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DEVELOPMENT OF ACTIVATED CARBON FROM
COFFEE RESIDUE FOR GOLD EXTRACTION

Mr Werayuth Juewatanasirikul

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

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 COFFEE RESIDUE FOR GOLD EXTRACTION
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ทำการเตรียมถ่านกัมมันต์จากกากกาแฟโดยเผาที่สภาวะบรรยากาศและการกระตุ้นด้วยซิงค์คลอไรด์ ตรวจหาลักษณะทางกายภาพของถ่านกัมมันต์ที่เตรียมได้ พบว่ามีพื้นที่ผิว 355 ตารางเมตรต่อกรัมและความกว้างของรูพรุน 1.9 นาโนเมตร ปรับปรุงคุณภาพถ่านกัมมันต์ที่เตรียมได้โดยใช้เทคนิค impregnation ด้วย ammonium thiosulfate (ATS) ศึกษาปัจจัยที่มีผลต่อการดัดแปรผิวและการสกัดทองในสารละลายทั้งในระบบแบทช์และคอลัมน์ ศึกษา adsorption isotherm ของถ่านดังกล่าว พบว่า การดูดซับที่เกิดขึ้นเป็นแบบ Langmuir มีความสามารถในการดูดซับทองได้สูงถึง 129.27 มิลลิกรัมต่อกรัม มีความเฉพาะเจาะจงกับทองในสถานะที่มีตัวรบกวนต่างๆซึ่งพบมากในน้ำเสียจากอุตสาหกรรมเครื่องประดับ นอกจากนี้ยังได้ออกแบบจำลองระบบคอลัมน์ขนาดใหญ่โดยใช้ตัวดูดซับเป็นถ่านกัมมันต์ที่ผ่านการปรับปรุงคุณภาพดังกล่าว พบว่าสามารถนำไปใช้ในการสกัดแยกทองออกจากน้ำทิ้งจากโรงงานอุตสาหกรรมเครื่องประดับได้อย่างมีประสิทธิภาพ (>90%) อีกด้วย

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....
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The activated carbon was prepared from the disposed coffee residue by atmospheric pyrolysis and activated with zinc chloride. The obtained activated carbon was characterized by surface area analysis and found to have the surface area and the pore diameter of $355 \text{ m}^2 \cdot \text{g}^{-1}$ and 1.9 nm respectively. These activated carbons were subsequently modified by impregnation with ammonium thiosulfate (ATS). Various parameters were optimized around the preparation and utilization of this modified carbon for gold extraction in both batch and column methods. The maximum sorption capacity of gold derived from Langmuir adsorption isotherm was approximately $129.27 \text{ mg} \cdot \text{g}^{-1}$. The adsorption of gold by the modified sorbent was relatively free from interference ions commonly found in gold jewelry waste. The sorbent was subsequently packed into a larger scale column and used for the extraction of gold from real jewelry wastes and successful recoveries of gold (>90%) were achieved.

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LIST OF ABBREVIATIONS

AC	Activated carbon
CRAC	Activated carbon prepared from coffee residue
ATS	Ammonium thiosulfate
BET	Brunauer, Emmett and Teller method
AC _{com}	Commercial activated carbon
°C	Degree celsius
D.I.	Deionized water
FAAS	Flame atomic absorption spectroscopy
FT-IR	Fourier transforms infrared spectroscopy
g	Grams
hr	Hours
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
LLE	Liquid liquid extraction
mg.L ⁻¹	Milligrams per litre
mL	Millilitres
µm	Microns
min	Minutes
ppm	Part per million
%	Percent
rpm	Revolutions per minute
SEM	Scanning electron microscope
SPE	Solid phase extraction
TGA	Thermal gravimetric analysis
w/v	Weight by volume
XRD	X-ray diffractometry

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Gold is a precious metal that has long been recognized. Besides its role as monetary reserves, gold is widely used in various industries such as raw materials in jewelry industry and components in electronic equipment, because metallic gold also possess excellent electrical and conductivity properties. Due to the considerable increase in the demand of gold for technological and industrial advances, its natural resource is rapidly depleted. For this reason, special attention should be given to the recovery of this precious metal from every possible resource, especially in wastes from jewelry and electronic industries.

A great deal of waste was generated from the manufacturing and processing of jewelry and electronic industries, which consist of gold-containing sludge and gold solution. Typically, techniques such as precipitation and electrolysis are used to purify the valuable metal from these wastes. Both methods are quite complex and incomplete. Adsorption technique is an interesting choice for the gold recovery because of its simplicity and suitability for high-volume samples. In mining process, the gold bearing cyanide solution was contacted with a sorbent, commonly the activated carbon [1] and later on stripped out by appropriate leachant for further purification.

Activated carbon is a carbonaceous material with extremely high surface area and micro-porous structure, hence it has been established as a decent adsorbent in a wide range of applications. A variety of carbon-rich materials can be transformed into an activated carbon via carbonization and activation processes. By far most commercialized activated carbon have been prepared from coconut shell. Recently, the attention has been focused on the use of carbonaceous agricultural solid wastes such as rice husk [2], almond shell [3] and hulls [4] to produce activated carbons.

Nowadays, coffee is the most popular beverages consumed worldwide. As a result, coffee residues generated from its production have become a great concern in the management and disposal. Turning these seemingly useless materials into a valuable activated carbon would be worthy in terms of waste management. A previous work [5] reported the use of activated carbon prepared from coffee residue for the adsorption of heavy metals. Although the results were quite satisfactory, no attempt has ever been made on using the activated carbon from such material for gold extraction.

Some of the problems associated with the use of activated carbon for the gold extraction are its slow adsorption kinetics, non-selectivity, and limited sorption capacity. These results in an incomplete extraction and unintentional loss of the precious element. Therefore, in this work, we aim to improve the efficiency of gold extraction in solution by using a low cost activated carbon derived from the coffee residues. The activated carbons prepared were surface-modified with ammonium thiosulfate in order to enhance its gold adsorption efficiency.

1.2 Scope of the research

The scope of this research was firstly a production and characterization of the activated carbon from coffee residues. The prepared carbon was then modified with ammonium thiosulfate with the modifying conditions optimized and assessed by means of gold extraction efficiency through batch method. Thereafter, the adsorption isotherm and interferences of the ATS-modified carbon were studied. The column extraction was then adopted with the effects of flow rate and breakthrough curve studied. A more industrial-like cylinder column was later on used to evaluate the gold extraction efficiency of high volume sample. Finally, the developed sorbent along with the column method was applied to extract gold from real jewelry industrial wastes.

1.3 The benefit of this research

Turning disposal waste in coffee residues into a valuable adsorbent with remarkable improvement in the extraction of gold.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Gold

2.1.1 Properties of gold

Pure gold has a bright yellow color and luster traditionally considered attractive, which it maintains without oxidizing in air or water. Gold is a noble metal that is generally found in nature as metallic gold and gold compounds, both of which are very useful in many aspects. Metallic gold also has high electrical and conductivity properties that lead to widespread uses in various industries. A list of some key physical properties of gold is shown in Table 2.1.

Table 2.1 Physical properties of gold

Physical properties	
atomic number	79
molar atomic weight	196.966 g.mol ⁻¹
melting point	1064°C
boiling point	2808°C
density	19.32 g.cm ⁻³
electronegativity	2.4

Gold is a soft and ductile metal. It is known that gold can occur in one of the six oxidation states from -1 to +5. The typical forms of gold ions are aurous (Au¹⁺) and auric (Au³⁺). The coordination number of aurous ion is 2, and the formation of this ion is a linear. For auric ion, the common coordination number is 4 and a square

planar geometry are usually found [6]. Gold is attacked by aqua regia which consists of nitric acid and hydrochloric acid resulting in chloroauric acid (HAuCl_4). In addition gold can also form complex with cyanide in an alkaline solution. In water, aurous and auric can form complexes such as $\text{Au}(\text{H}_2\text{O})_2^+$ and $\text{Au}(\text{H}_2\text{O})_4^{3+}$, respectively. In chloride media, the distributions of gold species as a function of pH are as depicted in Figure 2.1.

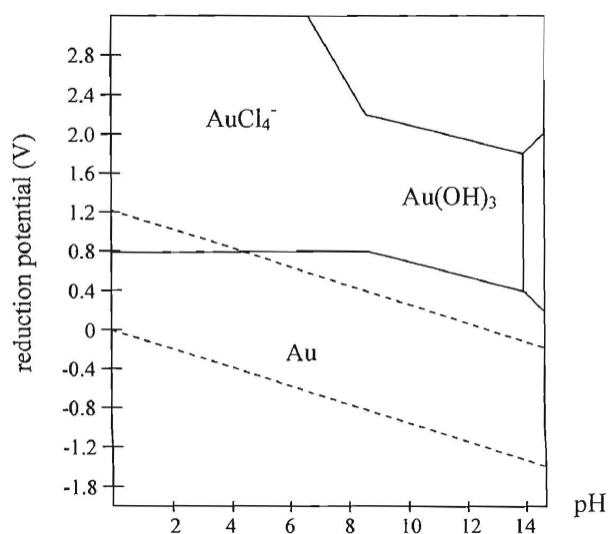


Figure 2.1 Diagram of the Au-H₂O-chloride ion system at 25°C when $[\text{Au}^{3+}] = 0.01 \text{ mol L}^{-1}$ and $[\text{Cl}^-] = 2.0 \text{ mol L}^{-1}$ [7]

2.1.2 Applications

Gold is currently used in a growing number of several applications. The demand and supply dynamics of the gold market in 2009 can be ranked in the descending order of jewellery 51%, investment 18%, official sector 17%, industries 12% and unaccounted for 2% [8]. The major gold applications are in the jewelry [9] and the electronic industries [10].

2.1.2.1 Jewelry

Gold jewelry has existed for thousands of years. In fact, the precious element used to create such items has been valued by humans since before recorded history. With limited technology in the earlier times, the jewelry was hard to produce and most of the treasured-skills were required to work the metal into desirable designs. Nowadays, the technological advances in gemology are readily available which make the manufacturing of gold jewelry more accessible and affordable.

Because of the softness of pure gold (24k), it is usually alloyed with base metals for jewelry making, 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 such as silver and palladium in the alloy. Copper is the most commonly used base metal, yielding a reddish 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. While blue and purple gold can be made by respectively alloying with iron and aluminum, it is rarely done except in specialized jewelry. Blue gold is more breakable and difficult to work with, when it is in the process of making jewelry. Fourteen and eighteen carat gold alloys with silver alone appear greenish-yellow and are referred to green gold. Furthermore, 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 and thus its release from the white gold jewelry is restricted 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 either pure silver or sterling silver.

2.1.2.2 Electronics

Gold is the material of choice in many electronic applications, especially in telecommunication, information technology and other high performance and safety critical applications. The utilization of gold is commonly seen in the circuit board of

virtually all mobile phones and computers worldwide. As a result of the growth of these sectors, the consumption of gold in electronics is critically increasing. During 2007, it was estimated that around 280 tons of gold found its way into electronics and electrical components.

The beneficial properties of gold include outstanding resistance to corrosion, the ease with which it can be worked and high thermal and electrical conductivity. Only silver and copper are better conductors of electricity, but they do not have comparable resistance to tarnishing or corrosion. Under conditions that most other metals either tarnish or corrode away, gold remains inert and extremely durable. So where resistance to tarnish or corrosion is essential, it is therefore common to either use gold or a gold alloy, or to plate gold onto a less noble metal. For electronic applications, the resistance of gold to environmental effects is perhaps the most important property. It means that the technical performance of gold bonding wires or gold electroplating essentially remain unaltered with time.

2.1.3 Gold recovery

According to the gold investment worldwide, the demand for gold has shown an enormous increasing trend recently. The increase is not only to the jewelry market, but also to the increased uses of gold in electronic industry, as well as mobile phone circuit [10]. Recovery of gold from waste is more attractive than that for most other metals, therefore, the recycling of gold from scraps and the leaching of gold residue were studied with appreciate methods [11].

2.1.3.1 Precipitation

Precipitation processes are universal techniques to treat metal-contaminated wastewater. It is a simple method for the removal of several metals; however, these processes have some limitations and problems. For example, a maximum metal removal is limited by the metal solubility and the optimal pH for precipitation that may vary for different metals. Even though the targeted metals can be satisfactorily removed, a significant amount of waste from the chemical reagents used and the

residue sludge were unavoidably generated. In a classic gold precipitation [1], the copperas, which is an ancient name for ferrous sulphate was added in solution for reducing a gold chloride to solid gold. The reason for using copperas is that it is a less aggressive reducer and thereby leaves the platinum in a chemical state easily changed to an insoluble condition. Utilizing the sulfur dioxide and the sulfite are likely to reduce the platinum compound to later soluble state.

2.1.3.2 Electrolysis

Electrolysis processes are among the favorite methods utilized to recover valuable metal ions from solution. Very high purity gold can be produced by the electrolytic treatment of gold in a hydrochloric acid solution. When a voltage is applied, the electrons of gold and other metals are reduced at the anode. The metallic gold deposits itself on the surface of the pure gold cathode. This method is somewhat costly and a relatively high concentration of gold is required. [1,12]. Typically, the gold slag from jewelry industry is extracted by a cyanidation process and refined by electro-winning process, a method based on electrolysis, to recover and purify of gold. Based on previous studies, the residual gold-cyanide solution from processes could not be refined at low concentration (1-4 mg/L) [13].

2.1.3.3 Adsorption

In the adsorption process [14], analytes in gaseous or liquid form diffuse to the exposed surface of a solid, where they were bound to the adsorbent or held there by weak intermolecular forces. There is an appreciable enhancement in the concentration of a particular component. Moreover, the overall effect is dependent on the extent of the interfacial area. From this reason, adsorbents should have a large specific surface area and highly porous nature or consist of very fine particles. Gold is fairly selectively sorbed on a carbon sorbent, thus, this method can be applied to extract and recover the precious metal. The adsorption of auro-cyanide complexes onto activated carbon is a well-established process, as well as more recently adsorption by ion-exchange resins that has been used [15-16].

2.2 Activated carbon

Activated carbon is a carbonaceous material of appreciable specific surface area, extending from at least $300 \text{ m}^2\text{g}^{-1}$ to well above $2000 \text{ m}^2\text{g}^{-1}$ for industrial adsorbents [17]. It is an amorphous material consisting of a large number of pores. Channels and pores with diameters less than 2 nm are commonly known as micropores. These micropores practically enclose a great portion of the external-carbon area. On the other hand, pores with diameters between 2 and 50 nm are identified as mesopores and pores with diameters higher than 50 nm are defined as macropores. The factors that lead to adsorptive properties of the activated carbon include surface area, a micro-porous structure, and a high degree of surface reactivity [18]. Hence, it has been established as a decent adsorbent for the treatment of industrial effluents.

The starting materials and the activation method used for the production of activated carbon determine its surface functional groups. A variety of carbon-rich materials can be transformed into an activated carbon by a process that consists of two basic stages: the carbonization of precursor by pyrolysis and the activation. Generally, coconut shell is the most common raw material used in the manufacturing of activated carbon. Recently, the attention has been focused on utilizing other carbonaceous agricultural solid wastes to prepare the activated carbons [19-21].

2.2.1 Preparation of activated carbon

Almost any carbonaceous raw materials can be used for manufacturing activated carbon, though the properties of the final product will be different, depending upon the nature of the raw material used, the nature of the activating agent, and the conditions of the activation process. Figure 2.2 illustrated common steps involved in the preparation of activated carbon.

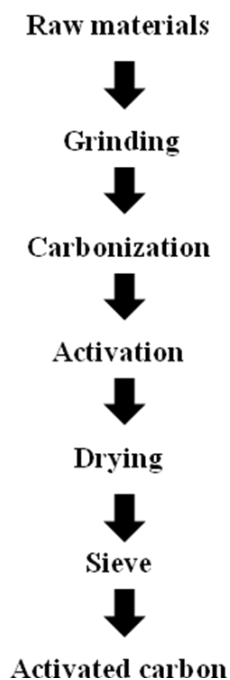


Figure 2.2 Schematic representation of the preparation of activated carbon

2.2.1.1 Carbonization

The raw materials are firstly subject to carbonization, in which the materials are pyrolyzed at temperature $<700^{\circ}\text{C}$, resulting in the loss of water, carbon dioxide and a wide range of organic molecules e.g. alcohols, ketone, acids [14]. Carbonization results in a progressive increase of the C/H and C/O ratio, and bonding of the remaining heteroatoms and aromatic macromolecules onto the carbon-surface.

2.2.1.2 Activation

The activation processes of charcoal are used to improve the accessibility of the pore structure as well as to increase a pore width and a pore volume. This process can be classified into two types; physical activation and chemical activation, [14, 20]. During the activation process, the spaces between the elementary crystallites are increased by the elimination of other compounds of the carbonaceous materials. The resulting channels through the graphite regions, the spaces between the elementary

crystallites, together with cracks within and parallel to the graphite planes constitute the porous structure with a large surface area [22].

2.2.1.2.1 physical activation

The precursor can be physically transformed into activated carbons by using gases. This method is generally done by a combination of the following processes [20]. Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600-900 °C, in the absence of air (commonly in inert atmosphere with gases like argon or nitrogen). Activation/Oxidation: Raw material or carbonized 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 [23-24].

2.2.1.2.2 Chemical activation

The precursor material is impregnated with appropriated chemicals that improved inner character of the activated carbon. The raw material is carbonized at lower temperatures (450-600°C) and then soaked with common activated reagent i.e. an acid, strong base or a salt (phosphoric acid, potassium or sodium hydroxide and zinc chloride, respectively) [25]. It is noticed that the carbonization and activation steps simultaneously proceed with this chemical reagent. The chemical activation has some problems in observed cases, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating material.

2.2.2 Modification of activated carbon

In general, carbon adsorption is not nearly effective at removing metals and inorganic pollutants as it is in removing organic compounds. This finding is attributed to the relatively non-polar surface characteristics, which inhibits attraction between charged metal species and its surface. In addition, one critical drawback of carbon is less adsorption selectivity [26]. Thus, the modification of AC has been studied for the

purpose of enhancing its selectivity for the targeted metal species. Modifications of activated carbon can be categorized into two types, namely physical modification and chemical modification.

2.2.2.1 Physical modification

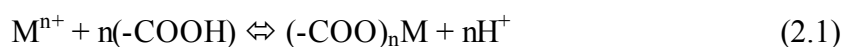
The physically modified activated carbon can be changes in its physical characteristics. The process is aimed to improve its physical characteristics such as BET surface area and pore volume which in turn should enhance the removal efficiency of target species, especially in the case of organic adsorptions [27]. These improved physical characteristics can be achieved with, for example, the thermal treatment. A disadvantage of thermal treatment of sorbent is the oxygen surface functional groups, which are thermally unstable and can be destroyed at high temperature [28]. It can be argued that heat-treated carbon is generally favorable for enhancing adsorption of organic compounds from aqueous solution, since basic characteristics of the activated carbon is amplified at such condition.

2.2.2.2 Chemical modification

The activated carbon surface can display acidic, basic and/or neutral characteristics, depending on the presence of surface functional groups [29]. It has been widely reported that chemical species can be adsorbed by AC via surface complex formation between the chemical species and the surface functional groups of the carbon. The functional surface such as carbonyl group can be created via two major oxidation methods, including dry and wet methods. The dry oxidation involves the reactions with gas phase, such as CO_2 at high temperature ($> 700^\circ\text{C}$), while the wet oxidation is based on the reactions between carbon surfaces and oxidizing solutions such as HNO_3 , H_2O_2 , NaOCl [30]. The chemical modification can be classified into 3 types that include acidic treatment, basic treatment and impregnation method.

2.2.2.2.1 Acidic treatment

The acidic treatment is intended to increase their acidic surface functional groups [31]. These specific functional groups such as carboxyl, carbonyl, lactone, hydroxyl and carboxylic anhydride 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 of complexes as following equation;



The reaction above is caused by cation exchange mechanism where the metal cation exchanges site with the hydrogen ion previously attached as a whole of carboxylic group. In general, acidic reactions with carbon have been associated with oxide structures. The conventional treatments using oxidizing agents in carrier medium can reduce the surface area of activated carbon.

2.2.2.2.2 Basic treatment

The basic treatment is beneficial in enhancing uptake of organic-based substances from aqueous solution but it may decrease the uptake of metal ions. There were studies achieved to determine the effect of basic treatment of AC on metal adsorption capacity. The adsorption of Cr(VI) was reduced by using NaOH treated activated carbon [32]. This reduction is due to the decrease of specific surface area or micropore volume. Under basic condition, it is expected that OH⁻ ion will react with immersed surface functional groups. 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 [33].

2.2.2.2.3 Impregnation method

The impregnation with appropriate chemicals is generally recognized that it can be strongly supported by greater adsorption capacity of activated carbon to

remove hazardous substances [34]. The three main specifications for impregnating carbons are to optimize the existing properties 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 carbon as inert porous carrier. The immobilized carbon is particularly significant, as impregnated materials can be distributed on the large internal surface area, making them accessible to incoming reactants. In many applications, the impregnating materials are present in the form of hydroxides, carbonates, chromates or nitrates, which the carbon impregnated are subjected to thermal after treatment at elevated temperature (150-200°C) to decompose the anions.

2.2.3 Application

Activated carbon is used in several applications such as water purification, metal extraction, gold adsorption, sewage treatment, gas purification, air filters in gas masks, filters in compressed air, medicine and other applications [35]. The conventional carbon has been established in water filtration. People using other forms of filtration for household requirements are presently switching over to activated carbon induced filtration for drinking water as well as for washing purposes, all harmful and toxic chemicals from the water and makes the water safe for drinking purposes. At the same time, such minerals are still retained in the water, which are essential for the body. Moreover, the use of activated carbon in the metal finishing field is a major industrial application. It is very widely employed for purification of electroplating solutions.

2.3 Sorption

Sorption is defined as being the attraction of an aqueous species to the surface of a solid [14] as a partitioning phase that occurs when analytic component passed into the bulk of the extracting phase and are retained. In the explainable term, the sorbing species are called the sorbate and the solid media, in which the sorbate is attracted are known as the sorbent. For the interfacial term, adsorption is a mass

transfer at interfacial layer that can generally be defined as the accumulation of materials at the interface between two phases. Absorption results from stronger interactive forces than that of adsorption. Adsorption and/or absorption processes are sometimes difficult to distinguish experimentally and often occurs simultaneously.

Carbon surface has an uncommon character. It has a porous structure, which determines its adsorption capacity and has a chemical structure, influencing its bonding on both polar and nonpolar sorbates. There is a previous confirmation of two types of the adsorption sites on activated carbons; Graphite-like basal planes that enable adsorption through van der Waals forces especially in π -electron interaction, as well as polar groups like carbonyl, hydroxyl and carboxyl that may interact via ionic interaction of hydrogen bonding [14]. As a consequence, the adsorption behavior of an activated carbon cannot be interpreted on the background of surface area, but it is prepared by either the different methods or given different activation treatments showing markedly different adsorption properties [25]. The determination of a correct model for adsorption on activated carbon adsorbents with complex chemical structure is a complicated problem. A proper model must take into consideration both the chemical and the porous structure of the carbon, which includes the nature and concentration of the surface chemical groups, the polarity of the surface, the surface area, and the pore size distribution. Furthermore, the physical and chemical characteristics of the sorbents were considered as its chemical structure, polarity, and molecular dimensions. In the case of adsorption from solutions, the concentration of the solution and its pH are also important additional factors.

2.3.1 Solid phase extraction (SPE)

Although liquid-liquid extraction (LLE) has long been recognized as an extraction method, it has many drawbacks, such as using the organic solvent for the extraction, high cost for waste disposal, long extraction time and the formation of emulsion during the extraction [36]. Solid phase extraction (SPE) is an alternative method that can overcome those problems with the enhanced advantages, achieving high recoveries along with possible elevated enrichment factors. Moreover, it can be

easily automated and afford a broader range of applications than LLE due to the large choice of solid sorbents.

The SPE technique always consists of three to four successive steps [37], as demonstrated in Figure 2.3. The first step is washing or conditioning with an appropriate solvent that is applied to condition the solid sorbent and to remove the basic impurities on the sorbent surface or the packing material. In the second step, referred to as loading, the sample is adsorbed onto the sorbent with the suitable sample flow-rate. During this step, the analytes are retained on the sorbent surface. The third step is washing, in which the sorbent is optionally washed by a proper solvent. The appropriate solvent should have lower elution strength and can eliminate matrix components on the surface of sorbent while having no effect on the analytes retained. If desired, the analytes in the adsorbent can then be optionally subject to further recovery and/or purification.

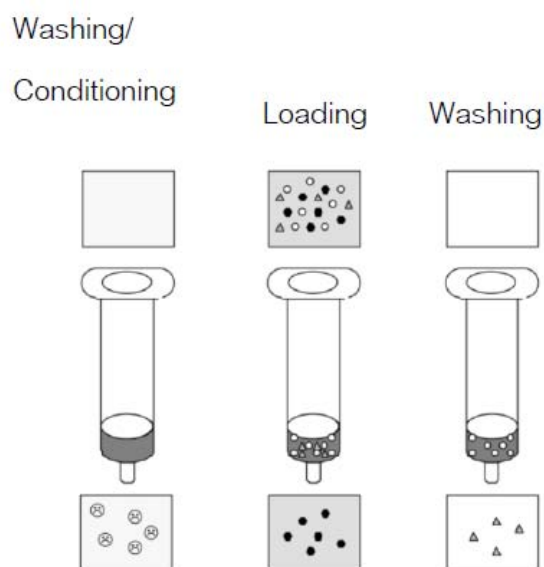


Figure 2.3 Common SPE procedures

2.3.2 Adsorption isotherm

The analysis and design of sorption process requires the purposed equilibrium sorption, which is the most determining information in understanding the sorption process. The different parameters and the essential thermodynamic assumption of these equilibrium models often provide some insight for the sorption mechanism, the surface properties, and the affinity of sorbent [38]. An expression of this type is termed an adsorption isotherm. The widely accepted adsorption isotherms utilized in the adsorption processes are the Langmuir isotherm and the Freundlich isotherm [39].

2.3.2.1 Langmuir adsorption isotherm

Langmuir isotherm is based on the monolayer sorption of determined species on the surface of sorbent and is used to describe the adsorption behavior of analytes on the sorbent. The Langmuir isotherm is represented by the following equation:

$$\frac{C}{N_f} = \frac{1}{bN_f^{S_f}} + \frac{C}{N_f^{S_f}} \quad (2.2)$$

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

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

$N_f^{S_f}$ = the maximum sorption capacity of the sorbent (mol.g^{-1})

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

By plotting C/N_f versus C (illustrated in Figure 2.4), the linearity of model and the slope of $1/N_f^{S_f}$ are obtained.

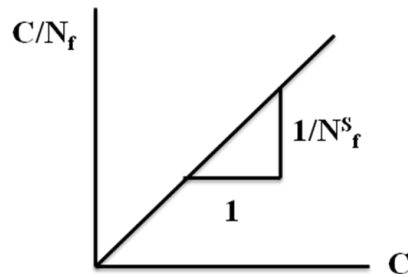


Figure 2.4 Langmuir adsorption isotherm

2.3.2.2 Freundlich adsorption isotherm

Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption that is expressed by the following equation:

$$\log N_f = \log K_f + \frac{1}{n} \log C_e \quad (2.3)$$

where N_f = the amount of solute adsorbed per unit weight of sorbent (mg.g^{-1})

C_e = the saturation concentration of solute in the solution (mg.L^{-1})

K_f and n = the constant and $n > 1$

By plotting $\log N_f$ versus $\log C_e$ (presented in Figure 2.5), it gives a linear with a slope of $1/n$ and the intercept that is equal to the value of $\log K_f$. The intercept is an indicator of adsorption capacity and the slope, $1/n$, of adsorption intensity.

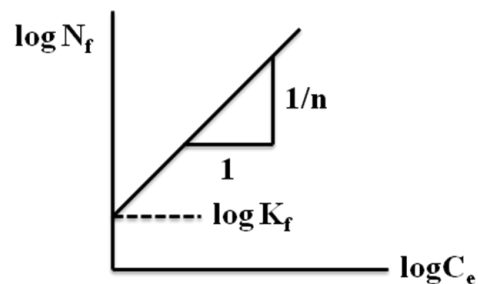


Figure 2.5 Freundlich adsorption isotherm

2.4 Analytical techniques

There are various analytical techniques that are employed in this research as detailed below.

2.4.1 Flame atomic absorption spectroscopy (FAAS)

Flame atomic absorption spectroscopy (FAAS) is one of the common techniques, which is utilized to quantitatively determine the elemental composition of samples. A continuous feed of sample solution is aspirated, mixed in an aerosol by combustible gases, i.e. acetylene gas and air, and then ignited in a flame with atomized temperature ranging from 1500 to 3000°C [40]. During combustion, metal atom in the sample is reduced to the atomic state and a light beam from a hollow cathode lamp of analyte is working through the flame into a monochromator and detector, respectively. A block diagram of atomic absorption spectrometer is shown in Figure 2.6.

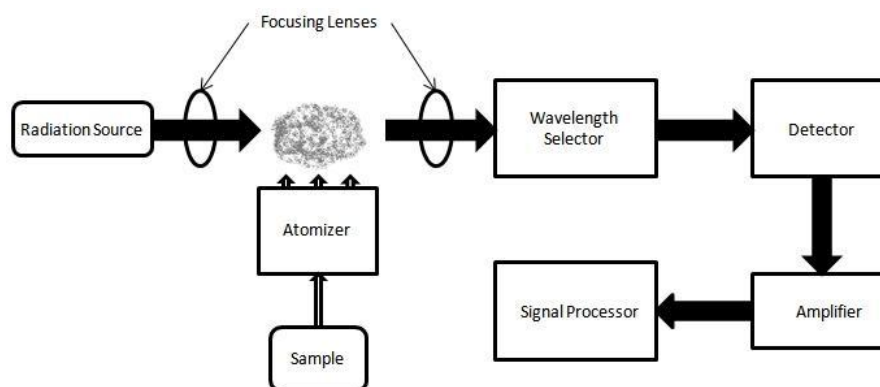


Figure 2.6 Schematic diagram of an atomic absorption spectrometer



Figure 2.7 Flame atomic absorption spectrometer, AAnalyst100, Perkin Elmer

2.4.2 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is a specific technique, which is used to perform qualitative and quantitative multi-elemental analysis. The technique is based on the measurement of emission from excited atoms or ions in a hot plasma. Typically, the gas temperature in the axial channel of the plasma can be as high as 7000 to 8,000 K [40]. The solution sample is nebulized into this hot plasma, which combustion leads to nearly complete solute vaporization, atomization/ionization, and eventually excitation. The excited atoms or ions are unstable and emit radiation of characteristic wavelength. This emitted radiation is then focused on a spectrometer where the light is dispersed and detected as illustrated in Figure 2.8

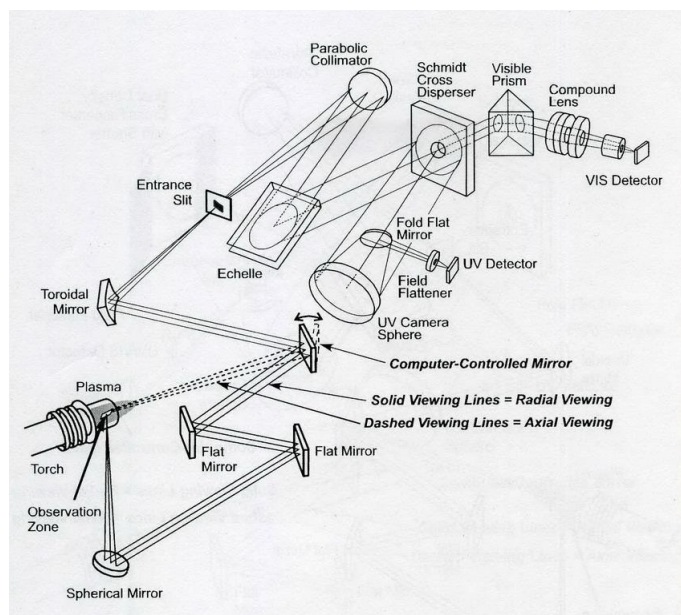


Figure 2.8 Schematic indication of ICP-OES instrument

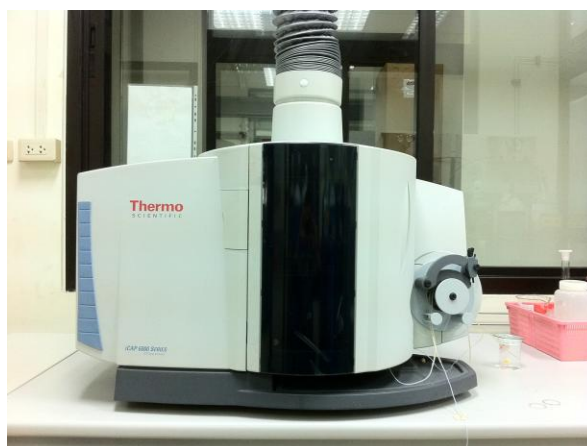


Figure 2.9 Inductively coupled plasma optical emission spectrometer, iCAP 6500, Thermo Scientific

2.4.3 Surface area analysis (BET)

The physical properties of carbon-sorbent such as total surface area (S_{BET}), the total porous volume (V_{tot}), and the average pore diameter (D_p) are determined by using BET method. The structural carbon-heterogeneity of materials are characterized

by N₂ adsorption-desorption isotherms measurements at 77 K. In this research, the determination of physical characterization between the prepared and the typical commercial activated carbons were investigated.

2.4.4 Fourier transforms infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy is a common technique for identifying the types of chemical bonds and functionalities in a molecule by producing an infrared absorption spectrum. Each chemical functional group has the individual vibration frequency in the infrared absorption spectrum [40]. Moreover, the vibration of bond can take place due to the interaction of infrared radiation with a sample molecule. The chemical functionality surface of the activated carbon prepared from coffee residues and the ATS-modified carbons were identified in the infrared spectral in the range of 4000 to 400 cm⁻¹.

2.4.5 Scanning electron microscope (SEM)

Scanning electron microscope [41] has unique capabilities for the determination of surface and morphology of the materials. This technique uses electrons for imaging, much as a light microscope uses visible light. The advantages of SEM include much higher magnification (>100,000X) and greater depth of field up to 100 times. The reflecting of light of microscope is served to create the required image, whereas the SEM controls the focused electrons for image formation. Also, the surface structures of the prepared activated carbon before and after the gold extraction were characterized using SEM.

2.4.6 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis [42] is a simple analytical technique for measuring a changed weight as loss or gain mass of a material as a function of temperature. Heated materials can lose weight from a simple process, such as drying, or from chemical reactions that release gases while some materials can gain weight by

reacting with the atmosphere. In this study, it is employed to study the thermal decomposition of the modifying reagent, ammonium thiosulfate, to confirm of its impregnation into the activated carbon.

2.4.7 X-ray diffractometry (XRD)

X-ray diffractometry is one of the non-destructive analytical techniques, which provide information regarding the crystallographic structure, chemical composition, and physical properties of analyzed materials. When the X-ray beam strikes a surface of crystalline sample at an angle, a portion of the radiation is scattered by the layer of atoms on the surface. The effect of scattering from the regularly spaced centers of the crystal is a diffraction of the beam. Furthermore, it reveals a suitable characteristic of the sample. The composition and possible speciation of gold on the extracted sorbent can be verified by this technique.

2.5 Literature review

2.5.1 Activated carbon from coffee residues

Activated carbon is a material that is widely used as adsorbent in many applications. This sorbent is produced from carbonaceous materials. Generally, attention is focused on the use of carbonaceous agricultural solid wastes as it resolves the problems of managing and disposing into the environment. Coffee residues are lignocellulosic and renewable low-cost materials that can be successfully converted to activated carbon.

Boonamnuayvitaya et al. [5] studied the preparation and utilization of adsorbent made from coffee residues binding with clay at a weight ratio of 80:20. Following the pyrolysis at 500°C for 2 hours, the resulting sorbent was shaped into cylindrical granules of 10 mm in length and 4 mm in diameter and then used to remove heavy metals in the solution of various pH (8-10) and temperature (30-80°C). The adsorption capacities of the coffee residues binding with clay derived from the

Langmuir isotherm model were found to be 39.5, 31.2, 19.5, 13.4 and 11.0 mg.g⁻¹ for Cd²⁺, Cu²⁺, Pb²⁺, Zn²⁺ and Ni²⁺, respectively.

Boonamnuayvitaya et al. [43] evaluated various activating agents such as zinc chloride, nitrogen, carbon dioxide and steam to produce a coffee sorbent for the adsorption of formaldehyde. The coffee activated carbon that was prepared with ZnCl₂ impregnation (3:1 ratio of ZnCl₂ to coffee residue), dehydration (110°C for 12 hours) and pyrolysis (600°C for 4 hours) under nitrogen activation demonstrates its highest capacity of formaldehyde adsorption owing to the hydrophilic functional groups of O-H, C=O, C-O on the surface. The total surface area and pore volume of prepared activated carbon were 470 m².g⁻¹ and 0.454 cm³.g⁻¹ respectively.

Boudrahem et al. [38] studied the influence of impregnation ratio (ZnCl₂/coffee residue) as well as the physical and chemical properties of the prepared carbons in order to optimize parameters for the removal of lead in batch sorption. The coffee residues were mixed with zinc chloride at a weight ratio of 1:1 at 85°C for 7 hours and then carbonized at 600°C under nitrogen flow for 1 hour. The total surface area and pore volume obtained are 890 m².g⁻¹ and 0.772 cm³.g⁻¹ respectively. Also, the maximum uptake of lead (II) at 25°C about 63 mg.g⁻¹ of optimized adsorbent at pH 5.8.

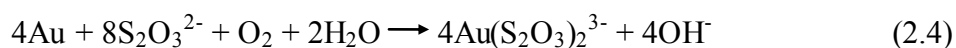
Khenniche and Aissani [44] studied the preparation of activated carbons from coffee residue by chemical activation, mainly ZnCl₂, varying ZnCl₂ from 0 to 100 % at 85°C for 7 hours. The activated sorbent was heated in an oven at 110°C for 24 hours and then nitrogen-pyrolyzed at 600°C for 1 hour. It was shown that the adsorption of salicylic acid is most effective with the activated carbon prepared with 25 % of ZnCl₂ (about 29.03 mg.g⁻¹).

2.5.2 Modification of activated carbon and its applications

The weaknesses associated with using activated carbon for the extraction of gold are its slow adsorption kinetics, non-selectivity, and limited sorption capacity, which consequently results in an incomplete extraction and unintentional loss of the

precious metal. Thus, the modified carbon has been studied in order to enhance the selectivity of targeted species.

Zhang and Dreisinger [45] studied the recovery of gold and copper from ammonium thiosulfate (ATS) solution by using anion-exchange resins in batch method. The adsorption of gold on resin followed a Freundlich isotherm. In the presence of ammonia and copper in the solution, the elution of gold from resins can be readily eluted by thiosulfate at alkaline pHs to form a gold–thiosulfate complex as shown.



The high-elution (over 70 %) of gold and copper from resins has been preliminarily studied with an eluent solution of 2 M Na_2SO_3 and 1 M NH_3 .

Navarro et al. [46] studied the adsorption of gold on commercial activated carbon in ammoniacal thiosulfate solution. The study showed that the rate of initial adsorption was fast, when it was compared to that of the overall adsorption process. Increasing ammonium hydroxide concentration results in a decrease in activity and diffusivity of gold ion, leading to a decrease in gold adsorption.

In terms of the modification of activated carbon, Monser et al. [47] studied the activated carbon impregnated with Tetrabutyl ammonium iodide (TBAI) to extract CN^- from solution and obtain the improved sorption capacity. It was concluded that the strong affinity of TBAI toward CN^- was attributed to the ion pairing effect between the ammonium ion and the cyanide ion.

In this work, we aim to improve the efficiency of gold extraction in solution by using low-cost activated carbon produced from coffee residues. The activated carbon prepared from coffee residues was surface-modified with ammonium thiosulfate in order to enhance its gold adsorption efficiency.

CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

Table 3.1 Instruments list

Instruments	Model, Manufacturer
Flame atomic absorption spectrometer	AAAnalyst 100, Perkin Elmer
Inductively coupled plasma optical emission spectrometer	iCAP 6500, Thermo Scientific
Surface area analyzer	Belsorp-mini
Fourier transforms infrared spectrometer	NICOLET 6700, Thermo Scientific
Scanning electron microscope	JSM-5800LV, JEOL
Thermal gravimetric analyzer	Pyris 1 TGA, Perkin Elmer
X-ray diffractometer	Ultima+, Rigaku
Furnace	NABERTHERM
Balance	SI-234, DENVER
Multi-position hotplate stirrer	KIKA-WERKE
pH meter	Ultrabasic, DENVER
Peristaltic pump	ISM827B, ISMATEC
Vacuum pump	Vacubrand
Oven	Memmert

3.2 Chemicals

Table 3.2 Chemicals list

Chemicals	Supplier
Ammonium thiosulfate	MERCK
Zinc chloride	CARLO ERBA
Gold standard solution	SCP SCIENCE
Copper standard solution	MERCK
Iron standard solution	SCP SCIENCE
Nickel standard solution	SCP SCIENCE
Platinum standard solution	SCP SCIENCE
Rhodium standard solution	ACROS
Zinc standard solution	MERCK
Hydrochloric acid	MERCK
Nitric acid	MERCK
Coconut shell activated carbon	T.M.D.Co.,LTD

3.3 Preparation and modification of adsorbent

3.3.1 Preparation of activated carbon

Coffee residue, the raw material for the production of activated carbon in this work, was obtained from K.V.N. import export (1991), Inc. The coffee residue was washed with water several times and then dried in an oven at 90°C until dryness. The dried residue was atmospherically pyrolyzed at 300°C for 1 hour. The pyrolyzed carbon was then activated by zinc chloride at the weight ratio of 1:2 at room temperature for 24 hours and pyrolyzed again at 600°C for 1 hour to transform into activated carbons. The obtained carbon was treated with 10% HCl to remove any residual salts followed by washing with hot distilled water to displace the acidity of

the carbons and chlorides. The resulting carbon was dried in an oven at 90°C for 12 hours. Finally, the activated carbon was sieved through a sieve No.35 and No.50 to obtain particle size in the range of 300-500 μm and kept in a desiccator until further use.

3.3.2 Modification of activated carbon

The activated carbon prepared from coffee residue was surface-modified with ammonium thiosulfate in order to enhance its gold adsorption efficiency. The prepared activated carbon was impregnated with 50 mL of 1% (w/v) aqueous solution of ammonium thiosulfate. Approximately 0.20 g of carbon was immersed and stirred (~ 60 rpm) in the ATS solution at room temperature for defined durations. The impregnated carbons were then filtered, dried at 60°C for 4 hours and kept in a desiccator until further use.

3.4 Characterization of activated carbon

3.4.1 Surface area analysis

The structures of the activated carbon obtained from the coffee residue and comparative commercial activated carbon were characterized by nitrogen adsorption and desorption isotherms measured at 77 K using a Belsorp-mini analyzer to determine the specific surface area (S_{BET}), the total pore volumes (V_{tot}) and the average pore diameter (D_p).

3.4.2 Fourier transforms infrared spectroscopy

The functional groups on the surface of the original coffee residue and the resulting activated carbons with varying concentration of impregnated ammonium thiosulfate were determined by FTIR analysis. Infrared spectra were recorded from 400 to 4000 cm^{-1} in attenuated total reflectance mode.

3.4.3 Sulfur content analysis

The amounts of sulfur retained on the modified activated carbons were determined to assess the impregnation efficiency of ammonium thiosulfate. Approximately 0.15 g of the modified carbon was digested with 5 mL conc. HNO₃. The mixture was heated and sonicated for 15 minutes, filtered and then centrifuged at 3000 rpm for 10 minutes. Finally, the solution was decanted, made up with D.I. H₂O and analyzed for sulfur content by inductively coupled plasma optical emission spectrometer (ICP-OES).

3.5 Batch extraction

3.5.1 Gold extraction efficacy of the ATS-modified activated carbon

To compare the efficiency of the raw material (coffee residue), the activated carbon prepared from coffee residue, the ATS-modified carbon impregnated with 1% ammonium thiosulfate, and a typical commercial activated carbon for the extraction of gold, these materials were subjected to the following study. Each adsorbent was weighted nearest to 0.020 g, mixed in 50 mL standard solution of 20 ppm Au and the mixture was then stirred (~ 60 rpm) at room temperature. The samplings of the solution for gold determination were carried out at the intervals of 5, 10, 20, 30, 60 and 120 minutes, in which the stirrer was temporarily stopped and 5 mL of the solution was withdrawn and filtered to remove any suspended carbon. The gold concentrations in the solution before and after the extraction at each interval were determined by FAAS. All experiments were performed in triplicate (n=3). From the obtained results, the efficiency of gold extraction was calculated on the basis of the following equation.

$$\% \text{ Gold extraction} = ((C_i - C_f) / C_i) \times 100 \quad (3.1)$$

Where C_i is the initial gold concentration (ppm)
 C_f is the residual gold concentration at each sampling time (ppm)

3.5.2 Effect of impregnation time

This experiment aims to evaluate the impregnation time of ammonium thiosulfate onto the surface of activated carbon. Approximately 0.20 g of carbon was impregnated with 50 mL of 1.0% (w/v) aqueous solution of ammonium thiosulfate. The mixture was stirred (~ 60 rpm) at room temperature for 1, 2, 4, 8 and 12 hours, respectively. The impregnated carbons were then filtered, dried at 60°C for 4 hours and kept in a desiccator until further use.

For comparison, the effectiveness of the modified carbons was determined by the gold extraction efficiency through batch extraction. The adsorbent was weighted closest to 0.020 g, mixed in 50 mL diluted solution of 20 ppm Au and stirred (~ 60 rpm) at room temperature. The samplings of the solution were taken at the intervals of 5, 10, 20, 30, 60, and 120 minutes for the gold content determination. The gold concentrations in the solution before and after each extraction period were determined by FAAS. Finally, the measuring changes in gold solution were applied to calculate the gold extraction efficiency according to equation (3.1).

3.5.3 Effect of impregnation temperature

The impregnation temperature of the modifying reagent was typically actuated to enhance the ability of impregnating method. This experiment was also carried out to investigate such effect at a relatively higher temperature. A portion of approximately 0.20 g of carbon was impregnated with 50 mL of 1.0% (w/v) aqueous solution of ammonium thiosulfate. The mixture was stirred (~ 60 rpm) at 70°C for 1, 2, 4, 8 and 12 hours, respectively. The impregnated carbons were then filtered, dried at 60°C for 4 hours and kept in a desiccator until further use.

The ATS-modified activated carbon was weighted nearest to 0.020 g, mixed in 50 mL standard solution of 20 ppm Au and stirred (~ 60 rpm) at room temperature. The samplings of the solution for gold determination were carried out at the intervals of 5, 10, 20, 30, 60 and 120 minutes. The gold concentrations in the solution before and after the extraction were determined by FAAS. Also, the measuring changes in

gold solution were applied to calculate the gold extraction efficiency as in previous sections.

3.5.4 Effect of concentration of the impregnating reagent

In this experiment, the effect of ammonium thiosulfate concentration was studied so as to determine the optimum loading for the impregnation of activated carbon. The variable amounts of modifying reagent were used to impregnate on the surface of the prepared activated carbons. Approximately 0.20 g of carbon was each impregnated with 50 mL of 0.1, 0.5, 1.0 and 5.0% (w/v) aqueous solution of ammonium thiosulfate, respectively. The mixtures were then stirred (~ 60 rpm) at room temperature for 8 hours. The impregnated carbons were filtered off, dried at 60°C for 4 hours and kept in a desiccator until further use.

The activated carbon with varying load of ATS was each weighted nearest to 0.020 g, mixed in 50 mL standard solution of 20 ppm Au and stirred (~ 60 rpm) at room temperature for 60 minutes. The gold concentrations in the solution before and after the extraction were determined by FAAS. The gold extraction efficiency of each system was calculated similarly to the previous section.

3.5.5 Adsorption isotherm

Under the optimum condition for gold extraction, the ATS-modified activated carbon was used to study the adsorption phenomena of gold on the surface of carbon by means of the adsorption isotherm. Approximately 0.020 g of the ATS-modified activated carbon, prepared under optimum condition, was suspended in 50 mL of gold solution with variable concentrations between 20 and 70 ppm. The suspensions were stirred (~ 60 rpm) at a controlled temperature (298 K) for 60 minutes to ensure of the adsorption equilibrium. The residual gold concentrations in each solution were then determined by FAAS and the adsorption isotherm analysis was executed.

3.5.6 Interference study

In the practical applications, not only gold but other metal ions such as Cu, Fe, Ni, Pt, Rh and Zn can be commonly found in jewelry industry wastes. Therefore, the influence of these potential interfering metal ions on the ATS-modified carbon was studied. Roughly 0.020 g of the activated carbons impregnated with ATS was soaked in 50 mL of a solution containing 20 ppm Au and mixed metal ions (Cu, Fe, Ni, Pt, Rh and Zn) of which the concentration were 20 and 100 ppm. The mixtures were stirred (~ 60 rpm) at room temperature for 60 minutes. The initial and residual concentrations of gold along with all interfering metal ions in the solutions were determined by ICP-OES. Likewise, the extraction efficiency of these metals were calculated in accordance with equation (3.1).

3.6 Column extraction

The column method is a typical technique that is applied to extract target metals from industrial wastes. The waste feed is continuously flown through a column packed with appropriate adsorbent. Two types of columns were fabricated in this experiment, i.e. mini-column and cylinder column, as shown in figure 3.1(A) and 3.1(B). Both columns were employed to investigate the gold extraction performance of the developed sorbent.

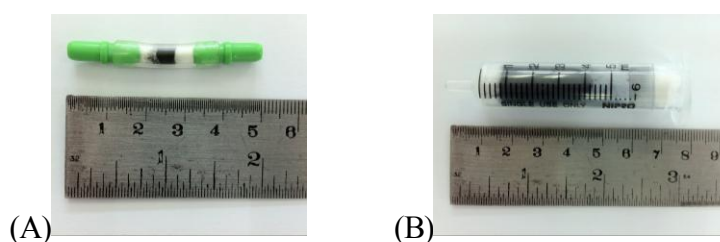


Figure 3.1 Photograph of (A) the mini-column and (B) the cylinder column

3.6.1 Effect of flow rate

A homemade mini-column (2.8 cm length and 6.0 mm i.d. Tygon tubing) was packed with 0.020 g of the ATS-modified carbon, prepared under the optimal conditions from the previous studies. Cotton balls were placed at both ends of the column to prevent the loss of sorbent. One end of the column was connected to a peristaltic pump while the other was placed in a collecting beaker. The actual flow rates of the solution passing through column were pre-calibrated with deionize water. Thereafter, 20 mL of 20 ppm Au solution was passed through the column with controlled flow rate of 1.0, 3.0, 5.0, 7.0 and 10.0 mL.min⁻¹. The filtrate was collected and analyzed for the residual gold concentration by FAAS.

3.6.2 Breakthrough curve

To determine the sorption capacity of this method, the gold extraction efficiency of the ATS-modified carbon and the commercial activated carbon were compared. The mini-column loaded with 0.020 g ATS-modified carbon was prepared as described in the previous section. The flow rate was controlled at 1.0 mL.min⁻¹. Twenty millilitres of 20 ppm Au solution was passed through this column. The residual gold concentration of the solution was determined by FAAS. Additional increments of 20 mL Au solution were then successively passed through until the column was completely exhausted. For a direct comparison, the same procedures were repeated with the commercial activated carbon.

3.6.3 Cylinder column

In order to demonstrate its potential application for real industrial wastes, a cylinder column was fabricated to handle higher volume and flow rate. A syringe piston was packed with approximately 1.0 g of the ATS-modified CRAC and blocked at both end with cottons. The column was aligned vertically while the solution was continuously pumped upward by means of a vacuum pump connected at the lower end of the column. With the operation of this pump, the apparent flow rate of roughly

$50 \text{ mL}\cdot\text{min}^{-1}$ was estimated with the circulation of deionized water. A synthetic waste solution of 10 ppm Au was passed through the column in portions of 100 mL each for a total of 1000 mL. The residual gold concentrations of each portion were determined by FAAS.

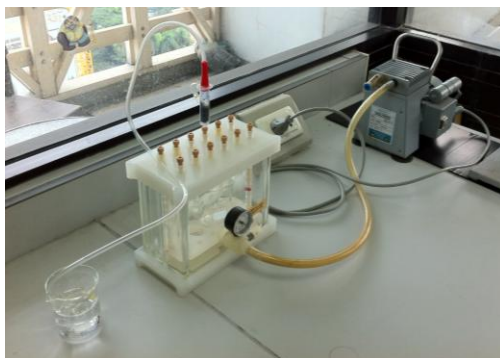


Figure 3.2 Photograph of instrumental cylinder column

3.7 Gold extraction from jewelry industry wastes

A genuine industrial waste in this work was provided by Brilliance Jewelry Company. The wastes obtained are comprised of aqueous waste from the factory water treatment (waste A) and organic waste (waste B). Both of these wastes contain solid wastes which were filtered to sludge A and B. These sludges were digested with 10 mL of aqua regia at 50°C for 30 minutes. Consequently, 5 mL of obtained solution was filtered and made up with deionized water. The first 1000 mL of filtered waste A, 500 mL of digested sludge A and B solution were consecutively passed through this cylinder column. The gold concentrations in the solution before and after the extraction were determined by FAAS.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation and modification of activated carbon

The discarded coffee residues used in this experiment are displayed as dark-brown solids in Figure 4.1 (A). After undergoing the pyrolysis and activating processes, these materials were transformed into activated carbon. The resulting carbon was then sieved to obtain the granular activated carbon with particle size in the range of 300-500 μm which appears as a black char as shown in Figure 4.1 (B). To increase its gold-binding efficiency, the obtained carbon was impregnated with 1% (w/v) aqueous solution of ammonium thiosulfate. The ATS-modified activated carbon is shown in Figure 4.1 (C).

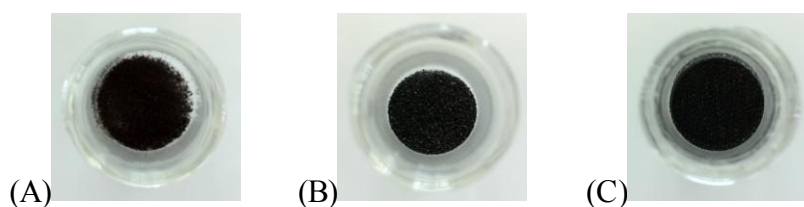


Figure 4.1 Appearance of (A) coffee residues, (B) the activated carbon produced from the coffee residue and (C) the ATS-modified activated carbon

4.2 Characterization of activated carbon

4.2.1 Surface area analysis

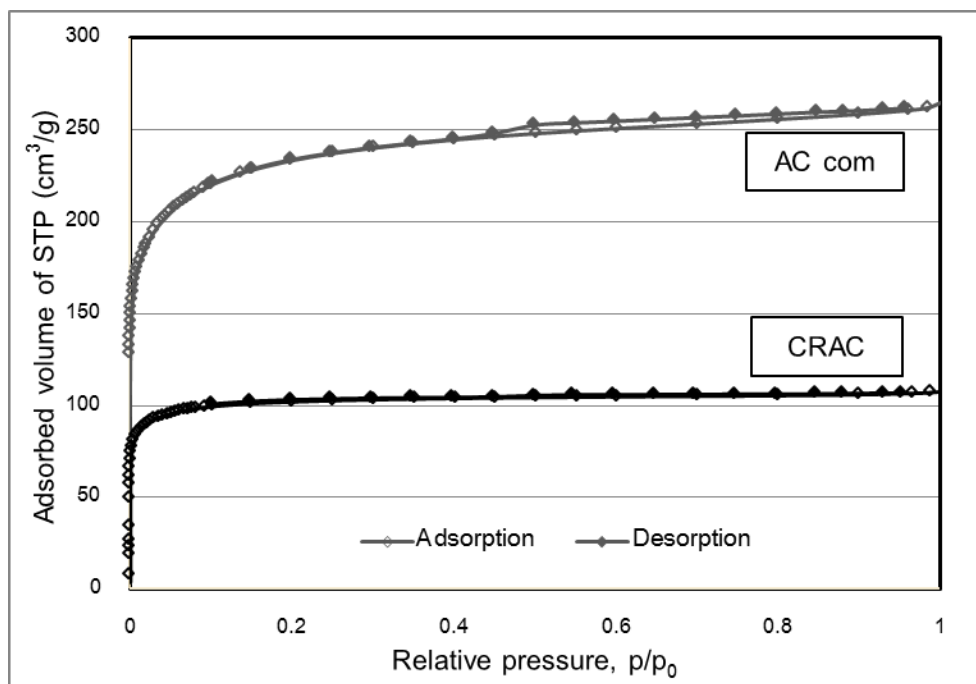


Figure 4.2 Adsorption and desorption isotherms of N_2 for CRAC and AC_{com}

The N_2 adsorption–desorption isotherms of the commercial activated carbon (AC_{com}) and the activated carbon prepared from coffee residue (CRAC) are shown in Figure 4.2. The amount of N_2 adsorbed was plotted against the relative pressure, P/P_0 of N_2 , where P is the vapor pressure and P_0 is the over-filled vapor pressure. It is observed that the N_2 isotherms of both types of carbon exhibited type I isotherms, which are typical for micro-porous solids. The values corresponding to the physical characteristics such as total surface area (S_{BET}), the total porous volume (V_{tot}), and the average pore diameter (D_p), resulted from the N_2 adsorption-desorption isotherms of the commercial activated carbon and the activated carbon obtained from coffee residue are summarized in the Table 4.1. It is noticed that the total surface area and the total porous volume of the commercial activated carbon are higher than those of the coffee residue carbon, while its pore diameter is smaller. Typical commercial

activated carbons are prepared from coconut shell and fabricated with more complex activation processes such as controlled atmosphere pyrolysis, therefore resulting in the activated carbon with higher surface area and total porous volume.

Table 4.1 Surface characteristics of carbons determined from N₂ adsorption-desorption isotherms at 77 K

Carbon	S _{BET} (m ² .g ⁻¹)	V _{tot} (cm ³ .g ⁻¹)	D _p (nm)
CRAC	354.77	0.166	1.87
AC com	825.54	0.407	1.97

4.2.2 Fourier transforms infrared spectroscopy

The FT-IR spectrum in ATR mode of the original CR carbon and the ATS-modified activated carbons are illustrated in Figure 4.3. The C=C and C≡C stretching, which are characteristic peaks of the carbon material from coffee residue [42], were clearly observed around 1550 and 2170 cm⁻¹ for all types of carbon. For the ATS-modified activated carbons, a weak S=O stretching was additionally observed at approximately 1040 cm⁻¹, increasing proportionally with the ammonium thiosulfate concentration. These results preliminarily confirmed the successful impregnation of ammonium thiosulfate onto the modified activated carbon. This finding was further supported by the result from thermal gravimetric analysis in which a significant mass loss was observed at 150°C, presumably due to the decomposition of ammonium thiosulfate.

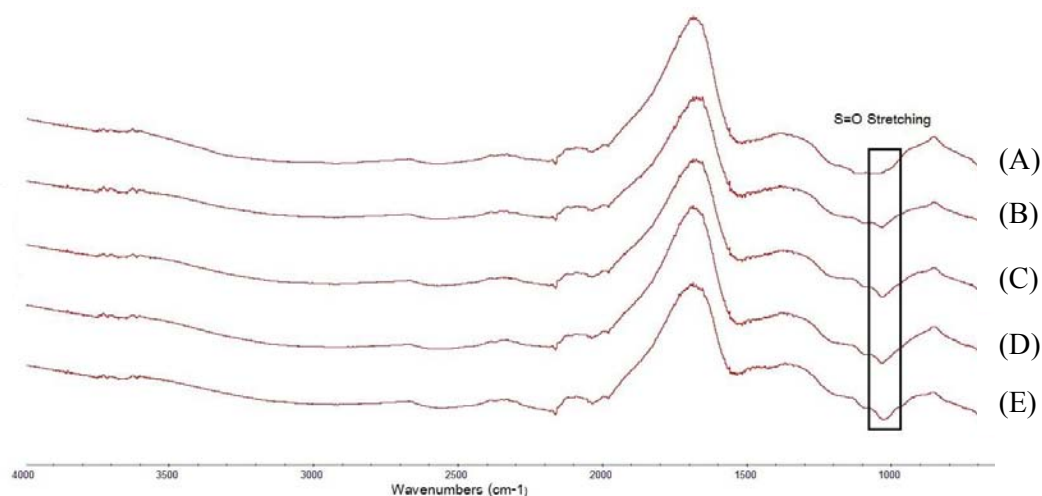


Figure 4.3 FT-IR spectra of (A) CRAC,(B) CRAC+0.1%ATS,(C) CRAC+0.5%ATS, (D) CRAC+1.0%ATS and (E) CRAC+5.0%ATS

4.2.3 Sulfur content analysis

To further investigate the impregnation efficiency of ammonium thiosulfate into the carbon, the amount of sulfur in the ATS-modified AC were determined. The prepared carbons were digested with conc. HNO_3 and analyzed for sulfur by ICP-OES. The amounts of sulfur were determined for each of the various ATS loading of the activated carbons as reported in Table 4.2. It can be seen that increasing ATS-loading on the activated carbons result in higher sulfur content, consequently confirming the deposition of ammonium thiosulfate on the carbon. A seemingly constant amount of sulfur ($\sim 0.8\text{-}1.0 \text{ mg.g}^{-1}$) on the carbons was obtained when the ATS concentration was above 0.5% (w/v), probably limited by the surface area of the coffee residue carbon.

Table 4.2 Sulfur content in the modified activated carbons

Carbon	Sulfur content (mg.g ⁻¹)
CRAC	0.09 ± 0.04
CRAC+0.1%ATS	0.65 ± 0.08
CRAC+0.5%ATS	0.90 ± 0.14
CRAC+1.0%ATS	0.84 ± 0.14
CRAC+5.0%ATS	1.03 ± 0.15

4.3 Batch extraction

4.3.1 Gold extraction efficacy of the ATS-modified activated carbon

The gold extraction efficiency of the coffee residue (CR), the activated carbon obtained from this material (CRAC), the carbon impregnated with 1% ammonium thiosulfate for 1 hour (ATS-modified CRAC) and the commercial activated carbon (AC_{com}) were evaluated. The extraction of 20 ppm Au solution was performed with each material and the samplings taken at 5, 10, 20, 30, 60 and 120 minutes were subjected to the determination of residual gold concentration by FAAS. The gold extraction efficiency as demonstrated by % gold extraction, of the tested materials are displayed in Figure 4.4.

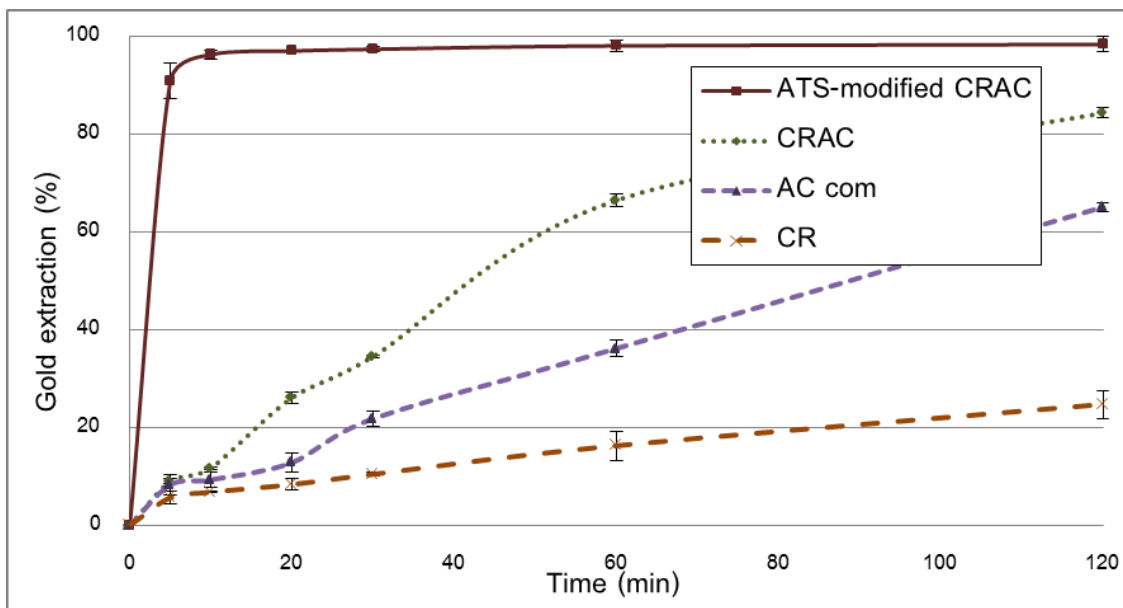


Figure 4.4 Gold extraction profiles of all carbons

A general weakness of utilizing activated carbon as adsorbent in the gold extraction process is related with its slow adsorption, non-selectivity and time consuming process. This problem may have been overcome by the modification of activated carbon. This potential improvement was clearly demonstrated in Figure 4.4. At all extraction periods, the gold extraction efficiency of the carbons can be ranked in the ascending order of CR, AC_{com}, CRAC and ATS-modified carbon. It can readily be seen that the overall improvement of gold extraction was established for the carbon modified with ATS. Although the typical commercial activated carbon has larger surface area and total pore volume, the ATS-modified CRAC proved to be a much better gold adsorbent. Ammonium thiosulfate is known to be a good complexing agent for gold ($\log K_f=28$) [48]. Impregnating the carbon surface with this reagent would definitely create more active sites with gold binding affinity and enhance its gold extraction efficiency as is evidenced by the above results.

4.3.2 Effect of impregnation time

The effect of impregnation time as a parameter influencing the extraction efficiency of gold was investigated. The activated carbon was impregnated with 1.0%

(w/v) aqueous solution of ammonium thiosulfate at room temperature for 1, 2, 4, 8 and 12 hours, respectively. The extraction efficiency of gold by the modified carbons were evaluated through batch extraction of 20 ppm Au solution at room temperature. The remaining concentrations of gold in the solutions after various extraction times are presented in Table 4.3.

Table 4.3 The residual gold concentration at each extraction time by various impregnation times

Time(min)	Impregnation time				
	1hr	2hrs	4hrs	8hrs	12hrs
	Residual gold concentration (ppm)				
5	17.63	18.57	16.93	1.87	1.30
10	16.29	17.15	14.84	0.77	0.74
20	13.31	14.64	12.74	0.61	0.55
30	10.78	11.69	9.34	0.54	0.54
60	3.18	1.27	1.53	0.40	0.41
120	0.52	0.47	0.48	0.34	0.32

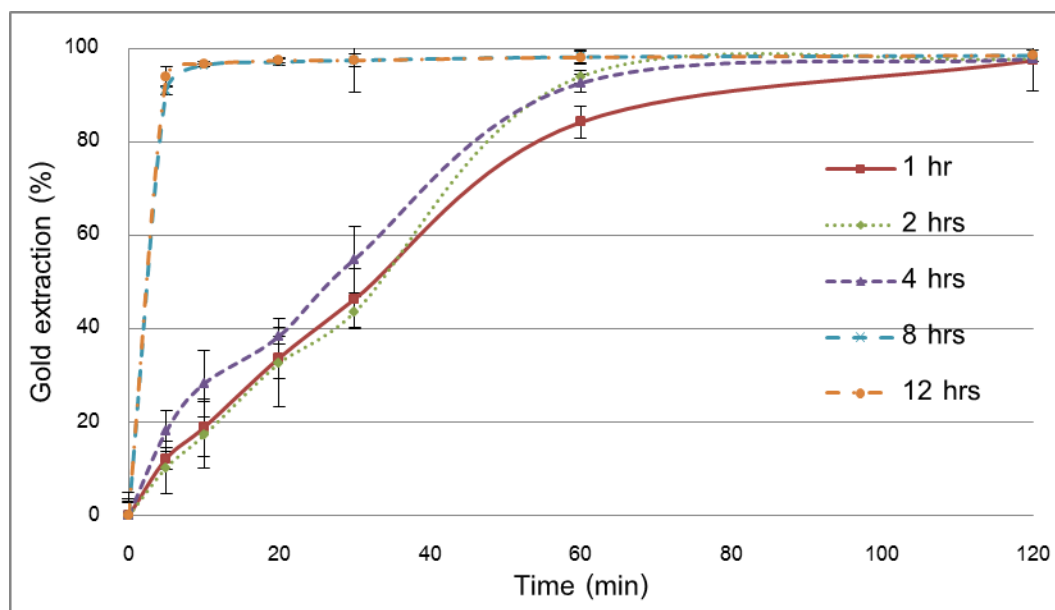


Figure 4.5 Gold extraction profiles of ATS-modified carbons prepared by various impregnation times

The initial and residual gold concentrations were used to calculate the gold extraction percentages. Figure 4.5 demonstrated the gold extraction profiles of these modified adsorbents. It can be noted that the gold extraction efficiency of all modified carbons increased proportionally with contact time. Although a virtually complete extraction of gold could be accomplished in just 60 minutes with all ATS-coated carbons, it was clearly shown that the extraction efficiency of the ATS-modified carbon impregnated for over 8 hours were distinctly exceptional. Under these conditions, over 85% gold extraction was readily attained in just under 5 minutes, while those with lower impregnating times were able to extract merely less than 20% of gold for the same extraction periods. The extraction profile of the 12-hour impregnated carbon was similar to the one with 8-hour impregnation in which the maximum extraction was established approximately after 10 minutes. This remarkable improvement in the gold extraction at shorter times could be extremely valuable in the industrial applications where operating cost and time consumption are of great concerns.

It should also be noted that the particle size of the carbon with 8 and 12 hours of impregnation were clearly smaller than the rest due to prolonged period of

mechanical stirring during the impregnation process. This small particle size and its subsequent increased surface area were initially believed to play an important role in the better extraction efficiency but further investigation with the non-impregnated carbon of the same size proved that the effect was negligible. These results indicated that the gold extraction enhancement was a direct consequence of longer exposure and thus, increased penetration and retention of the modifying reagent on the surface of activated carbon, resulting in numerous active sites for gold adsorption. The impregnation time of 8 hours was therefore executed for further experiments.

4.3.3 Effect of impregnation temperature

Temperature is a common parameter that enhances the kinetics of most reactions in general. Based on the above observation in which a better Au extraction was obtained with increased penetration and retention of the modifying reagent on the carbon, it was then speculated that higher temperature would lead to better impregnation efficiency and a probable reduction of the impregnation time. The experiments similar to those of the previous section were carried out with the exception that the impregnation temperature was controlled at 70°C. The values corresponding to the gold concentration results are tabulated in Table 4.4.

Table 4.4 The residual gold concentration at each extraction time by various impregnation times at 70°C

Time(min)	Impregnation time (controlled at 70°C)				
	1hr	2hrs	4hrs	8hrs	12hrs
	Residual gold concentration (ppm)				
5	18.30	18.41	17.76	10.47	9.39
10	17.19	17.23	16.40	7.74	6.32
20	14.18	13.99	12.54	2.84	2.14
30	11.12	10.64	9.39	0.72	0.61
60	4.58	3.18	2.92	0.38	0.31
120	0.76	0.41	0.52	0.23	0.15

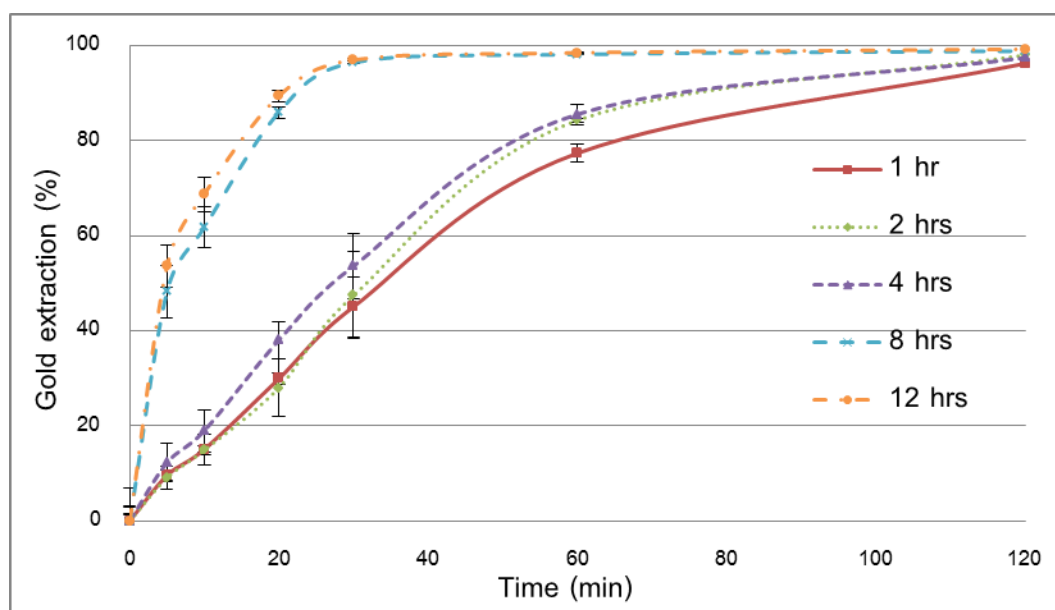


Figure 4.6 Gold extraction profiles of ATS-modified carbons prepared by various impregnation times at 70°C

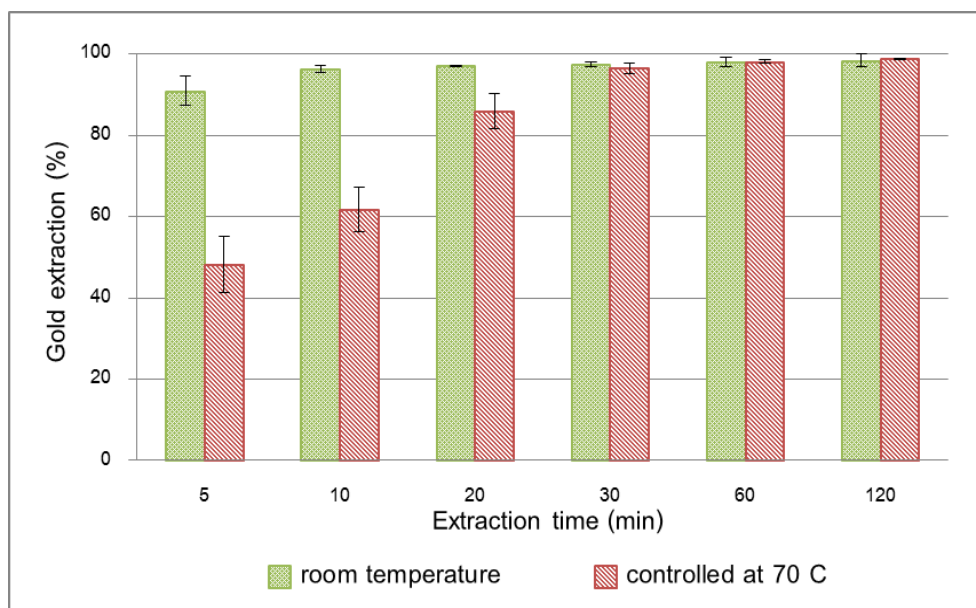


Figure 4.7 The extraction of gold in comparison of the activated carbon impregnated with 1% ATS for 8 hours prepared at room temperature and controlled at 70°C

The gold extraction profiles of ATS-modified activated carbons prepared by various impregnation times at 70°C were illustrated in Figure 4.6. An enhancement behavior in the gold extraction trends was similar to those of the carbons impregnated at room temperature. For the same extraction period of 30 minutes, approximately 85% Au extraction was achieved with the carbons impregnated over 8 hours, and 45-55% for the lower impregnating times. Figure 4.7 directly compared the influence of the impregnation temperature on the gold extraction of the carbon prepared under the optimum impregnation time (8 hours). It is obvious that the overall extraction figures are far less superior than those obtained with the room temperature impregnated carbon, indicating that higher temperature proved to be no advantageous in this instance. Presumably the better penetration of ammonium thiosulfate at higher temperature may have been superseded by its leaching kinetics which result in the dissolution of ammonium thiosulfate out of the sorbent.

4.3.4 Effect of concentration of impregnating reagent

The effect of concentration of ammonium thiosulfate was studied so as to determine the optimum loading for impregnation of activated carbon. The activated carbon was impregnated with 0.1, 0.5, 1.0 and 5.0% (w/v) aqueous solution of ammonium thiosulfate at room temperature for 8 hours, respectively. The maximum concentration of the impregnating reagent was limited to only 5.0% (w/v) as the ammonium thiosulfate became insoluble beyond this concentration. The modified carbons loaded with varying amount of ATS were applied to capture gold from the 20 ppm Au solution for 60 minutes. The remaining concentrations of gold in the solutions were determined and demonstrated in Table 4.5.

Table 4.5 The residual gold concentration of ATS-modified carbons prepared by various ATS loadings after 60 minutes of extraction

Carbon	Residual gold concentration (ppm)
CRAC+0.1%ATS	2.74 ± 0.36
CRAC+0.5%ATS	0.53 ± 0.05
CRAC+1.0%ATS	0.54 ± 0.12
CRAC+5.0%ATS	0.39 ± 0.04

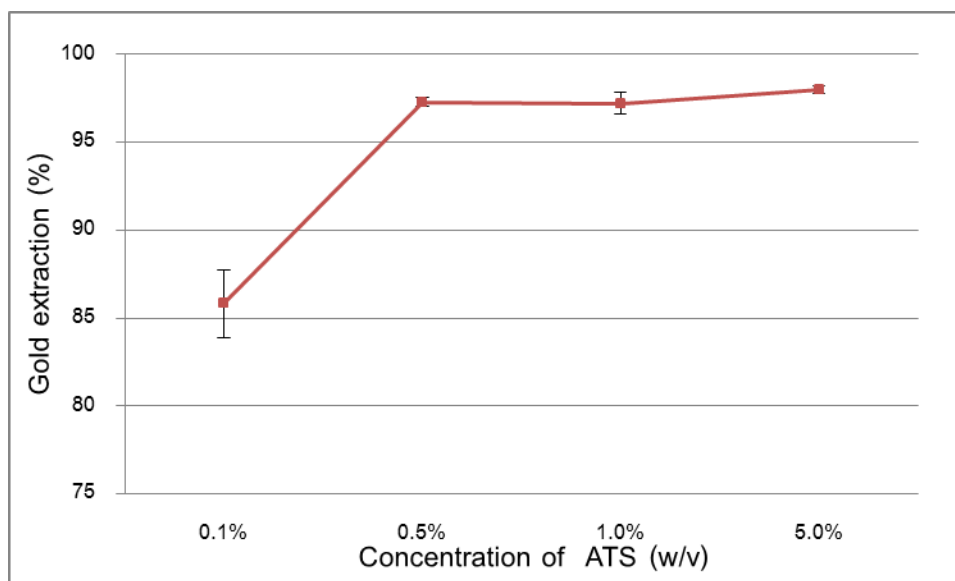


Figure 4.8 The gold extraction of ATS-modified carbons prepared by various ATS loadings for 60 minutes

The gold extraction of the modified carbons with various ATS loadings were presented in Figure 4.8. The contact time of 60 minutes were used for all batches to ensure that the extraction equilibrium was reached. Approximately 85.8% gold extraction was achieved with the carbon impregnated with 0.1% ATS. The extraction efficiency was increased to roughly 97.3% and seemingly stabilized around this figure as the concentration of impregnating reagent was extended to 0.5% and higher, indicating that the maximum efficiency might have been established beyond this point. The extraction efficiency pattern observed here apparently correspond to the findings of the sulfur content analysis (Table 4.2), in which the saturation of ammonium thiosulfate on the activated carbon and thus maximum gold binding sites would be assumed after its concentration exceeded 0.5% (w/v). The impregnation with 1% ammonium thiosulfate was selected for further experiments to ensure that the carbon thoroughly and sufficiently impregnated.

4.3.5 Adsorption isotherm

The sorption capacity is a key analytical figure that can be estimated by the adsorption phenomena between an ion of gold (AuCl_4^-) in the solution and the sorbent. The ATS-modified activated carbon that was prepared under the optimum condition (impregnation with 1% (w/v) ATS for 8 hours at room temperature) was employed to extract gold solution in the range of 20 to 70 ppm. The sorbents were allowed to extract gold from the solution for 60 minutes at a constant temperature (298 K). A plot of adsorption isotherm of the ATS-modified carbon is shown in Figure 4.9.

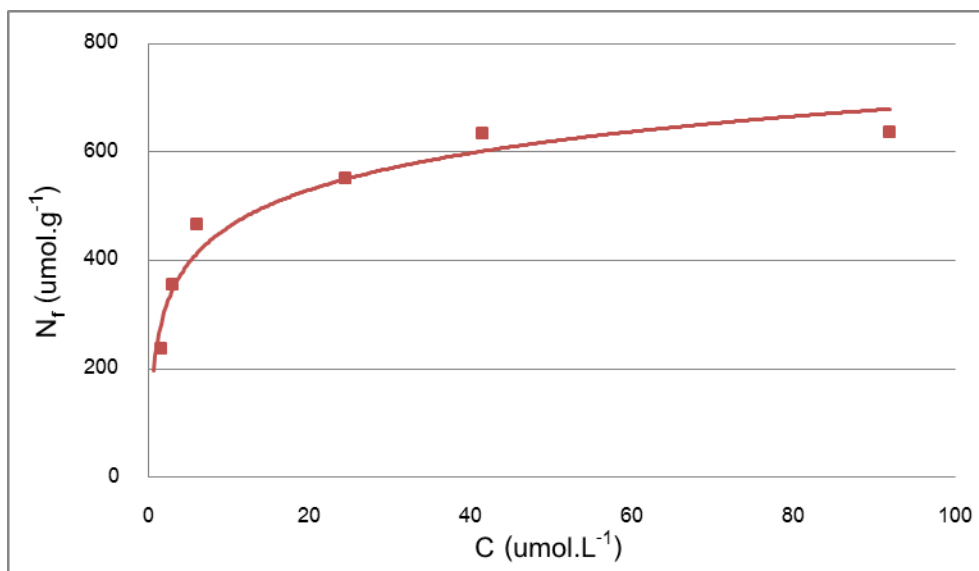


Figure 4.9 The sorption capacity of ATS-modified carbons prepared under the optimum condition for 60 minutes

The Langmuir and Freundlich adsorption isotherms are the two common models used to study the adsorption behavior on the structure of adsorbent. The Langmuir relation describes the analyte uptake that occurs by a monolayer sorption on the surface, i.e. each restrictive site has an affinity with only one analyte ion. In addition to the Langmuir relation, the Freundlich relation describes the adsorption that

occurs by a multilayer sorption. The Langmuir adsorption isotherm was plotted in Figure 4.10, while the Freundlich adsorption isotherm in Figure 4.11.

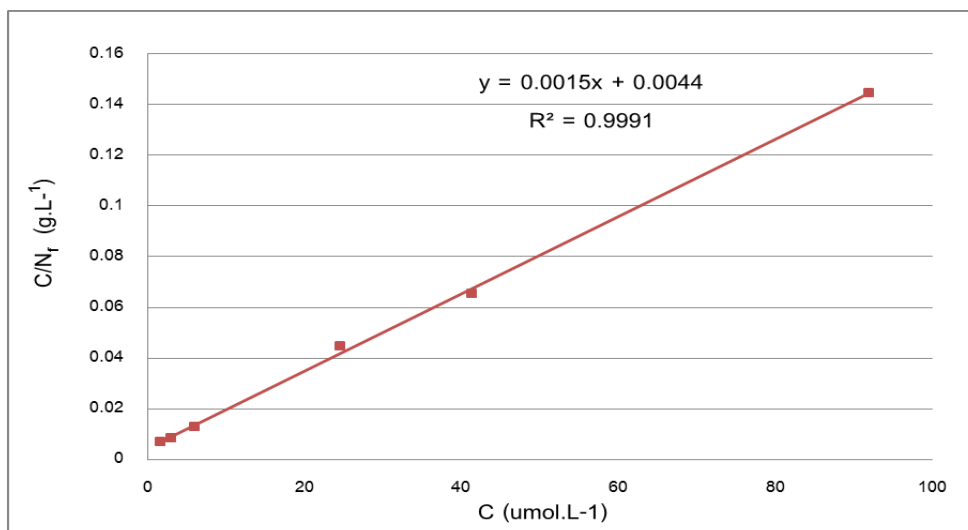


Figure 4.10 Langmuir plot for gold adsorption

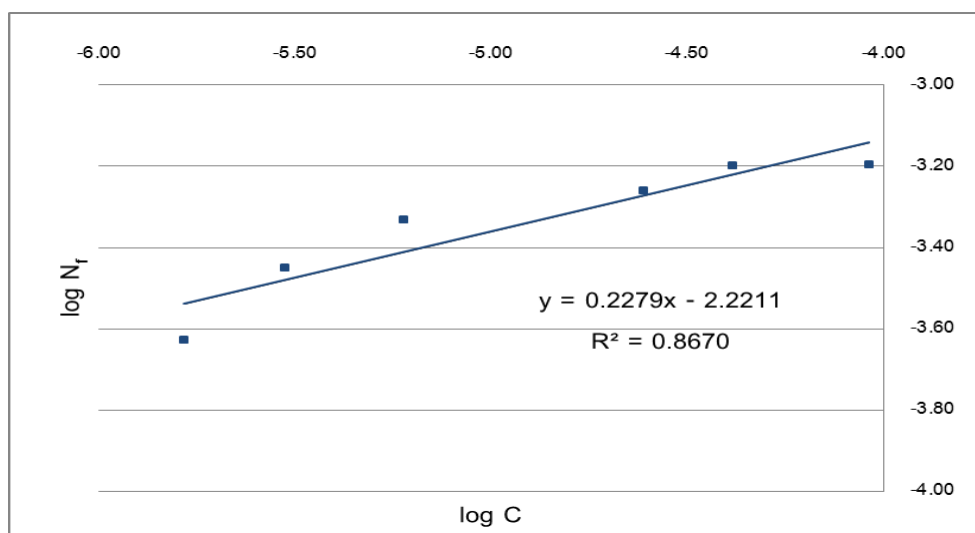


Figure 4.11 Freundlich plot for gold adsorption

The Langmuir adsorption isotherm is accomplished with a near perfect correlation coefficient (R^2) of about 0.9991. This indicated that the sorption of gold on the ATS-modified carbon fit very well with the Langmuir adsorption model. The

Freundlich adsorption isotherm, on the contrary, yielded an unacceptable correlation coefficient (R^2) of merely 0.8670. The maximum sorption capacity of the ATS-modified carbon estimated from the Langmuir model was 129.27 mg.g^{-1} , an unprecedented figure as compared to those obtained from the previous works [49].

4.3.6 Interference study

A variety of potential interfering metal ions, commonly found in jewelry industrial wastes, i.e. Cu, Fe, Ni, Pt, Rh and Zn were chosen to study its interference effect against the gold extraction of the investigated adsorbent. The ATS-modified carbon prepared under the optimum condition was brought to extract a mixed metal ions solution, of which the concentrations of the interfering metal ions were 20 and 100 ppm, for 60 minutes. The initial and residual concentrations of all metal ions in the solution were determined by ICP-OES. The efficiency of each metal ions extraction was illustrated in Figure 4.12.

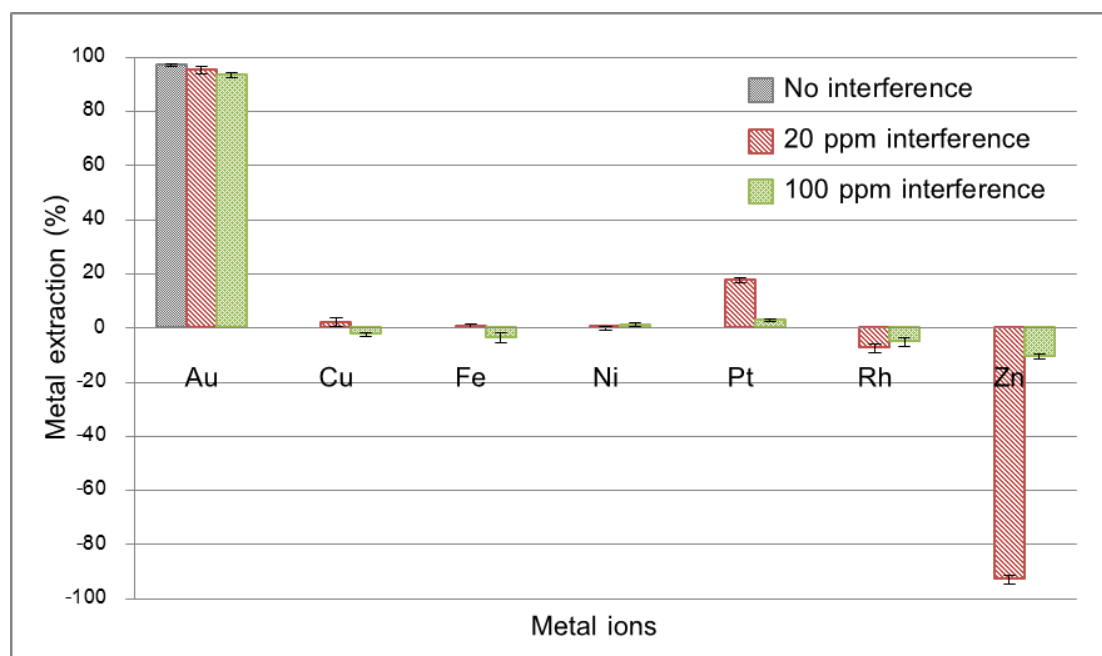


Figure 4.12 The extraction profiles of various metal ions obtained with the ATS-modified carbon

As seen earlier, a typical extraction of gold in the absence of interferences was nearly complete (~97-98%). This number was slightly reduced to around 95 and 93% when the interfering elements were present at 20 and 100 ppm, respectively. It is clearly noticed that the presence of these common interfering metal ions insignificantly affected the gold-binding efficacy of the ATS-impregnated carbon. With the exception of platinum, all other interfering metal ions studied were essentially not adsorbed on the sorbent indicating the modified sorbent has excellent selectivity toward the noble metal. A noticeable quantity of platinum (17.71%) was extracted by the modified carbon when the interferences were introduced. According to the hard-soft acid base principle, platinum is a soft acid which commonly exists as PtCl_4^- in the acidic medium. These ions therefore behave similarly to AuCl_4^- and possibly compete with gold in the extraction process. Increasing the weight of the sorbent may be used to solve this problem. In case of zinc, negative extraction values were obtained suggesting that additional amount of zinc were eluted. This extra mass of Zn could be attributed to the elution of zinc chloride, a chemical catalyst used excessively during the activation process, yet the phenomena apparently had no impact on the extraction of gold.

4.4 Column extraction

Column extraction is a typical method that is applied to extract target species from industrial wastes. This method is readily available and is capable of handling large volume circulation. Based on previous observations, the ATS-modified carbon has exceptional performance in a short extraction time and thus should be able to accommodate fast sample intake in the column extraction method. In the following experiments, various parameters influencing the gold extraction were investigated and optimized through the use of a laboratory made mini column and its potential applicability was extended to the larger and more industrial-like cylinder column.

4.4.1 Effect of flow rate

In the column system, the sample flow rate is a critical parameter to obtain quantitative retention of gold with the modified carbon. The ATS-modified carbon was packed in a laboratory mini-column and evaluated for its gold extraction efficiency under the controlled flow rates ranging from 1.0 to 10.0 mL.min⁻¹. The flow rate that is higher than 10.0 mL.min⁻¹ cannot be handled due to the limitation of the peristaltic pump power and the problem of back pressure. The residual gold concentration of the solution is tabulated in Table 4.6.

Table 4.6 The residual gold concentration of the ATS-modified carbon with various flow rates

Flow rate (mL.min ⁻¹)	Residual gold concentration (ppm)
1	1.13 ± 0.17
3	3.36 ± 0.21
5	6.69 ± 1.39
7	6.82 ± 0.71
10	5.97 ± 0.83

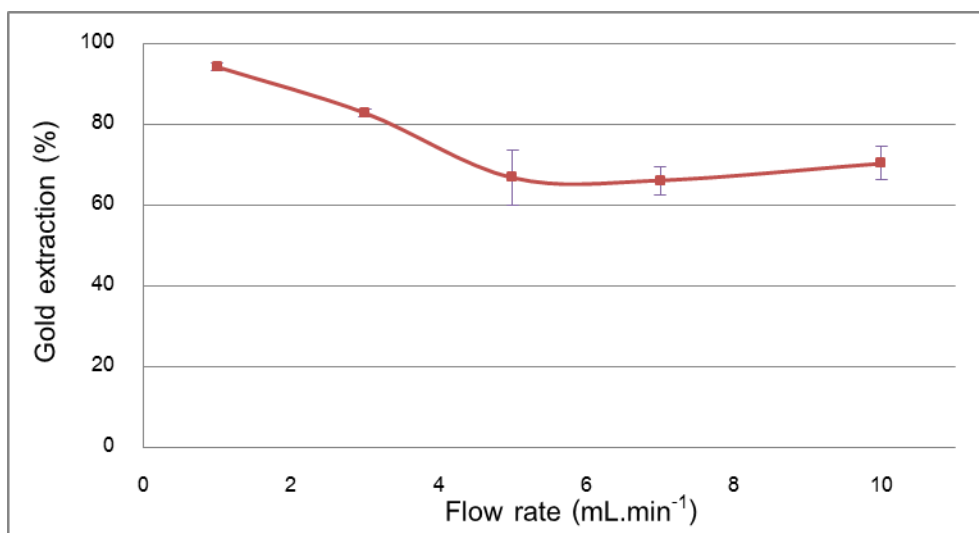


Figure 4.13 Gold extraction profiles of the ATS-modified carbon with various flow rate

The efficiency of gold extraction obtained from the column at varied flow rates (in Figure 4.13) were found to be 94.23, 82.83, 66.81, 66.14 and 70.34% for the controlled flow rate of 1.0, 3.0, 5.0, 7.0 and 10.0 mL.min⁻¹, respectively. The sorption efficiency of gold continually decreased as the sample flow rate was increased because of less exposure period between gold and the binding sites of the ATS-modified carbon. To ensure a complete extraction of gold, the sample flow rate of 1.0 mL.min⁻¹ was used to study in the subsequent experiments.

4.4.2 Breakthrough curve

A breakthrough study was carried out to determine the sorption capacity of gold on a laboratory-made mini column. This experiment compares the extraction efficiency of gold between the ATS-modified carbon and the commercial activated carbon. The mini column was each loaded with the modified carbon and the commercial activated carbon and then allowed to retain gold from the solution passing through at the column-optimized flow rate (1.0 mL.min⁻¹). The filtrate was then subject to gold content analysis by FAAS.

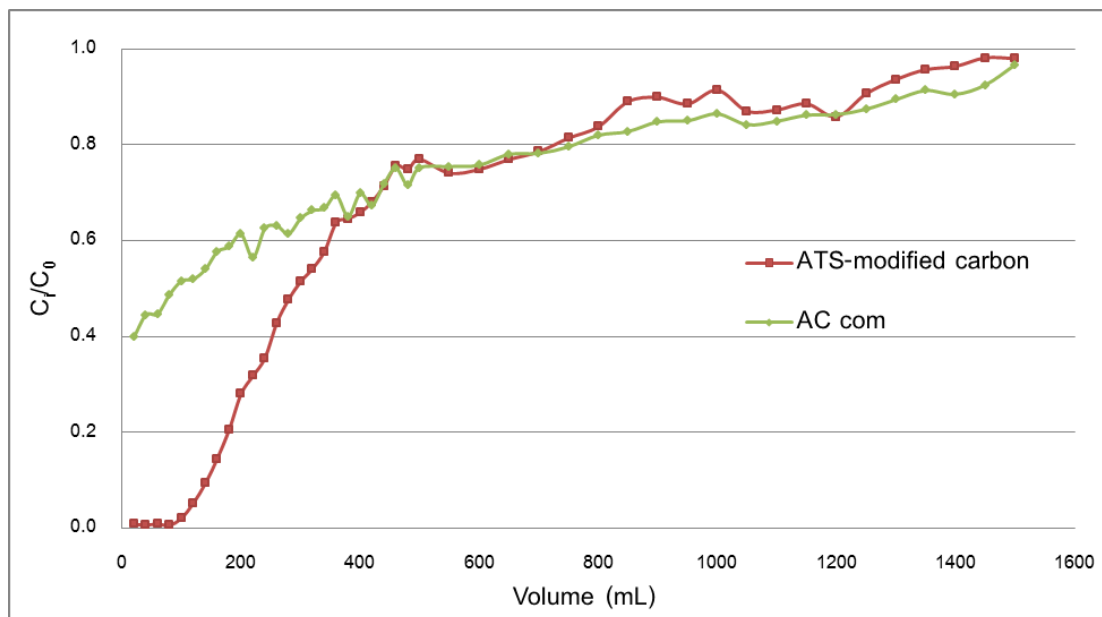


Figure 4.14 Breakthrough curves of the ATS-modified and the commercial activated carbons

A plot of the ratio of the remaining gold concentration that passed through the mini column (C_i) versus the initial gold concentration (C_0) was illustrated in Figure 4.14. It can be seen that, with the ATS-modified carbon, a virtually complete retention of gold ($C_i/C_0 \sim 0$) was achieved earlier in the extraction process up to 100 mL of sample volume. On the other hand, a C_i/C_0 of approximately 0.4, i.e. 40% leak, was attained right from the beginning of the extraction process with the commercial carbon. The drastic differences in the retention ability of the two columns observed here were gradually diminished and merged at the approximate volume of 500 mL. The ratio progressively increased to roughly 0.95, a point to which it was considered that the column completely failed to retain gold at approximately 1500 mL of the sample volume. The breakthrough capacity of the column can be estimated from the amount of gold retained on the column prior to a predefined breakthrough point. Since gold is a very precious material, any significant loss would be considered a disastrous consequence. In this experiment, therefore, a ratio (C_i/C_0) of only 0.05 was used as a breakthrough point and the integrated area of the breakthrough curve below this ratio was calculated to determine the quantity of gold retained. This methodology

cannot be applied in the case of the commercial carbon column as the gold leak was already over the limit. A further experiment was then performed with increased amount ($5\times$) of sorbent ($0.10\text{ g AC}_{\text{com}}$) and lower gold concentration (10 ppm) to establish a breakthrough curve below the defined ratio. The breakthrough capacity of the ATS-modified carbon was found to be $98.90\text{ mg}\cdot\text{g}^{-1}$ while those obtained with the commercial carbon was merely $25.36\text{ mg}\cdot\text{g}^{-1}$, a remarkable improvement by nearly a factor of four.

To clearly get an insight of what happen at the surface of the sorbent, both of the plain coffee residue activated carbon and the ATS-modified carbon fully loaded with gold from the breakthrough column were subject to scanning electron microscopy (SEM) analysis. The SEM images of the activated carbon obtained from coffee residues at 200 and 600 magnifications were shown in figure 4.15 (A) and (B). The non-modified carbon is an amorphous material with extremely high surface area and micro pores. Elemental composition of the material was analyzed by an energy dispersive X-ray spectrometer integrated within the SEM. The sorbent was found to predominantly contain carbon, oxygen, chlorine and zinc at approximately 72.3%, 16.9%, 5.1% and 4.3% respectively. Meanwhile, the SEM images of ATS-modified carbon filled with gold were shown in the same illustration for $200\times$ (C), $600\times$ (D) and $1200\times$ (E) magnifications. The presence of metallic gold component was visually observed and abundantly distributed throughout the surface of the modified carbon.

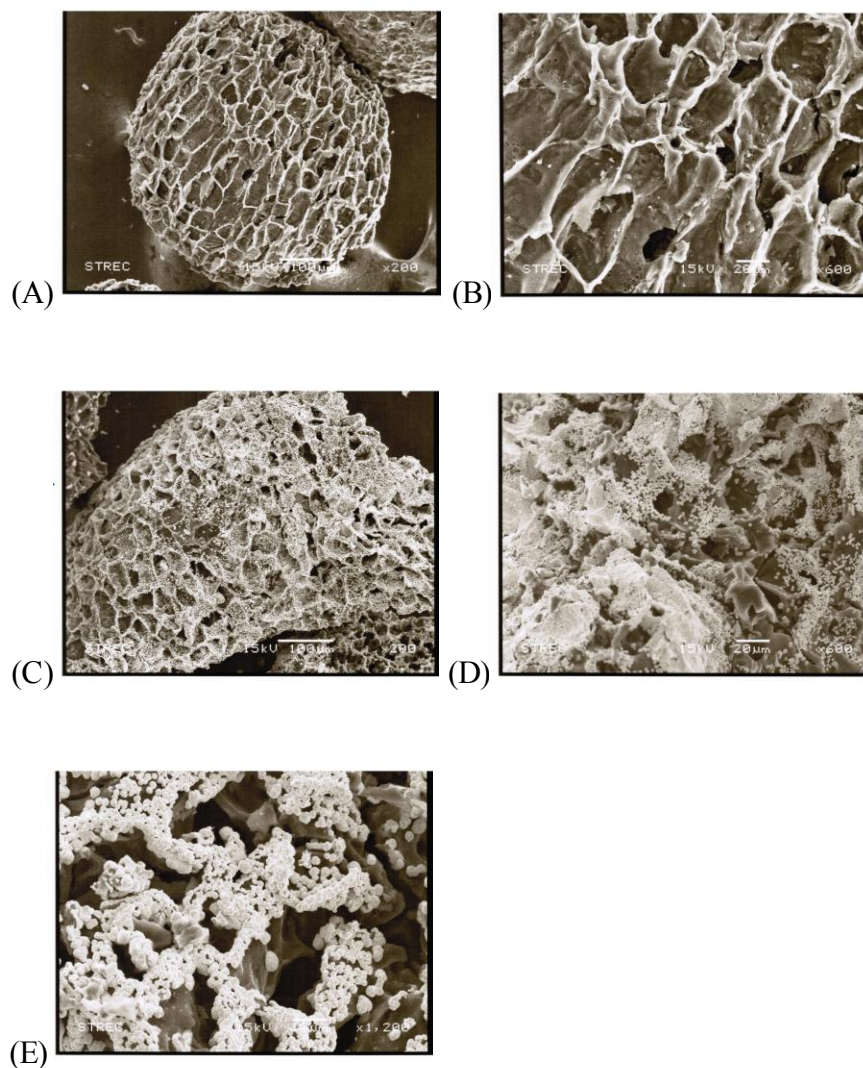


Figure 4.15 SEM images of the activated carbon prepared from coffee residues at 200 \times (A) and 600 \times (B), besides the ATS-modified carbon after gold adsorption at 200 \times (C), 600 \times (D) and 1200 \times (E).

The earlier finding was further supported by the characterization of the sorbent utilizing X-ray diffraction analysis. The XRD patterns in Figure 4.16 presented the composition of gold crystallites on the sorbent with the characteristic peaks located at about 37, 44 and 64 $^{\circ}$ two theta. At this point it is undoubtedly confirmed that a significant portion of the adsorbed gold were reduced into metallic gold (Au^0). This can be attributed to the fact that gold, both in the form of Au^{3+} and its thiosulfate complex $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$, have relatively high reduction potential (E°). The reduction of

gold can possibly be accomplished by several potential reducing agents present in the system, among which are zinc and other reducing functional groups on the carbon surface as well as thiosulfate itself.

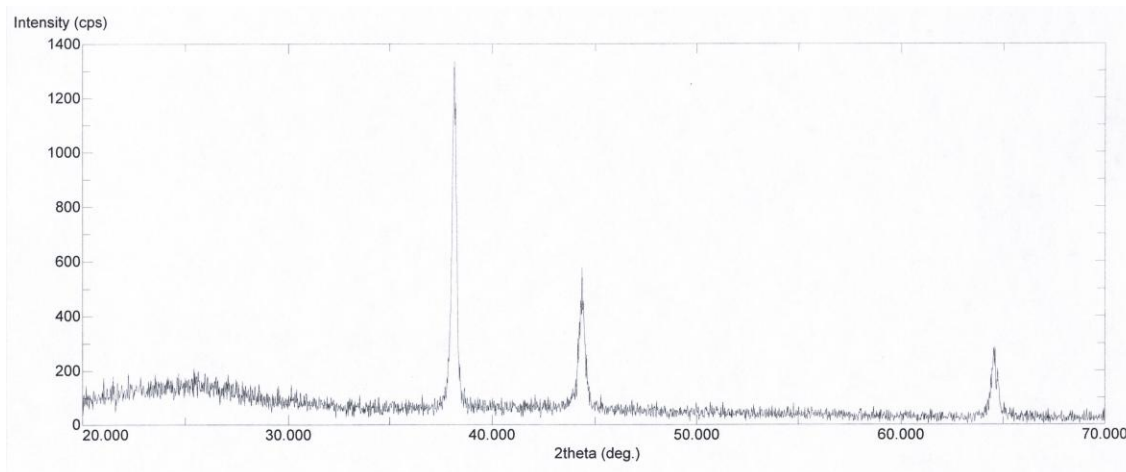


Figure 4.16 XRD pattern of gold-surfacing on the ATS-modified activated carbon

4.4.3 Cylinder column

The flow-through column extraction was proven to be a successful technique in the recovery of gold solution, however, its merit is practically obscured by the limitations of applicable flow rate and intake volume. To further demonstrate the potential of the developed sorbent, its capability to handle faster flow rate and larger volume of gold solution were evaluated. The ATS-modified carbon, prepared under the optimized condition, was packed in a larger cylinder column. Portions of gold solution were pumped upward through the packed column by a vacuum pump at an approximate flow rate of $50.0 \text{ mL}\cdot\text{min}^{-1}$. This setup is a closer imitation to what is used in the extraction of gold in mining industries. The solution passing the column at each increment was then collected and analyzed for the remaining gold concentration. The extraction efficiency of this system is tabulated in Table 4.7 for an accumulated volume of 1000 mL.

Table 4.7 The efficiency gold extraction of the ATS-modified carbon applied with cylinder column

Volume (mL)	Residual gold concentration (ppm)	Gold extraction (%)
0	10.29	-
100	0.022	99.79
200	0.045	99.56
300	0.069	99.33
400	0.157	98.47
500	0.013	99.87
600	0.066	99.36
700	0.175	98.30
800	0.154	98.50
900	0.039	99.62
1000	0.118	98.85
Average		99.17

Although the proposed system is still far from industrial scale, the modified sorbent has truly shown its competence for such challenge. With merely 1 g of the material, an average of over 99% extraction of 1000 mL Au solution was attained within less than 20 minutes. This result is a clear demonstration that the modified material can unquestionably extend its feasibility towards the industrial applications.

4.5 Gold extraction from jewelry industry wastes

In this experiment, the recovery of gold from real jewelry wastes were exemplified. The aqueous waste (A) and its sludge were collected from the dissolution and washing processes of scrap gold while the organic waste (B) were mainly solvents used to remove debris left on the wax setting in the manufacturing

process. As the organic solvent is not compatible with FAAS, only the solid waste (sludge B) was analyzed. Both types of waste were filtered to obtain sludge A and sludge B which were subsequently digested with aqua regia and diluted as detailed below. All three specimens were passed through the exact same column, one by one, for a total of three replicates each. The gold concentrations of all wastes before and after the extraction were measured, extraction efficiency calculated, and depicted in Table 4.8.

Table 4.8 Gold extraction of jewelry wastes

Cylinder column 1.011 g	Waste classification		
	Waste A	Sludge A	Sludge B
weight (g)	-	0.102 ± 0.001	0.104 ± 0.003
volume (mL)	1000	500	500
Initial concentration (ppm)*	0.83 ± 0.38	0.37 ± 0.06	0.27 ± 0.07
gold extraction (%)	88.27 ± 5.58	94.11 ± 6.89	88.78 ± 8.70

*Dilute 100 times

The obtained results showed satisfactory extraction efficacy (~88-94%) from all real wastes with large volume and relatively low Au concentration (<1ppm). To eliminate any doubt in the capability of this system for handling wastes with higher Au concentration and acidic content, additional wastes were prepared with larger amount of sludge A and B and less dilution factor which resulted in the initial concentration of 16.89 and 14.82 ppm Au as exhibited in Table 4.9. With significantly higher amount of gold loaded onto the column, somewhat less than satisfactory extraction were obtained for both types of waste, 60.82 and 56.18 % respectively. This lower extraction efficiency could be partially attributed to the higher leaching power of less diluted aqua regia as well. Nonetheless, following additional circulations of these wastes through the same existing column, the Au extraction efficiency were improved dramatically to over 93 and 92 % respectively. These

results evidently confirmed that the modified activated carbon was indeed capable of administering such rather extreme conditions.

Table 4.9 The condition and result of real-wasted experiment confirmed by cylinder column

Cylinder column 1.046 g	Waste classification	
	Sludge A	Sludge B
weight (g)	1.004 ± 0.004	1.002 ± 0.003
volume (mL)	100	100
Initial concentration (ppm)*	16.89 ± 2.78	14.82 ± 1.14
% gold extraction after 1 st circulation	60.82 ± 11.78	56.18 ± 7.01
% gold extraction after 2 nd circulation	79.95 ± 8.12	79.90 ± 4.29
% gold extraction after 3 rd circulation	93.47 ± 2.67	92.28 ± 2.14

*Dilute 10 times

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The activated carbon in this experiment was prepared with disposed coffee residues by atmospheric pyrolysis at 300°C, activated with zinc chloride at a weight ratio of 1:2 and re-pyrolysed at 600°C. The obtained coffee residue activated carbon (CRAC) was then impregnated with ammonium thiosulfate (ATS) for improving its gold extraction efficiency. Various parameters influencing the gold extraction of the ATS-modified carbon were studied and optimized through batch extraction, i.e. impregnation time, impregnation temperature and concentration of ammonium thiosulfate. The resulting carbons were characterized by surface area analysis (N₂ adsorption and desorption), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and sulfur content analysis which in turn indicated a successful impregnation of ammonium thiosulfate. The modifying carbon was optimized by impregnation with 1% (w/v) ammonium thiosulfate at room temperature for 8 hours. An outstanding gold extraction efficiency of over 85% could be readily achieved in just under 5 minutes with the impregnated carbon as compared to only less than 10% of its commercial counterpart. The adsorption isotherm study of the ATS-modified CRAC revealed that its affinity toward gold correspond to Langmuir adsorption model with the maximum sorption capacity of approximately 129.27 mg.g⁻¹. The adsorption of the ATS-modified carbon was relatively free from potential interference by ions commonly found in gold jewelry waste such as Cu, Fe, Ni, Pt, Rh and Zn.

The activated carbon impregnated with ATS was applied in the column extraction method. The flow rate of a home-made mini column was optimized at 1 mL.min⁻¹. The remarkable sorption capacity of this column for the gold extraction was demonstrated by a breakthrough curve in which the column breakthrough

capacity ($C_i/C_0=0.05$) obtained were, 98.90 $\text{mg}\cdot\text{g}^{-1}$ and 25.36 $\text{mg}\cdot\text{g}^{-1}$ for the ATS-modified CRAC and the commercial activated carbons, respectively. A fabricated cylinder column was then used to illustrate the potential applicability of the developed sorbent in handling larger volume and higher flow rate of challenging real jewelry wastes with satisfactory results. Overall the ATS-modified CRAC proved to be an extremely remarkable sorbent for the gold extraction process and possibly a good alternative and sustainable solution for the coffee residue waste management.

5.2 Suggestions for future work

The following issues could be of particular interests for future work:

- Automation of the gold extraction system using the ATS-modified carbon
- Adoption of the modified sorbent into the gold leaching and refining methods
- Development and modification of the new activated carbons from other carbonaceous waste materials

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