively complete extraction of 20 ppm Au was effected at the flow rate of 1 mL.min^{-1} and decreased appreciably down to approximately 50% as the flow surged to 10 mL.min^{-1}. This finding came at no surprise as smaller flow rate would be expected to yield better adsorption due to longer contact time. A similar trend was observed for the commercial activated

carbon with the Au extraction descending from roughly 60% at 1 mL.min^{-1} to merely 30% at 10 mL.min^{-1}. The extraction of 100 ppm Au solution by the two carbons generated nearly equivalent patterns but with proportionally smaller extraction efficiency, presumably due to a limited adsorption capacity on each column. Based on these results, 1 mL.min^{-1} was definitely the obvious choice of flow rate for further experiments.

4.3.2 Breakthrough curve and sorption capacity

A breakthrough curve is a means that can be used to describe the effectiveness of the column extraction. The curve is typically a plot of the ratio of the remaining concentration of the adsorbed species (C), gold in this case, passing the column over its initial concentration (C$_i$) versus the amount of gold or the Au solution loaded through the column. The experiment was carried out by passing Au solution through the column loaded with an accurately weighed carbon. The remaining gold concentrations in the effluents were monitored as a function of volume and the curve was constructed. The breakthrough curves of both the commercial and the TBA-impregnated activated carbons are shown in Figure 4.11.
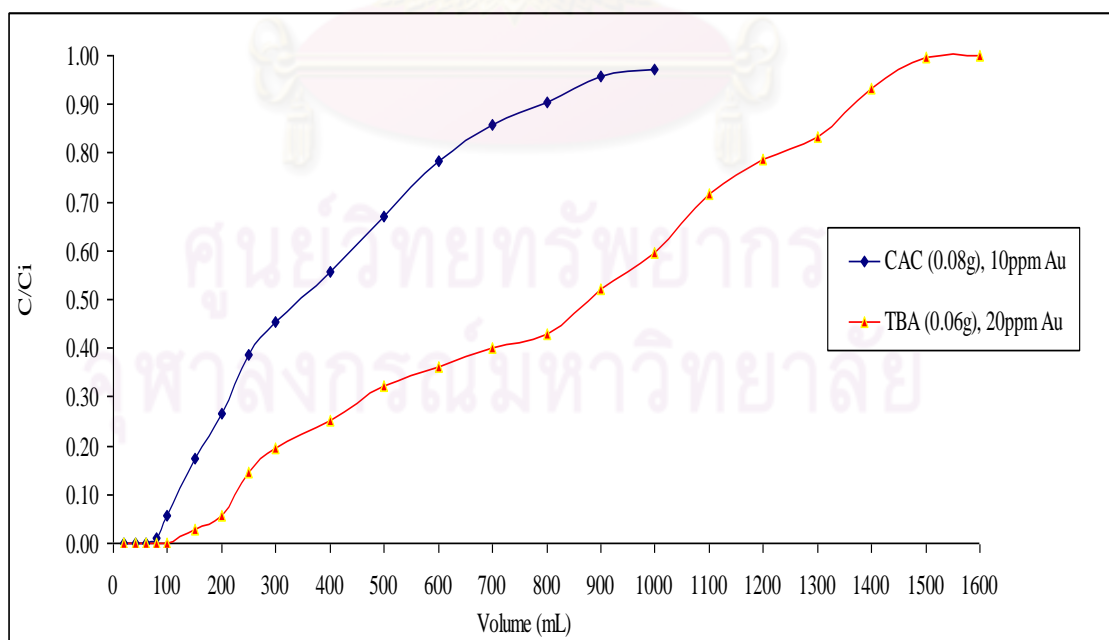

Figure 4.11 Breakthrough curves of the commercial and the TBA-impregnated activated carbon

A typical breakthrough curve was obtained with the TBA-carbon in which a complete extraction of gold ($C/C_i \sim 0$) was maintained up to roughly 100 mL. The ratio progressively increased to roughly 0.95, a point to which it was construed that the column essentially failed to retain gold at approximately 1500 mL of effluent volume (equivalent to 30 mg of gold loading). Meanwhile, the curve of the commercial activated carbon showed that the column failed to retain gold completely at roughly 900 mL of effluent volume (equivalent to 9 mg of gold loading). These numbers indicated that there is a large difference in the adsorption capacity between the two carbons.

A calculation method in the work of Zhou et al. [50] was adopted in order to determine the adsorption capacity of the carbons. In brief, this method utilized the integrated area of the curve up to a defined breakthrough point to calculate the amount of adsorbed species and the eventual breakthrough capacity. In this work, a breakthrough point of 15% ($C/C_i = 0.15$) was defined and the area was integrated. The breakthrough capacity obtained by the TBA-carbon was 90.62 mg/g while that of its commercial counterpart was merely 18.00 mg/g, a remarkable enhancement by roughly a factor of 5 for the modified carbon.

4.4   Gold extraction from industrial waste sample

The waste sample was initially analyzed for its composition. The gold content in this particular waste was found to be 8.52 ppm among with all other common base metals at substantially higher concentrations (30-100 ppm).

4.4.1 Batch extraction

The batch extraction experiment was designed to demonstrate a significant improvement in Au extraction of the TBA-carbon. Varying amounts of both TBA-carbon and CAC were allowed to adsorb Au in 100 mL of the jewelry waste solution under gentle stirring at room temperature for 60 min. The gold extraction percentages

of these adsorbents as a function of its dose were exhibited in Table 4.5 and Figure 4.12

Table 4.5 Au extraction from waste sample using batch method

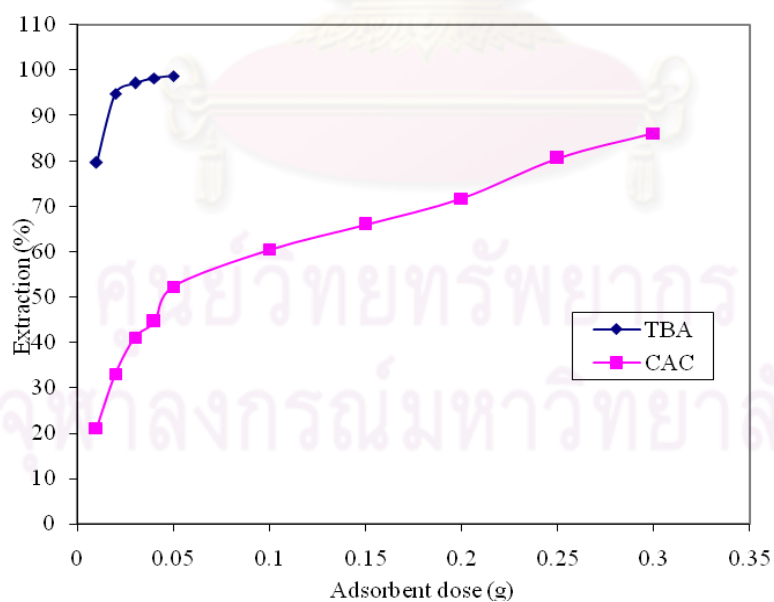| Sorbent (g)	TBA Extraction (%)	CAC Extraction (%)
0.01	79.58	21.13
0.02	94.84	32.98
0.03	97.18	41.08
0.04	98.24	44.60
0.05	98.71	52.23
0.1	-	60.45
0.15	-	65.96
0.2	-	71.71
0.25	-	80.63
0.3	-	86.03

Figure 4.12 Au extraction profiles of the commercial and the modified carbons from waste sample

It was clearly demonstrated that the TBA-carbon was far more effective than the CAC in term of the Au extraction from the real industrial waste. The extraction of gold from 100 mL of the waste was virtually completed with the use of TBA-carbon as little as 0.02 g. The additional amount of TBA-carbon was only able to improve the % extraction by a very slim margin and thus the experiment was discontinued after 0.05 g of TBA-carbon was used. On the other hand, only 33% extraction was achieved with 0.02 g of CAC. The extraction improved slightly as the amount of CAC increased but the extraction was still far from completion even with the highest amount of carbon being used.

4.4.2 Column extraction

A different strategy was employed in the column method. Two mini-columns containing fixed amount of TBA-carbon and CAC were used and 100 mL of the waste solution was passed through both columns under the optimum flow rate. The amount of non-retained Au in the eluted solution was determined. It was evidently established once again that the TBA-carbon owned a huge advantage as a gold sorbent over its commercial counterpart as seen in Table 4.6.

Table 4.6 The Au extraction efficiency of TBA-carbon and the commercial activated carbon

Sorbent	Remaining Au concentration (ppm)	Extraction (%)
CAC	3.98	53.29
TBA-Carbon	0.13	98.47

4.5   Scanning electron microscopy (SEM) analysis

To further demonstrate the improvement and adsorption capability of TBA-carbon over its commercial counterpart, both materials were immersed into a 1000 ppm Au solution and allowed to equilibrate for 1 hour. The dried carbons were then subject to the scanning electron microscopy (SEM) analysis. The SEM images of the commercial activated carbon at 2,000 and 10,000 magnifications were shown in figure 4.13(a) and 4.13(b) while those of the TBA-modified carbon were shown in figure 4.13(c) and 4.13(d) respectively. A uniform distribution of gold deposits was evidently noticed throughout the surface of the TBA-carbon while only negligible amount of gold was seen with the commercial carbon. The fact that gold was observed as solid Au(0) might have been the result of the auto-reduction of gold in which the mechanism is not yet clearly understood.
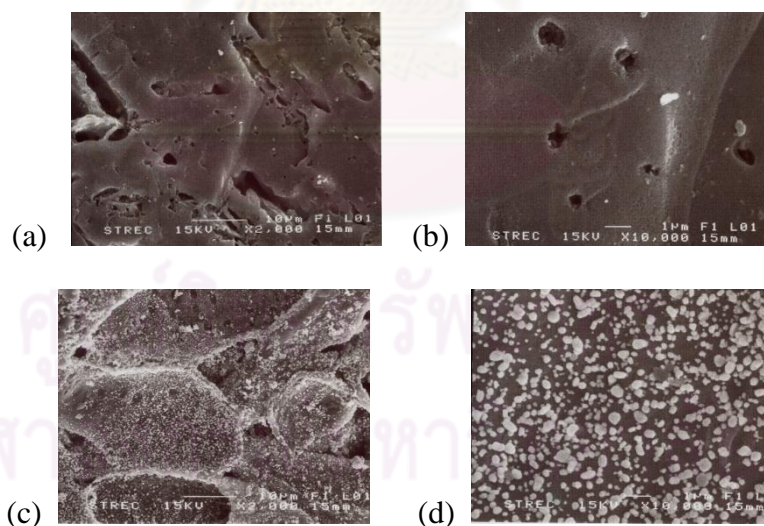

Figure 4.13 SEM images of the commercial activated carbon at 2,000x (a) and 10,000x (b) as well as the TBA-carbon at 2,000x (c) and 10,000x (d) following the immersion into 1,000 ppm Au(III) solution.

4.6   Gold recovery (Desorption study)

An excellent extraction of gold would be a worthless effort if the noble metal cannot be retrieved. Cyanide is the most commonly and satisfactorily used leachant in gold mining to recover the sorbed gold from the activated carbon, unfortunately, the reagent is extremely toxic and its use should thus be minimized or otherwise avoided. In this experiment, several other leachants were investigated for its potential in the recovery of gold from the TBA-carbon. Aqua regia, 1% and 5% ammonium thiosulfate and thiouria were chosen as leaching candidates to study the recovery of gold from the sorbed material. The effect of heating was also examined. The % Au recovery obtained under these conditions were summarized in Table 4.7.

Table 4.7 Summary of the gold recovery by various leachants

Leachant	Residual Au concentration (ppm)	Au $_{adsorbed}$ (mg)	Au $_{recovered}$ (mg)	Recovery (%)
Amonium thiosulfate 1%	33.79	0.97	0.34	34.78
Amonium thiosulfate 5%	65.38	0.97	0.65	67.65
Amonium thiosulfate 5%+heat	82.26	0.99	0.82	83.07
Thiourea 1%	59.63	0.98	0.60	60.59
Thiourea 5%	62.90	0.98	0.63	64.33
Thiourea 5%+heat	83.28	1.00	0.83	83.68
aqua regia 2hr	10.51	0.99	0.53	53.22
aqua regia 2hr+heat	11.49	0.99	0.57	57.85

1% ammonium thiosulfate and 1% thiourea exhibited a recovery of 34.78% and 60.59% respectively. The recovery was improved to 67.65% for ammonium thiosulfate and 64.33% for thiourea when higher concentration (5%) was employed. Under mild heating condition (60 ºC), the recovery was significantly elevated to over

83% for both substances. On the contrary, a somewhat unsatisfactory recovery was obtained with aqua regia (53.22%), even when the heating was provided (57.85%).

Explanations can be made on the capability of ammonium thiosulfate and thiourea as leachants for gold, assuming the 'Hard − Soft' acid base theory. For example $S_2O_3{}^{2-}$ which is used as a leachant, is a soft base, and is effective in acquiring the Au (soft acid) from the source rock. In an alkaline or near neutral solution of thiosulfate, gold dissolves slowly in the presence of a mild oxidant. The dissolution of the gold can be described as follows, where oxygen is an oxidant and thiosulfate is a ligand.[49]

$$4Au + 8S_2O_3{}^{2-} + O_2 + 2H_2O \rightleftharpoons 4[Au(S_2O_3)_2]^{3-} + 4OH^-$$
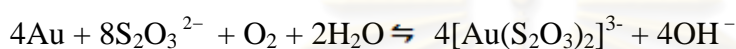
Two thiosulfate complexes of gold are known to form as $Au(S_2O_3)^-$ and $Au(S_2O_3)_2{}^{3-}$, in which the latter complex is known to be more stable.

In addition, Gold (I) can reportedly form a strong cationic complex with thiourea in an acidic solution [51] as shown by the following equation.

$$Au° + 2SC(NH_2)_2 \rightleftharpoons Au[SC(NH_2)_2]_2^+ + e$$
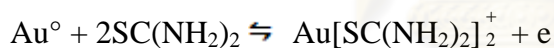
With over 80% of Au recovery as a starting point, we strongly believe that the complete recovery of gold can be accomplished with further improvement and/or optimization of the leaching agents and their methods in application. Unfortunately, that goal has not yet been succeeded due to the limitation of time.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1   Conclusion

The activated carbons were modified with various substances that conceivably have gold binding ability, namely Ammonium thiosulfate (ATS), Cetyltrimethyl ammonium bromide (CTA), N,N-dimethylformamide (NDF), Sodium dodecyl sulfate (SDS) and Tetrabutyl ammonium iodide (TBA), by impregnation technique. These modified carbons were evaluated for its gold extraction efficiency against the unmodified commercial activated carbon. The TBA-impregnated carbon demonstrated an exceptional extraction result and thus was adopted as a model modifying agent for subsequent studies. The effect of alkyl chain length (C_1-C_8) of the TBA analogs were assessed and it was reaffirmed that the best Au extraction was obtained with the TBA-carbon. The concentration of the modifying agent and the impregnation time for the preparation of the TBA-carbon were optimized at 1% (w/v) and 24 hours, respectively. Using this TBA-carbon, 50% extraction of gold was rapidly achieved within 10 minutes as compared to roughly 80 minutes for the commercial carbon and while a virtually complete extraction was achieved in less than an hour for the modified carbon, the same benchmark could not be accomplished even after 3 hours for the commercial counterpart. The interference study revealed that the base metals commonly found in gold wastes and gold pregnant solutions (eg. Cu, Zn, Fe, Ni, Rh and Pt) had absolutely no adverse effect to the gold extraction efficiency of the modified carbon. The adsorption isotherm was studied but no definitive correlation was found.

The modified carbon was applied to the column extraction method in which the flow rate was optimized at 1 mL/min. The remarkable improvement in Au extraction was again demonstrated by a breakthrough curve in which the column breakthrough capacity of the modified carbon was 90.62 mg/g whereas that of the commercial carbon was only 18.00 mg/g. The TBA-carbon was applied toward the recovery of gold from jewelry industrial waste sample with an extremely satisfactory

result in both batch and column extraction methods. The recovery of gold from this modified carbon was preliminarily studied using Aqua regia, Ammonium thiosulfate and Thiourea as leachants and promising results were obtained.

5.2 Suggestion for future work

The following issues could be of particular interests for future work:
- Selection of new and improved modifying agents and leachants
- Optimization of the leaching method
- Automation of the gold extraction system using the modified carbon

REFERENCES

[1] Miller, J. D.; Wan, R. Y.; Parga, J. R. Characterization and electrochemical analysis of gold cementation from alkaline cyanide solution by suspended zinc particles Hydrometallurgy 24 (1990): 373-392.

[2] Kenneth, N. Gold advances in precious metals recovery. Gordon and Breach, Science Publishers, Inc., Pennsylvania, USA, 1990.

[3] Johnson, B. F. G. The chemistry of gold. Recent advances in the coordination and organometalin field, Cambridge. 1-3

[4] Bandyopadhyay, M.; et al. Gold nano-particles stabilized in mesoporous MCM-48 as active CO-oxidation catalyst. Microporous and Mesoporous Materials 89 (2006): 158-163.

[5] Gold mining processes [Online]. Available from: http://www. e-goldprospecting .com/html/gold_plant_process_flow_sheet.html.[2010, January 2]

[6] The basic processes of gold recovery [Online]. Denver mineral engineers, Inc. Available from: http://www.denvermineral.com/basicp~1.html. [2010, January 4]

[7] Miller process [Online]. Wikimedia Foundation, Inc. Available from:. http://en.wikipedia.org/wiki/Miller_process [2010, March 4]

[8] Aqua Regia [Online]. 1999 Division of Chemical Education, Inc. Available from: http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA3/MAIN/AQREGIA/PAGE1.HTM. [2010, March 4]

[9] Leach gold by chlorination [Online]. Available from: http://www.e - goldprospecting.com/html/leach_gold_by_chlorination.html [2010, March 4]

[10] Gold Applications and Developments in the Electronics, Biomaterials and Catalysis [Online]. Azom. Available from: http://www.azom.com/Details.asp?ArticleID=1899 [2010, February 3]

[11] Leek, F. F. Did a dental profession exist in ancient Egypt. Society for the Advance of Anaesthesia in Dentistry 20 (1969): 18-21.

[12] Axthelm, W. H. Is the practice of dentistry in ancient Egypt an archaeological fact. Bulletin of the History of Dentistry 27 (1979): 71.

[13] Pastor, A. C.; Reinoso, F. R.; Marsh, H.; Martinez, M. A. Preparation of activated carbon cloths from viscous rayon. part I. carbonization procedures. Carbon 37 (1999): 1275-1283.

[14] Mohan, D.; Pittman Jr., C. U. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. Journal of Hazardous Materials B137 (2006): 762-811.

[15] Ng, C.; Marshall, W. E.; Rao, R. M.; Bansode, R. R.; Losso, N. L. Activated carbon from pecan shell: process description and economic analysis. Industrial Crops and Products 17 (2003): 209-217.

[16] Jankowska, H.; Swiatkowski, A. Active Carbon. Journal of Chromatography A 537 (1991): 167-180.

[17] Rodriguez-Reinoso, R. F.; Solano, A. L. Microporous structure of activated carbons as revealed by adsorption methods. Chemistry and Physics of Carbon 12 (1989).

[18] Sastri, V. A.; Aspila, K. I.; and Chakrabarti, C. L. Studies on the solvent extraction of metal dithiocarbamates. Canadian Journal of Chemistry 47 (1969):2320-2323.

[19] Yin, C. Y.; Aroua, M. K.; Duad, W. M. A. W. Impregnation of palm shell activated carbon with polyethyleneimine and its effects on Cd^{2+} adsorption. Colloids and Surfaces 307 (2007): 128-136.

[20] Perrich, J. R. Activated carbon adsorption for wastewater treatment. CRC Press (1981)

[21] Yin, C. Y.; Aroua, M. K.; Duad, W. M. A. W. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Separation and Purification Technology 52 (2007): 403-415.

[22] Wu, S. N.; Chen, P. J. Modification of a commercial activated carbon for metal adsorption by several approaches. Proceeding of the 2001 International Containment & Remediation Technology Conference and Exhibition, 10-13 June, Orlando, Florida

[23] Barton, S. S.; Evans, E.; Halliop, E.; MacDonald, J. A. F. Acidic and Basic sites on the surface of porous carbon. Carbon 35 (1997): 1361-1366.

[24] Aggarwal, D.; Goyal, M.; Bansal, R. C. Adsorption of chromium by activated carbon from aqueous solution. Carbon 37 (1999): 1898-1997.

[25] Park, S. J.; Jang, Y. S. Pore structure and surface properties of chemically modified activated carbon for adsorption mechanism and rate of Cr(VI). Journal of Colloid and Interface Science 249 (2002): 458-463.

[26] Chiang, H. L.; Huang, C. P.; Chiang, P. C. The surface characteristics of activated carbons as affected by ozone and alkaline treatment. Chemosphere 47 (2002): 257-265.

[27] Chen, W.; Cannon, F. S.; Rangel-Mendez, J. R. Ammonia-tailoring of GAC to enhance perchlorate removal, I : characterization of NH3 thermally tailored GACs. Carbon 43 (2005): 573-580.

[28] Adhoum, N.; Monser, L. Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater. Separation and Purification Technology 38 (2004): 233-239.

[29] Henning, K. D.; Schafer, S. Impregnated activated carbon for environmental protection. http://www.activated-carbon.com/enviro.html (1998)

[30] Torregrosa-Macia, R.; Martin-Martinez, J. M.; Mittelmeijer-Hazeleger, M. C. Porous texture of activated carbons modified with carbohydrates. Carbon 35 (1997): 447-453.

[31] Attia, A. A.; Rashman, W. E.; Khedr, S. A. Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment. Dyes Pigment 69 (2006): 128-136.

[32] Seke, M. D.; Sandenbergh, R. F.; Vegter, N. M. Effects of the textural and surface properties of activated carbon on the adsorption of gold di-cyanide. Minerals Engineering 13 (2000): 527-540.

[33] Abu-Salah, K.; Shelef, G.; Levanon, D.; Armon, R.; Dosoretz, C. G. Microbial degradation of aromatic and polyaromatic toxic compounds adsorbed on powdered activated carbon. Journal of Biotechnology 51 (1996): 265-272.

[34] Walker, G. M.; Weatherley, L. R. Biological activated carbon treatment of industrial wastewater in stirred tank reactors. Chemical Engineering Journal 75 (1999): 201-206.

[35] Stewart, M. H.; Woffe, R. L.; Means, E. G. Assessment of the bacteriology activity associated with granular activated carbon treatment of drinking water. Applied and Environment Microbiology 56 (1990): 3822-3829.

[36] Rivera-Utrilla, J.; Bautista-Toledo, I.; Ferro-Garcia, M. A.; Moreno-Castilla, C. Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. Journal of Chemical Technology and Biotechnology 76 (2001): 1209-1215.

[37] Ravodic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla, J. Carbon materials as adsorbents in aqueous solutions. Chemistry and Physics of Carbon 27 (2000): 227-405.

[38] Camel, V. Solid phase extraction of trace elements. Spectrochimica Acta Part B 58 (2003):1177-1233.

[39] Filho, N. L. D.; Gushikem. Y.; Polito. W. L.; Moreira, J. C.; and Ehirim, E. O. Sorption and preconcentration of metal ions in ethanol solution with a silica gel surface chemically modified with benzimidazole. Talanta 42 (1995): 1625-1630.

[40] Zhaoa, N; Weia, N.; Li , J.; Qiao , Z.; Cui , J.; He, F. Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI). Chemical Engineering Journal 115 (2005): 133-138.

[41] Gomez-Serrano, V.; Macias-Garcia, A.; Espinosa-Mansilla, A.; Valenzuela-Calahorro, C. Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon. Water Research 32 (1998): 1-4.

[42] Daorattanachai, P.; Unob, F.; Imyim A. Multi-element preconcentration of heavy metal ions from aqueoussolution by APDC impregnated activated carbon. Talanta 67 (2005): 59-64.

[43] Aworn, A.; Thiravetyan, P.; Nakbanpote, W. Recovery of gold from gold slag by wood shaving fly ash. Journal of Colloid and Interface Science 287 (2005): 394-400.

[44] Narita, H.; Tanaka, M.; Morisaku, K.; Abe, T. Extraction of gold(III) in hydrochloric acid solution using monoamide compounds. Hydrometallurgy 81 (2006): 153-158.

[45] Ubaldini, S.; Fornari, P.; Massidda, R.; Abbruzzese, C. An innovative thiourea gold leaching process.Hydrometallurgy 48 (1998): 113-124.

[46] Monser, L.; Adhoum, N. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. <u>Separation and Purification Technology</u> 26 (2002): 137-146.

[47] Yang, X.; Huang, K.; Wei, Q.; Huang, Z.; Chen, J.; Wu, J. Stripping of Au(I) from a Loaded Cetyltrimethylammonium Bromide/Tributyl Phosphate Organic Solution: Conversion and Reduction. <u>Solvent Extraction and Ion Exchange</u> 26 (2008): 556-569.

[48] Navarro, P.; Vargas, C.; Alonso, M.; Alguaci, FJ. The Adsorption of Gold on Activated Carbon from Thiosulfate-Ammoniacal Solutions. <u>GoldBulletin</u> 39/3 (2006): 93-97.

[49] Tagashira, S.; Kimoto, S.; Nosaki, K.; Murakami, Y. Surfactant Gel Extraction of Gold(III), Palladium(II), Platinum(II), and Lead(II) as Thiourea-complexes. <u>ANALYTICAL SCIENCES</u> 25 (2009): 723-726.

[50] Zhou, Q.; Zhang, C.; Fei, L.; Sun, J.; Qu, Y. The determination of dynamic adsorption curve, adsorption capacity and breakthrough capacity of powdered activated carbon for perfluorooctanoicAcid elimination from Water. [Online]. Available from: http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=05163588 [2010, March 9]

[51] Aylmore, M.G.; Muir, D.M. Thiosulfate Lenaching of Gold-A Review. <u>Minerals Engineering</u> 14 (2001): 135-174.

VITA

Mr. Jakraphan Suwanvijit was born on April 25, 1978 in Suphanburi, Thailand. He received a Bachelor's degree of Science in Industrial Chemistry from Rajamachala Industrial of technology in 2001. Subsequently, he has been a graduate student at the Department of Chemistry, Chulalongkorn University and a member of Environmental Analysis Research Unit (EARU). He finished his postgraduate study with a Master's degree of Science in Chemistry in 2010. His present address is 129/278 Mahasawat Road, Mahasawat, Bangkruay, Nontaburi, Thailand, 10330. Contact number is 081-4580360. Email: sjakraphan@git.or.th.