Adsorptive Recovery of Au(III) from Aqueous Solution Using Modified Bagasse Biosorbent

Theeraporn Rubcumintara

Abstract—The recovery of Au(III) from aqueous chloride solutions onto modified bagasse biosorbent was investigated. The parameters for biosorbent preparation as well as gold recovery were studied in detail. It was found that 99.8% of sugarcane bagasse could be modified as biosorbent having better physical properties for adsorption. The solution pH, sorbent dosage, initial Au(III) concentration and temperature were the studied variables that affect the efficiency of gold recovery as well as adsorption behavior. The efficiency of 99% for Au(III) recovery was obtained under the following conditions: 25 mg sorbent, 25 mL of 25-500 mg/L Au(III), pH 2, 150 rpm, 4 h and 25°C. The 99% of gold recovery still obtained in only 1 h or less with the increasing of dosage or temperature. The gold adsorption in this study was best fitted with Langmuir isotherm with the increasing of dosage or temperature. The gold adsorption kinetics was also evaluated in terms of the pseudo first-order and pseudo second-order kinetic models. The high activation energy of 45.8 kJ/mol was estimated which represents a chemisorption process. The adsorption mechanism in this study is clarified to be the oxidation of hydroxyl to carboxyl in biosorbent and reduction of trivalent gold ions to metallic gold simultaneously on biosorbent surface. The results from ORP measurement, FT-IR and EDS spectra including SEM images were the supported evidence for this adsorption mechanism. The modified bagasse biosorbent therefore has potential in gold recovery process.

Index Terms—Au(III) recovery, modified bagasse, biosorbent.

I. INTRODUCTION

Because the primary resource of gold has been declined due to the less abundant on earth crust, the world gold production from mining has then be limited [1]. About one-third of the precious metals available from electronic waste are recorded to be gold, then the secondary resource from used appliances or electronic scraps has gold as the composition now become the potential source for gold production and can be considered as the major economic driver for recycling of electronic waste [2], [3]. To extract gold from electronic waste, the hydrometallurgical routes such as gold precipitation, ion-exchange and solvent extraction has been selected for processing [3]. All the above recovery processes require chemical agents that need further treatment in the final step. The investigation to develop an environmentally friendly technique for the recovery of gold from electronic waste is still continuing. The separation of metal ions from solutions using biomass materials has gained more attentions due to their availability and cost. In recent years, the growing interest has been focused on the development of biosorbents prepared from plant materials or agricultural wastes as the adsorbent for gold ions [4]-[6]. Many research works are concerned with the utilization of bio-waste to directly prepare the novel adsorption gels which can be performed reductive adsorption of Au (III) from chloride medium solutions [7]-[19]. These bio-waste materials are generally composed of natural lignocellulosic fibers and tannin containing sufficient polyphenolic groups which have high capability for interaction with heavy metals such as iron and gold. At present, the adsorption technique to recover gold from aqueous solutions using biomass wastes has become the most promising method and gained more interest due to its low cost, high efficiency and eco-friendly method [20]-[24]. Thailand has been known as one of the leading countries for sugar production from sugarcane, massive amounts of bagasse from sugar industry are disposed as biowaste or utilized as raw material for paper industry. This sugarcane bagasse composes of cellulose and lignin which have many hydroxyl and/or polyphenolic groups that can be chemically reacted to produce adsorbent having a good capacity for Cu (II), Cd (II) and Pb (II) ions [25]. This work was attempted to prepare the adsorbent from sugarcane bagasse for gold separation, the efficiency of Au(III) recovery from aqueous chloride solution using the modified bagasse biosorbent as well as adsorption mechanism were investigated in this study.

A. Materials

Bagasse used in this work is come from sugar plant located at 14/1 Moo 10 Tambon Tamaka, Saengxuto Road, Amphur Tamaka, Kanchanaburi 71120, Thailand. The cellulose content in the bagasse was determined to be 40.1% (on dry basis). The Au(III) solutions used in this work were in the form of tetra-chloro complex of AuCl₄⁻ (HAuCl₄·4H₂O) and all other chemical reagents were of analytical grade.

B. Biosorbent Preparation

Sugarcane bagasse that washed, oven dried and ground to small size was refluxed with concentrated sulfuric acid for various time and solid liquid ratio at fixed temperature and stirring speed at 100°C and 200 rpm, respectively. The brown black precipitated product called as modified bagasse biosorbent was neutralized, washed, oven dried and ground to 100 - 140 mesh and used as biosorbent for all adsorption experiments.

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C. Biosorption Experiments

A given amount (25 mg) of modified biosorbent (on dry basis) was added to the gold solutions (25 mL) at the controlled conditions of initial concentration, pH and temperature for a given time with the fixed shaking rate at 150 rpm. At the end of adsorption period, the solution mixture was filtered and solid residue was washed and dried in the oven and then characterized using Fourier transform infrared (FT-IR), scanning electron microscope (SEM) and energy dispersive X-ray (EDS). The concentration of remaining gold in residual filtrate was measured by atomic absorption spectroscopy (AAS). The amount of gold adsorption, \( q_t \) (mg Au/g) was computed according to Equation (1) where \( C_i \) and \( C_t \) are the concentrations of gold in solution (mg/L) at initial time and at time \( t \), respectively; \( V \), the volume of solution (mL) and \( W \), the dosage of sorbent used (mg). The percentage of gold recovery from solution can also be calculated by Equation (2).

\[
q_t = \frac{(C_i-C_t)V}{W} \tag{1}
\]

\[
\% \text{Au(III) recovery} = \left( \frac{C_i-C_t}{C_i} \right) \times 100 \tag{2}
\]

The effects of solution pH, sorbent dosage, initial Au(III) concentration and temperature on adsorption capacity as well as the efficiency of gold recovery were also examined. The EDS pattern, SEM images and FT-IR spectra of the biosorbent before and after adsorption as well as oxidation-reduction potential (ORP) were all used to clarify the adsorption mechanism.

II. RESULTS AND DISCUSSION

A. Characterization of Modified Biosorbent

The 99.8% yield of modified biosorbent can be achieved from the reaction of sugarcane bagasse with concentrated sulfuric acid by using the conditions of bagasse to sulfuric acid ratio, time, temperature and stirring speed as follows: 1 to 3 g/mL, 6 h, 100 °C and 200 rpm, respectively. The cellulose content determined from acid detergent method as well as physical properties from BET analysis of bagasse and modified bagasse biosorbent were characterized as shown in Table 1. Decreasing of cellulose content from 40.1 to 16.8% from bagasse to modified biosorbent is due to the consumption of hydroxyl group in the cellulose during cross-linking condensation reaction with concentrated sulfuric acid to form brown black solid known as modified biosorbent having higher porosity and surface area. As shown in Fig. 1 with the assignments of the FT-IR absorption band, the main bands observed for bagasse are as follows: O-H stretching at 3406 cm\(^{-1}\), C-H stretching at 2907 cm\(^{-1}\), and O-H bending of absorbed water at 1639 cm\(^{-1}\) [26]. After condensation reaction, the broader band with less intensity of O-H stretching is observed at 3442 cm\(^{-1}\). The change of the intensity of the band at 3442 cm\(^{-1}\) which is slightly less broad for bagasse in comparison with broader for bagasse biosorbent suggests this condensation result. The new peaks of biosorbent are shown at 1700 and 1196 cm\(^{-1}\) which represent the C=O stretching and C-O-C stretching, respectively. The formation of C-O-C stretching band after condensation reaction of bagasse is the evidence to support that the cross-linking occurs at the hydroxyl group of cellulose [13]. The higher surface area as well as porosity of biosorbent as shown from Table I is consequently resulted from the cross-linking reaction with concentrated sulfuric acid.

**TABLE 1: PHYSICAL PROPERTIES OF SUGARCANE BAGASSE IN COMPARISON WITH MODIFIED BIOSORBENT**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bagasse</th>
<th>Bagasse biosorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m(^2)/g)</td>
<td>0.948</td>
<td>4.858</td>
</tr>
<tr>
<td>Pore volume (cm(^3)/g)</td>
<td>3.777×10(^{-1})</td>
<td>1.752×10(^{-1})</td>
</tr>
<tr>
<td>Pore size (Å)</td>
<td>67.33</td>
<td>133.9</td>
</tr>
</tbody>
</table>

![Fig. 1. FT-IR spectra of bagasse before and after modification reaction.](image1)

![Fig. 2. Effect of pH on gold recovery.](image2)
C. Effect of Sorbent Dosage

The effect of sorbent dosage on gold adsorption and gold recovery was observed, the gold recovery increases with the increase of sorbent dosage as shown in Fig 3a-3b. The adsorption rate as well as % recovery increased rapidly at initial time and finally reached equilibrium value of 99% after 1 h for 35 mg dosage, whereas more than 95% recovery can be accomplished after 4 h of contact time using 15-25 mg of dosage. It should be noted that only 30% of Au(III) can be recovered with 5 mg of dosage in 6 h but with the high adsorption capacity. Therefore, to maximize the adsorption capacity, the 1 mg of dosage at 170 h was used for the next experiment, the result was shown in Fig. 4. The gold loading capacity can be maximized to 1497.5 mg of gold per g of adsorbent (7.6 mmol/g).

D. Effect of Initial Au(III) Concentration

The initial Au(III) concentration of 25, 50, 100, 300, 500 and 800 mg/L were chosen to be adsorbed by using 25 mg of biosorbent at equilibrium time of 48 h and at pH 2, 25 °C, and 150 rpm. It was found from the result that the Au(III) concentration and adsorption capacity at equilibrium (C_e and q_e) strongly depends on the initial concentration of Au(III) ions. Equilibrium gold adsorption capacity was increased with the increase of initial Au(III) concentration from 25 to 800 mg/L. The gold recovery reached almost 100% for the initial Au(III) concentration up to 500 mg/L. The results are shown in Table III and Fig. 5 (a) and (b).

<table>
<thead>
<tr>
<th>Au(III) mg/L</th>
<th>C_e (m/mL)</th>
<th>q_e (mg/g)</th>
<th>% Au recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.096</td>
<td>17.38</td>
<td>99.6</td>
</tr>
<tr>
<td>50</td>
<td>0.014</td>
<td>32.83</td>
<td>99.9</td>
</tr>
<tr>
<td>100</td>
<td>0.205</td>
<td>63.39</td>
<td>99.8</td>
</tr>
<tr>
<td>300</td>
<td>0.395</td>
<td>204.30</td>
<td>99.9</td>
</tr>
<tr>
<td>500</td>
<td>1.023</td>
<td>278.96</td>
<td>99.7</td>
</tr>
<tr>
<td>800</td>
<td>61.4</td>
<td>537.85</td>
<td>92.6</td>
</tr>
</tbody>
</table>

Table III: Effect of Initial Au(III) Concentration onto Modified Biosorbent. (Solution Volume 25 mL, Biosorbent Dosage 25 mg, pH 2, 25 °C, 150 rpm, 48 h)

E. Biosorption Isotherm

In this study, the two commonly used isotherms namely, Langmuir and Freundlich isotherm were applied to explain or predict their equilibrium parameters for Au(III) adsorption onto biosorbent. The Langmuir model is based on the
monolayer adsorption on active sites of biosorbent. The Langmuir isotherm can be expressed in the form of non-linear and linear equations as shown in Equations (4) and (5);

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad \text{(non-linear form)} \quad (4)
\]

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{1}{q_{\text{max}}} C_e \quad \text{(linear form)} \quad (5)
\]

where \( C_e \) is the concentration of Au(III) solution at equilibrium (mg/L), \( q_e \) and \( q_{\text{max}} \) are the equilibrium and maximum of Au(III) adsorbed at equilibrium (mg/g), and \( K_L \) is the Langmuir equilibrium constant which is related to the adsorption energy. The linear plot between \( C_e/q_e \) and \( C_e \) using data available from Table III was shown in Fig. 6 (a).

The Frundlich isotherm explains the adsorption based on the assumption of multiple layer on heterogeneous surface. The empirical equation and its logarithmic form can be expressed as Equations (6) and (7), respectively.

\[
q_e = K_F C_e^n \quad \text{(non-linear form)} \quad (6)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(linear form)} \quad (7)
\]

where \( K_F \) and \( n \) are the Frundlich constant related to adsorption capacity of adsorbent and adsorption intensity, respectively. The values of \( K_F \) and \( n \) can be evaluated from the intercept and slope of the linear plot between \( \log q_e \) and \( \log C_e \) as shown in Fig. 6 (b).

It was shown from the results of linear plots in Fig. 6 that the Au(III) adsorption onto biosorbent follows the Langmuir model due to the higher in correlation coefficient value \( (R^2) \). This suggests that the monolayer adsorption of Au(III) dominates on biosorbent surface.

**F. Biosorption Kinetics**

The kinetic models for adsorption namely pseudo-first order and pseudo-second order model were considered. The rate of adsorption capacity over the contact time for the first order and second order can be written as Equations (8) and (9).

By integrating Equations (8) and (9) using boundary conditions from \( t = 0 \) to \( t = t \) and \( q_e = 0 \) to \( q_e = q_e \), the equations after rearrangement were shown as Equations 10 and 11 for pseudo-first order and pseudo-second order, respectively.

\[
\frac{d q_t}{d t} = k_1 (q_e - q_t) \quad (8)
\]

\[
\frac{d q_t}{d t} = k_2 (q_e - q_t)^2 \quad (9)
\]

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (10)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)
\]

where \( k_1 \) and \( k_2 \) are the rate constant of pseudo-first order (min\(^{-1}\)) and pseudo-second order (kg mol\(^{-1}\) min\(^{-1}\)), respectively. The temperature at 25, 35, 45 and 55 °C were varied for adsorption experiments, the adsorption capacity is increased with time and increased with temperature as observed in Fig. 7. The \( R^2 \) values of the plots of \( \log (q_e-q_t) \) versus time \( t \) in Fig. 8 (a) for each temperature were between 0.94-0.99 which is a little higher than the \( R^2 \) values from the plots of \( t/q_t \) versus time \( t \) represented as pseudo-second order model as shown in Fig. 8(b). The evaluated pseudo-first order rate constants \( k_1 \) for each temperature were then calculated and use in the Arrhenius plot (Equation (12) and Fig. 9). The activation energy of 45.8 kJ/mol can be evaluated from the slope of this plot. Chemical adsorption is usually between 8.4-83.7 kJ/mol [13]. This reveals that the chemical adsorption dominates in this adsorption process.

\[
\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad (12)
\]

where \( R \) is the gas constant, \( A \) is constant and \( E_a \) is the activation energy for gold adsorption process.

![Fig. 6. The linear plots based on Langmuir isotherm (a) and Frundlich isotherm (b) : (Solution volume 25 mL with initial gold concentration 25-800 mg/L, biosorbent dosage 25 mg, pH 2, 25 °C, 150 rpm, 48 h).](image)

![Fig. 7. Effect of contact time on gold adsorption capacity at different temperature. (Solution volume 25 mL with initial gold concentration 97.6 mg/L, biosorbent dosage 35 mg, 25-55 °C, 150 rpm, 3 h).](image)
Fig. 8. Adsorption kinetics of Au(III) by modified bagasse biosorbent at different temperatures for pseudo-first order (a) and pseudo-second order (b). (Solution volume 25 mL with initial gold concentration 97.6 mg/L, sorbent dosage 35 mg, 25-55 °C, 150 rpm, 3 h).

Fig. 9. Arrhenius plot from kinetics data of Au(III) by modified bagasse biosorbent at different temperatures. (Solution volume 25 mL with initial Au(III) concentration 97.6 mg/L, sorbent dosage 35 mg, 25-55 °C, 150 rpm, 3 h).

Fig. 10. FT-IR spectra of modified bagasse biosorbent before and after adsorption.

Fig. 11. SEM images of modified bagasse biosorbent after adsorption at different magnification (a for 750 magnification and b for 10,000 magnification) reveals the gold particle on the surface.

Fig. 12. Elemental gold peak from EDS spectra of modified bagasse biosorbent after adsorption.

Fig. 13. Oxidation-reduction potential versus time. (Solution volume 25 mL with initial gold concentration 97.6 mg/L, biosorbent dosage 35 mg, 55 °C, 150 rpm)

G. Adsorption Mechanism

The results from FT-IR spectra, SEM images and EDS patterns as shown in Fig. 10-Fig. 12 are confirmed the oxidation of hydroxyl to carbonyl group in biosorbent and the reduction of gold(III) ions that occur simultaneously on the surface of synthesized biosorbent as expressed by Equations 13 and 14 and the overall reaction (Equation (15)). From FT-IR spectra (Fig. 10), the peak for O-H (3442 cm$^{-1}$), C=O (1700 cm$^{-1}$) and C-O-C (1196 cm$^{-1}$) bands were shifted after adsorption as shown in Fig. 10. The hydroxyl peak has become broader, the intensity of carbonyl peak has increased and the sharp peak of C-O-C has become less intense and broader. All these appearance are signified that the redox reaction take place on the surface of biosorbent. The hydroxyl group is oxidized to the carbonyl group as well as the binding of Au ions. The other supports came from SEM images (Fig. 11) at 10,000 time of magnification, the metallic gold particle can be observed on the biosorbent surface. The EDS patterns shown in Fig. 12 is the supportive evidence for the appearance of gold in metallic form on biosorbent after adsorption.

\[
\begin{align*}
\text{R-OH} & \rightarrow \text{R=O} + \text{H}^+ + e^- \\
\text{AuCl}_3^- + 3e^- & \rightarrow \text{Au}^0 + 4\text{Cl}^- 
\end{align*}
\]
AuCl₄⁻ + 3R-OH → Au⁰ + 4Cl⁻ + 3R=O + 3H⁺ (15)

Fig. 13 shows that the measurement of oxidation-reduction potential or ORP as a function of time, the decrease of ORP in the first hour indicates the reduction of gold ions in solution to metallic gold and then level off after one hour which is coincided with the maximum percentage of gold recovery after one hour of adsorption.

IV. CONCLUSION

It can be concluded from this investigation that sugarcane bagasse can be modified by the reaction with concentrated sulfuric acid to produce biosorbent for gold recovery effectively. The 99% gold recovery was accomplished when using the initial gold concentration in the range from 25 to 500 mg/L. The adsorption behavior represent Langmuir model. The activation energy of 45.8 kJ/mol suggests that the adsorption process is chemically control. The adsorption mechanism was elucidated to be the oxidation of hydroxyl group to carbonyl group in synthesized biosorbent and reduction of Au(III) on the surface of adsorbent simultaneously. The sugarcane bagasse might be the low cost material for gold recovery as the alternative choice.

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REFERENCES


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