BIOSORPTION OF GOLD(III), PALLADIUM(II) AND SILVER(I) FROM AQUEOUS SOLUTION ONTO LOW–COST *DURIO ZIBETHINUS* HUSK

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UNIVERSITI TEKNOLOGI MALAYSIA

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ABSTRAK

Biopenjerapan adalah salah satu proses kos-rendah untuk menjerap ion logam berharga daripada larutan akueus. Kajian ini mengkaji biopenjerapan ion emas(III), palladium(II), dan perak(I) dari larutan akueus menggunakan *Durio zibethinus* husk (DZH) sebagai penjerap biojisim. DZH telah dicirikan dengan menggunakan spektroskopi FT-IR, menunjukkan bahawa ia mempunyai kumpulan hidroksil, karboksil dan fenol yang berupaya untuk menarik ion logam berharga dari larutan akueus. Keupayaan DZH untuk menjerap ion logam berharga itu telah dikaji dengan sistem biopenjerapan kelompok dibawah pelbagai paramater seperti masa sentuh, pH, dos penjerap, kepekatan awal logam dan suhu. Keadaan optimum telah dicapai untuk memberi peratus penjerapan masing-masing sebanyak 98.50, 93.88 dan 67.18 (%) untuk emas(III), palladium(II) dan perak(I), masing-masing. Data eksperimen masing-masing adalah memenuhi model kinetik tertib-kedua-pseudo untuk kedua-dua emas(III) dan palladium(II), dan tertib-pertama-pseudo untuk perak(I). Keputusan eksperimen juga telah dianalisis dengan persamaan isoterma Langmuir, Freundlich dan Dubinin-Reduskevich pada suhu yang berbeza. Data menunjukkan bahawa pejerapan gold(III), palladium(II) dan perak(I) mematuhi isotema Langmuir dengan penjerapan maksimum yang diperolehi masing-masing adalah sebanyak 500.00, 30.30 and 3.66 mg g^{-1}. Fakta bahawa model Langmuir memenuhi data eksperimen dengan tepat menunjukkan bahawa permukaan DZH adalah homogen. Sifat termodinamik ($\Delta G°$, $\Delta H°$ and $\Delta S°$) juga telah dipelajari pada tiga suhu berlainan (30, 40 and 50^{o}C). Nilai negatif $\Delta H°$ untuk emas(III) dan perak(I) mengesahkan proses penjerapan semulajadi eksotermik, manakala nilai positif bagi penjerapan palladium(II) menunjukkan sifat endotermik kesemulajadiannya. Tenaga pengaktifan (E_a) biopenjerapan telah dianggarkan dari persamaan Arrhenius adalah didapati sebanyak 15, 70.28 and 31.56 kJ mol^{-1}, masing-masing, dan menunjukkan bahawa semua logam yang dipelajari adalah dikawal oleh mekanisme kimia, memandangkan nilai dari tenaga pengaktifannya adalah lebih dari 4 kJ mol^{-1}. Pengesahan emas(III) yang terjerap telah dilakukan menggunakan mikroskop pengimbasan elektron pancaran medan dan analisis sinar-x sebaran tenaga (FESEM-EDX) menunjukkan bahawa peratus atom emas(III) telah dikenalpasti sebanyak 4.12 (%).

ABSTRACT

Biosorption is one of efficient low-cost process of precious metal ions recovery from aqueous solution. This study investigated the biosorption of gold(III), palladium(II) and silver(I) ions from aqueous solution using *Durio zibethinus* husk (DZH) as a biosorbent. The DZH characterized by FT-IR (Fourier transform infrared) spectroscopy, showed that it has hydroxyl, carboxyl and phenolic groups, which have possibility to adsorb precious metal ions from aqueous solution. The ability of DZH was investigated using batch biosorption system. Several parameters were studied such as contact time, pH, adsorbent dosages, initial metal concentration, and temperature. The optimum conditions were achieved to give the adsorption percentage of 98.50, 93.88 and 67.18 (%) for gold(III), palladium(II) and silver(I), respectively. The experimental data was fitted very well the pseudo-second-order kinetic model for both of gold(III) and palladium(II), and pseudo-first-order kinetic model for silver(I), respectively. Experimental results were also analyzed by the Langmuir, Freundlich and Dubinin-Reduskevich isotherm equations at different temperatures. The results shows that the biosorption of gold(III), palladium(II) and silver was follow Langmuir isotherm model for all temperatures with the maximum biosorption capacity was obtained to be 500.00, 30.30 and 3.66 mg g^{-1}, respectively. The fact that the Langmuir model fits the experimental data very well shows that the surface of DZH was homogeneous. The thermodynamic properties ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were also studied at three different temperatures (30, 40 and 50^{o}C). Negative value of $\Delta H°$ for gold(III) and silver(I) confirmed the exothermic nature of adsorption processes, whereas the positive value of palladium(II) adsorption showed endothermic in nature. The activation energy (E_a) of the biosorption of gold(III), palladium(II) and silver(I) were estimated from the Arrhenius equation and found to be 21.15, 70.28 and 31.56 kJ mol^{-1}, respectively, shows that all the metal studied was controlled by chemical mechanism since the value of activation energy more than 4 kJ mol^{-1}. The verification of adsorbed gold(III) on DZH surface was done by Field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX), indicating that the atomic percentage of gold was detected by 4.12 (%).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectrometer
AG25	-	Acid Green 25
ASEAN	-	Association of South East Asian Nations
Ag	-	Argentum (Silver)
Au	-	Aurum (Gold)
Br	-	Bromium
C	-	Carbon
C	-	Celcius
Cd	-	Cadmium
Cl	-	Chlorine
cm	-	Centimeter
CP	-	Citrus Pectin
Cu	-	Copper
DP	-	Durian Peel

DRP	-	Durian Rind Pectin
DZH	-	*Durio Zibethinus* Husk
EDX	-	Energy Dispersion X-Ray
Fe	-	Ferrum
FESEM	-	Field Electron Scanning Electron Microscopy
FT-IR	-	Fourier transform infrared
g	-	gram
GMCCR	-	Glycine Modified Crosslinked Chitosan Resin
H	-	Hydrogen
J	-	Joule
K	-	Kalium
K	-	Kelvin
L	-	Liter
M	-	Molarity
m	-	Mass
MCP	-	Modified Citrus Pectin
mDRP	-	Modified Durian Rind Pectin
mg	-	Miligram
min	-	Minutes

mol	-	Mol
N	-	Nitrogen
O	-	Oxygen
Pd	-	Palladium
pH	-	Potential Hydrogen
Pt	-	Platinum
T	-	Temperature
V	-	Volume

LIST OF SYMBOLS

E_a	-	Activation energy
q_t	-	Amount adsorbed at any time
R	-	Coefficient correlation
ΔH^o	-	Enthalpy change
ΔS^o	-	Entropy change
C_e	-	Equilibrium concentration in solution
C_{Ae}	-	Equilibrium concentration on sorbent
K_c	-	Equilibrium constant
K_F	-	Freundlich equilibrium constant
R	-	Gas constant
ΔG^o	-	Gibbs energy
C_o	-	Initial concentration
B	-	Langmuir constant
K_f	-	Langmuir constant related to adsorption capacity
n	-	Langmuir constant related to intensity
q_m	-	Maximum adsorption capacity
%	-	Percentage

k_1	-	Rate constant pseudo-first-order
k_2	-	Rate constant pseudo-second-order
R_L	-	Separation factor constant
q_e	-	Sorption capacity
$q_{e,cal}$	-	Sorption capacity, calculation
$q_{e,exp}$	-	Sorption capacity, experimental

CHAPTER 1

INTRODUCTION

1.1 Research Background

Gold, palladium and silver are precious metals that have been in high demand for centuries, which were widely applied in many fields such as catalysts in various chemical processes, electrical and electronic industries, medicine and also jewelry (Zereini and Alt, 1999). Gold was extensively used in many high technology areas, particularly in computer applications that demand the highest reliability. Meanwhile, palladium is a well known catalyst in organic synthesis and combustion gas treatment (Suyama *et al.*, 1996). Due to the excellent malleability, ductility, electrical and thermal conductivity, silver is a useful raw material in industries such as for the production of electrical contacts and switching gear, batteries, catalysts and mirrors.

Despite the continuous demand of these materials, consumption of precious metals by the industry grows and expected to increase further in the years to come. Simultaneously, these industries in its development, which not only contribute to water deterioration but also adverse effect to the aquatic ecosystem (Begum, S., 2003).

The toxicity of these precious metal ions to the marine ecosystem can also effect to the human body, which the presence of chloroauric acid can cause extremely destructive to tissues of the mucous membrane and upper respiratory tract, while palladium and silver may cause burn to skin and eyes. As a response, the development of the adsorption methods of these precious metal ions became an imperative task. Currently, there are still no satisfactory methods of removing these metal ions that fulfill environmental regulations and industrial company.

Many studies have been recently focused on conventional methods for the sorption of precious metal ions include membrane filtration (Bessbousse *et al.*, 2008), chemical precipitation (Gonzalez-Munoz *et al.*, 2006), ion exchange (Kiefer *et al.*, 2007), etc. A part from being economically expensive, these techniques have disadvantages of incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products (Pejic *et al.*, 2009).

In recent years, adsorption on solid-solution interface is used as an important method for controlling the extent of heavy metal ions in wastewater (Bulut and Tez, 2007b). Activated carbon is traditionally used to adsorb precious metal ions form aqueous solution, however, its manufacturing and regeneration poses several constrains and represents a major portion of the operating cost, which limits their usage. This has led many researchers to find low-cost material such as coal, fly ash, agricultural wastes and biosorbents (Bulut and Tez, 2007a). In general, an adsorbent can be assumed as “low-cost” if it requires little processing, abundant in nature, or could be waste material from industry (Bulut and Tez, 2007b).

A lot of sorbents have been proposed to be used for precious metal sorption, including chitosan (Arrascue *et al.*, 2003), egg shell membrane (Ishikawa *et al.*, 2002), dealginated seaweed waste (Romero-González *et al.*, 2003), persimmon tannin gel (Nakajima *et al.*, 2003), etc. There has been a continuous interest in finding a potential biosorbent, a property of certain types of biosorbents that can remove precious metals from aqueous solution, to gain the maximum profit from the process.

Due to the need to find a new and inexpensive adsorbent for metal adsorption, this work focused on the study of potential of *Durio zibethinus* husk (DZH), an abundant tropical fruit waste founded in Malaysia. In addition, Khedari *et al.* (2003) reported that the DZH contained a large amount of cellulose, which has a great potential to attract metal ions from aqueous solution. Detail studies on the physical properties and sorption characteristics of the DZH toward adsorption of precious metal ions were done.

1.2 Problem Statement

The growing amount of electrical and electronic industrial waste, especially precious metals, such as gold, palladium and silver were creating negative impacts to the human and environment. Besides, that metals also bringing problems with regards to the supply of raw materials, due to the highly valuable and the limited source. Recovering precious metals are important, because it is not only beneficial to reduce cost, but it also could reserve the resources of precious metals and protect the environment. Thus, the need of economical and effective methods for the recovery of precious metal ions is became an imperative concern.

Therefore, the use of biomass from tropical fruit wastes as a biosorbent could be investigated. Due to high consumption of Durians, massive amount of the husk waste caused several problems to the environment. In accordance to this problem, this research was proposed to use this agricultural waste as a low-cost biosorbents for adsorption of precious metal ions.

1.3 Research Objectives

The objectives of this study are:

1. To study the physico-chemical properties of DZH.
2. To optimize the adsorption of precious metal ions onto DZH under various parameters.
3. To study the kinetic and thermodynamics models of those precious metal ions adsorption onto DZH.

1.4 Scopes of Research

Scopes of this study consists of:

1. Characterization of DZH by Fourier transform infrared (FT-IR) and Field electron scanning energy microscopy spectrometer-electron dispersion x-ray spectrometer (FESEM-EDX) before and after adsorption.

2. Optimization of biosorption condition of gold(III), palladium(II) and silver(I) under several parameters, such as contact time (30-240 min), pH solution (pH 2-10), biosorbent dosage (0.005-0.04 g), initial metal concentration (10-700 mg L^{-1}) and temperature (30-50^{o}C).

3. Study of the kinetic behaviour of precious metal ion using a Lagergren pseudo-first-order and pseudo-second-order and the thermodynamics parameters such as the equilibrium studies (Langmuir, Freundlich and Dubinin-Raduskevich isotherm models) and also enthalpy (ΔH^o), enthropy (ΔS^o), Gibbs Energy (ΔG^o) as well as activation energy (E_a) for all of those three metals.

1.5 Significant of Study

This work was conducted to study the biosorption of precious metal ions (gold(III), palladium(II) and silver(I)) onto DZH. Due to the presence of high content of cellulose, DZH was expected to demonstrate high ability of adsorbing precious metal ions from aqueous solution. Since the DZH could be prepared easily, the expenditure on adsorbent usage could be reduced. Moreover, DZH was an abundant and low-cost material which could be easily obtained. In term of efficiency and effectiveness, this biosorbent was viable to be applied in the industrial wastewater treatment. Furthermore, the biosorption process does not generate large amount of sludge or any contaminant. As a consequence, DZH was predicted to boast a great and potential biosorbent, as well as contributing a green and sustainable method.

1.6 Outline of the Thesis

This thesis reported the biosorption of precious metal ions from aqueous solution onto low-cost DZH. Chapter 1 described the research background, problem statement, research objective, scope of research, significant of study and also outline of the thesis.

Chapter 2 reviewed literatures those related to precious metal ions, adsorption, treatment technology for the removal of heavy metals ions, adsorption, biosorption of precious metal ions, and equilibrium of biosorption, as well as biosorption kinetics and also *Durio zibethinus* husk as biosorbent.

Chapter 3 revealed the research design and methodology employed in this work. This chapter described all of raw materials used and the experimental procedures. The research design and independent variables were clarified at the end of this chapter.

Chapter 4 discussed all of the experimental results have been conducted in this research. The first part of this chapter dealt with the characterization of DZH followed by optimization of the biosorption. Finally, the kinetics and thermodynamic studies were discussed for gold(III), palladium(II) and silver. The comparison of DZH with other biosorbents was stated at the last part of this chapter, as well as the proposed biosorption interaction mechanism.

Chapter 5 illustrated the general conclusion derived from this study and also suggested recommendations for future work.

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