THE ADSORPTION CHARACTERISTICS OF GOLD
ONTO 3-AMINOPROPYLTRIETHOXYSILANE
GRAFTED COCONUT PITH

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To my beloved mother and father

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ABSTRACT

Increased use of gold in the various industries has raised significant quantities of such compounds into environment. Gold is persistent and non-biodegradable. Precious metal (gold) becomes serious threat to human health in the form of ionic compounds. They can cause damage to nervous system, skin problem, cancer, kidney problem, bone marrow and hearing damage. Also their high price and limited sources makes it economical to recover them. In this study, coconut pith was investigated for the biosorption studies of Au(III). The chemical modification of coconut pith was done using 3-aminopropyltriethoxysilane. The Scanning Electron Microscopy (SEM) results reveal that the surface of grafted coconut pith (GCP) has cracks and coarse surface as compared to virgin coconut pith (VCP) which shows smooth surface. These cracks and irregularities help to increase the biosorption on the interior and surface of GCP. The Fourier Transform Infrared (FTIR) spectroscopy shows different silanization bonds on GCP; Si-O-Si (1032 cm^{-1}), Si-CH_2 ($1411 cm^{-1)}$) and NH_2 (1569.56 cm^{-1}) which were absent in VCP. The effect of different parameters such as pH, contact time, temperature, and initial Au(III) concentration on biosorption was studied. The optimum conditions for biosorption of Au(III) onto GCP and VCP were at Au(III) concentration of 500 ppm, pH 4, contact time of 360 minutes, and temperature of 60 ^{o}C. The highest biosorption capacity of 262.19 mg/g was recorded for Au(III) biosorption onto GCP biosorbent at pH 4 and dosage of 1 gm/ml. The biosorption of Au(III) onto VCP and GCP biosorbents was best fitted to the Langmuir isotherm model while the pseudo-second order model was found to best describe experimental data. Au(III) biosorption selectivity of the GCP was better compared to VCP. The regenerability of GCP and VCP biosorbents in gold (III) biosorption was completed in three cycles revealing excellent durability of GCP as compared to VCP.

ABSTRAK

Peningkatan penggunaan emas dalam pelbagai industri telah meningkatkan kuantiti bahan ini dengan ketara ke atas alam sekitar. Emas adalah bahan yang kekal dan tidak terbiodegradasi. Logam berharga (emas) dalam bentuk sebatian ion menjadi ancaman serius kepada kesihatan manusia. Ianya boleh menyebabkan kerosakan terhadap sistem saraf, masalah kulit, kanser, masalah buah pinggang, sumsum tulang dan kerosakan pendengaran. Selain itu, harganya yang tinggi dan sumber yang terhad menjadikannya ekonomikal untuk digunapakai. Dalam kajian ini, habuk kelapa telah disiasat untuk biojerapan Au(III). Pengubahsuaian kimia terhadap habuk kelapa telah dilakukan dengan menggunakan 3-aminopropyltriethoxysilane. Keputusan Mikroskop Elektron Imbasan (SEM) mendedahkan bahawa habuk kelapa yang diubahsuai (GCP) mempunyai keretakan dan permukaaan kasar berbanding habuk kelapa dara (BPV), yang menunjukkan permukaan yang licin. Keretakan dan permukaan kasar ini membantu meningkatkan biojerapan pada bahagian dalaman dan permukaan GCP. Fourier Tranformasi Infra-Merah (FTIR) menunjukkan perbezaan ikatan silana pada GCP; Si-O-Si (1032 cm^{-1}), Si-CH$_2$ (1411cm^{-1}) dan NH$_2$ (1569.56 cm^{-1}) yang mana tidak kelihatan dalam VCP. Kesan parameter yang berbeza terhadap biopenjerapan seperti pH, masa pengadukan, suhu, dan kepekatan logam awal telah dikaji. Keadaan yang optimum untuk biojerapan emas ke atas biopenjerap GCP dan VCP pada kepekatan logam awal 500 ppm, pH 4, 360 minit masa pengadukan dan suhu 60 ^{o}C. Kapasiti biojerapan yang tinggi adalah 262.19 mg/g yang dicatatkan untuk penjerapan Au(III) ke atas GCP biopenjerap pada pH 4 dan dalam nisbah (1:1) biopenjerap/biojerap. Biojerapan bagi biopenjerap GCP dan VCP mematuhi model isoterma Langmuir, manakala pseudo-tertib-kedua telah didapati sebagai yang terbaik untuk menerangkan data ekperimental yang diperolehi. Pilihan bagi biojerapan Au (III) adalah yang terbaik bagi biopenjarap GCP berbanding VCP. Kebolehgunaan biopenjerap GCP dan VCP terhadap biojerapan Au(III) telah dilaksanakan dalam tiga kitaran mendedahkan ketahanan yang terbaik bagi GCP berbanding VCP.

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LIST OF SYMBOLS

α	-	Elovich constant related to chemisorption rate(mg/gmin)
β	-	Elovich constant related to surface coverage
C	-	Gold concentration (ppm)
C_e	-	Equilibruim gold concentration (ppm)
C_o	-	Initial gold concentration (ppm)
K_1	-	Equilibruim rate constant of pseudo-first order kinetic model(1/min)
K_2	-	Equilibruim rate constant of pseudo-second order kinetic model(g/mg.min)
K_d	-	Dissociation constant
K_F	-	Freundlich constant (dm^3/mg)
K_L	-	Langmuir constant (dm^3/mg)
n	-	Intensity of adsorption
P_g	-	Percentage grafting(% grafting)
Qe	-	Amount adsorbed at equilibruim condition(mg/g)
Q_{max}	-	Maximum adsoption capacity(mg/g)
Q_t	-	Adsoption capacity at time t (mg/g)
R^2	-	Corelation coefficient
R_L	-	Langmuir parameter

LIST OF ABBREVIATIONS

VCP	-	Virgin coconut pith
GCP	-	Grafted coconut pith
APS	-	Aminopropyl Triethoxy Silane
AAS	-	Atomic Absorption Spectra
FTIR	-	Fourier transfrom Infrared Spectroscopy
H^+	-	Hydrogen Ions
OH^-	-	Hydroxyl Ions
NaOH	-	Sodium Hydroxide
ppm	-	Parts Per Million
SEM	-	Scanning Electron Microscopy
EDX	-	Energy Dispercive X-rays
Fe	-	Iron
K	-	Potassium
Na	-	Sodium

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CHAPTER 1

INTRODUCTION

1.1   Research Background

Earth surface contains large reservoirs of water up to 70% of earth surface. It is most valuable resource amongst all the natural resources. There are several ways by which, water contamination can occur but as general, they fall into two categories: direct and indirect contaminant sources. The direct sources contain wastes from industries, refineries and wastewater treatment plants and in later one they contain the sources which have potential to enter underground water. The pollutants, which have a potential to pollute the water falls under organic or inorganic class. Insecticides, pesticides and volatile organic compounds come under organic class while the metals, dyes and fertilizers comes under the inorganic class (Mack et al., 2007). Our concern will be inorganic. There effects on the human health are adverse and known to be carcinogenic and toxic.

Metals have found their use in various kinds of industries ranging from mining electronic electroplating to metal finishing. The wastewater being discarded by these industries if containing these metal ions become hazardous. Due to their increased concentration in the wastewater they can reach toxic levels and damage

life on earth by entering into ecological system (Vijayaraghavan and Yun, 2008). Taking these serious threats into consideration to human health, there is a need to find out the cheap and environmental friendly process which can act as a shield to these threats to increase the standard of living and to make world a better place to live (Bhatnagar et al., 2010). Countries having strong environmental laws to limit the use of contaminant being wasted in the environment (without being treated under consideration) are urged to developed on site or in plant facilities to treat the effluents to make the pollutants under the acceptable concentration (Banat et al., 1996; Vijayaraghavan and Yun, 2008).

Gold is a metal, which is widely used in various industries (electrical systems, fuel cells, catalysts, biomedical area, etc.) due to its unique physical and chemical properties. The increase in the industrial demand for gold has determined the need for gold recycling. This is the main reason in the finding of a better and safer technology for this purpose (Bulgariu and Bulgariu, 2011). Worldwide, billions of peoples are using mobile phones as fast communication devices. Nowadays, mobile phones serve not just as a personal luxury or an addition to traditional landline telephones but also as a primary means of communication in some areas of the world where communication infrastructure is not in place.

Due to rapid economic growth, technological advances and the obsolescence of electronic equipment in the market, the amount of waste mobile phones has been growing. The life time of these devices is reducing day by day. In fact, most users upgrade their phones due to technological advances and fashion obsolescence; mobile phones are usually taken out of use well before they cease to operate and consequently the potential lifespan of a mobile phone is under 3 years and all of them eventually have to be discarded.

This consumer behavior has resulted in hundreds of millions of mobile phones that are taken out of use each year. Worldwide estimates are that, by 2005, there were over 500 million mobile phones weighing 250,000t stockpiled in drawers,

closets and elsewhere, waiting for disposal. Mobile phones contain toxic elements, such as lead, mercury, chromium, nickel, beryllium, antimony and arsenic as well as valuable metals, such as gold, silver, palladium and platinum. Therefore, recycling of waste mobile phones is required for both environmental protection and resource conservation. Many kinds of technologies are being used still with varying ranges of efficiency and working in different kinds of conditions (Ha et al., 2010). Precious metals including gold are concentrated in anode slimes generated in the tank-house at the electro-refining step of nonferrous metals. In order to separate and recover each precious metal, the anode slimes are totally dissolved in hydrochloric acid each liquor containing chlorine gas or hypochlorite to obtain a concentrated chloride solution from which each precious metal is separated and recovered by mean of different processes (Parajuli et al., 2008).

However the prime focus was on the method, which should be cheaper and effective also even in low concentrations, because of the diversion from conventional methods, which have high operational and maintenance costs, and also the production of activated sludge formed becomes itself a problem to handle (Bhatnagar et al., 2010). The best approach to reduce their concentration or completely removing them is to omit metals from cycling/ entering into the food chain, with a promising recovery of these metals from their sources (Katarzyna, 2010). Precious metals demand is increasing progressively due to its increased use in electronic/electrical devices, catalyst and medical equipment's and mining industry because of their good physical and chemical characteristics (Nilanjana, 2010; Parajuli et al., 2006; Ramesh et al., 2008; Zou et al., 2007).

These precious metals are considered identical to currency internationally under ISO 4217 (Nilanjana, 2010). The recovery of gold from the sources, which contain them is profitable also because of the high price and also reduce the environmental threats (Parajuli et al., 2006). To reduce their concentration into very low amounts many methods are available. Scientists and engineers are using several methods to reduce the concentration of metals in the industrial wastewater, it

includes agglomeration, neutralization, complexation, ion-exchange resin, separation and elution (Zou et al., 2007).

Therefore, the development in this area finds a new method, which is called biosorption. It is more efficient than the previous methods and can reduce the concentration up to traces of precious metals. Because the other methods become less effective when used for low concentrations and also the recovery methods are expensive due to their high demand of labor and time (Nilanjana, 2010; Zou et al., 2007). In the biosorption process, the biosorbents used help in removing pollutants from wastewater and are usually known as biomass, which is easily available in the market throughout the country in cheap amount. Industrial crops produces a huge amounts of cheap material during their reaping and processing of food crops (Lehrfeld, 1996). Woody plants consist of a major part of lignocelluloses, which in turn consists of lignin, hemicelluloses and cellulose. Their structure and properties makes them important in biotechnology (Malherbe and Cloete, 2002). A most tragic situation is that most of lignocelluloses are disposed of by burning, which is even banned in developing countries and is also considered as a threat to environment (Howard et al., 2003).

To solve this residue problem and to use it for beneficiary effects it was studied and recommended to use these residue in removing the metals from the wastewater (Lehrfeld, 1996). The use of these non-living organisms in biosorption makes the process even more cost effective. The biosorbent used here was obtained from coconut. Coconut palm belongs to the family Arecaceae (palm family). Due to various uses it is called the tree of life (Bhatnagar et al., 2010). Coconut is one of the important agricultural crops in Malaysia and is abundantly available in Malaysia. The area over which coconut grows has increased from 117,000 ha (1998) to 147,000 ha in 2004 (Hameed et al., 2008).

1.2   Problem Statement

Increased population, vast industrialization activities and unplanned use of water resources in the world are creating a threat to the water quality in various regions of the world. Electrical and electronic usage has been increased to make our life comfortable but resulted in heaps of wastes popularly known as e-waste. The major concern related with e-waste is two way negative impacts on environment. One is the air water and soil contamination by the untreated e-waste and the other is excessive mining to meet the market demands (Parajuli et al., 2009). However, the problem associating with the recovery of gold is due to the ineffective and costly processes, when the concentration of gold is present in traces. Therefore, biosorption is used to recover traces of metals in comparison to other conventional methods. Conventional methods become costly, ineffective and labor intensive when treating traces of gold. Their removal from the wastewater helps to protect the environment and save the gold resources for future usage due to their rarity.

Biosorption process is preferred due to its cost effectiveness and efficiency. Adsorption capacity of the particular biosorbent to remove gold was studied. The biosorbent under consideration was coconut pith due to its abundance in Malaysia. Instead of its own natural adsorption capacity, a modification process is exercised by the attachment of functional groups called surface modification. This functional group helps greatly to increase the adsorption capacity and functionality of biosrobents (Park et al., 2010; Vijayaraghavan and Yun, 2008). The surface modification will be executed by grafting organosilanes on the sorbent surface. The effect of different parameters such as pH, initial metal concentration and time and temperature effect on the adsorption capacity was studied.

1.3   Research Objectives and Scopes

The objectives and scope of this research are:

i)   To synthesize, functionalize and characterize coconut pith waste as biosorbents for Au(III).

Coconut pith was obtained from T&H Coconut Fiber Sdn. Bhd., Johor. The sample was ground to a particular size of 75-150 μm. Coconut pith was treated chemically using graft polymerization method with the help of γ-aminopropyltriethoxysilane. The characterization of these adsorbents was done using Energy Dispersive X-ray (EDX), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy.

ii)   To study the gold adsorption capacity of virgin coconut pith and grafted coconut pith.

The batch equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models and various kinetic models. The biosorption experiment was carried out at the following conditions.

a) Contact time 1-2880 min

b) Agitation speed 200 rpm.

c) Gold concentration 10 - 500 ppm.

d) pH 2–10.

e) Temperature 30 – 60 $^{\circ}$C.

1.4   Thesis Outline

This thesis consists of five Chapters. Chapter 1 titled introduction contains research background highlighting the current situation and available methods, problem statement, research objectives and scopes, dissertation outline and summary. Objective and scopes lays the boundary of the study. Chapter 2 explains the past research done on gold adsorption, some discoveries on biosorption and technical aspects of gold adsorption system.

Chapter 3 discusses the materials and methods that was adopted during the sample preparation, characterization, and functionalization and in adsorption/desorption experiments. Chapter 4 represents the results and discussion about characterization, modification and biosorption performance of biosorbent. The results for effect of different parameters like pH, contact time, temperature and gold concentration are explained. Conclusions, recommendations and suggestions are presented in Chapter 5. In addition, the response of biosrobents towards metal selectivity and regenerability studies were also investigated.

1.5   Summary

The demand of gold (Au) is increasing because of extensive usage in electrical, electronic instruments, catalysts and medical devices. As a result their concentration in wastewater is increasing, thereby causing a serious threat to the environment. To keep the concentration in safe limits, a process called biosorption was initialized and used, which binds and concentrates the metal from the wastewater. The biosorbent used was abundantly and cheaply available. The attraction of biosorption process lies in low cost and its effective uptake of metal, even in traces of concentration. In Malaysia, coconut pith available in abundance

was used as biosorbent. Surface modification was used to increase its adsorption capacity. The effect of different parameters on the biosorption capacity was studied with VCP and GCP biosorbents. The detailed study of kinetic models and isotherms were also done. The selection of biosorbents was studied with different metals. Regenerability of biosorbents was studied in three cycles.

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