Response surface methodology (RSM) for optimization of silver biorecovery process from simulated silver electroplating wastewater using oil palm (*Elaeis guineensis*) leaves extract as the reducing and stabilizing agents

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Abstract. Oil palm (*Elaeis guineensis*) leaves extract is capable of acting as reducing and stabilizing agents to reduce and recover silver from simulated silver electroplating wastewater by chemical reduction method. First, Plackett-Burman design (PBD) was used to evaluate six factors that affecting silver biorecovery process. From the PBD analysis, only four factors were found to be significant. In order to maximize the biorecovery process, the significant factors were further optimized using response surface methodology (RSM). The optimum conditions were found to be 50% (v/v) of palm leaves extract, 1975 mg/L of initial silver ions concentration in wastewater, pH 7.5 of reaction medium and 70 °C of reaction temperature yielding 93.30% of silver being recovered. Characterization of the biorecovered solid particles revealed that elemental silver was successfully reduced and recovered from the wastewater with sizes ranging from 20 to 60 nm. On the other hand, characterization of the palm leaves extract revealed that hydroxyl and carboxyl groups compounds act as reducing agents to reduce silver ions into zero-valence silver atoms while polysaccharides, carboxylic acids and proteins act as stabilizing agents to cap and stabilize the silver solid particles formed.

1. Introduction

Silver is widely used in various applications especially in electrical and electronics industries owing to its excellent thermal and electrical conductivities. Depleted sources from its ores and increasing demands have encourage recovery of silver from secondary sources. Conventional silver recovery methods have several disadvantages such as high capital and operational costs due to expensive chemical reagents and electricity supply, and generation of silver-complexes sludge which requires further treatment and purification [1]. On the other hand, chemical reduction is one of the recovery methods where soluble silver cations are reduced by a reducing agent to form insoluble elemental silver solids [2]. The silver solids were then separated from the solution either by filtration, sedimentation or centrifugation. Commonly used reducing agents are sodium borohydride (NaBH₄) [3], hydrazine (N₂H₄) [4] and hydrogen peroxide (H₂O₂) [5]. Unfortunately, these commercial reducing agents are highly toxic and dangerously unstable [2].

Extracts of plants are known to possess high antioxidant activities and great reducing capacities which could act as both reducing as well as stabilizing agents [6] to reduce metal ions into zero-
valence metal atoms and cap the metal solids formed for stabilization [7]. Oil palm (*Elaeis guineensis*) leaves extract is rich in polyphenols content [8] and has high antioxidant activity [9]. In addition, oil palm trees are widely planted in Malaysia. Mature leaves are pruned during harvesting rounds and replanting [10], and hence there are plenty sources of oil palm leaves.

Optimization is one of the critical steps in developing any protocol of chemical process or synthesis. There are two most commonly used optimization methods: classical and statistical. The classical method is based on the “one-factor-at-a-time” method in which one independent factor is changed at a time while other factors are kept constant [11]. This method may lead to unreliable results and inaccurate optimized conditions since it does not include the interaction effects among the factors studied. Additionally, it also involves a relatively large number of experiments necessary to conduct the research, which makes it laborious, and great expenses due to high consumption of reagents and materials, and time-consuming, especially when the number of factors is large [12]. On the other hand, the statistical method, response surface methodology (RSM), uses quantitative experimental data obtained from appropriate experimental design to determine and simultaneously solve multivariate equations [11]. It is a collection of statistical techniques for designing experiments, building empirical models, evaluating the effects of factors, and analyzing optimum conditions of factors for desirable responses [13].

The objective of this present work was to apply RSM in optimizing the process parameters for maximizing silver biorecovery from simulated silver electroplating wastewater using oil palm leaves extract as the reducing and stabilizing agents.

2. Experimental

2.1. Chemicals and materials
Silver nitrate (AgNO₃), copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), nitric acid (HNO₃) and sodium hydroxide (NaOH). All chemicals were of analytical grade (Merck) and used as supplied. Palm leaves were pruned from oil palm (*Elaeis guineensis*) trees planted in UiTM Shah Alam campus. Only matured, dark green palm leaves were collected.

2.2. Preparation of palm leaves extract
Fresh palm leaves were collected, washed, cut into small pieces and oven dried at 70 °C for 12 hours. The dried palm leaves were ground into powder using a grinder. First, 500 mL of distilled water was heated until reaching 70 °C. Fifty gram of the palm leaves powder was weighed and mixed with the water bath. The mixture was stirred at 600 rpm for 10 minutes and filtered. The obtained extract was stored in refrigerator at 4 °C for further use [8].

2.3. Preparation of simulated silver electroplating wastewater
Silver nitrate was used as the silver precursor where 7.8738 g silver nitrate salt was dissolved in one liter of distilled water to produce simulated silver electroplating wastewater stock solution containing 5000 mg/L of silver ions (Ag⁺). The simulated wastewater stock solution was diluted later to prepare the working solutions according to the desired silver ions concentration. Measured amount of copper (II) nitrate trihydrate salt was also added according to the preferred mass concentration ratio of copper ions to silver ions (%w/w), varying from 10 to 50%. Copper was also present in the wastewater because copper was plated first as a base metal before plating with silver.

2.4. Silver biorecovery process
Palm leaves extract was mixed with 200 mL simulated silver electroplating wastewater and continuously stirred at 500 rpm. After certain minutes, the mixture was centrifuged at 10000 rpm for 10 minutes to separate suspended solids from residue solution [14]. The residue solution was subjected to atomic absorption spectroscopy (AAS) using Hitachi Z-2000 Flame AAS to determine the concentration of silver ions left.
2.5. Experimental designs

2.5.1. Screening of significant factors. Large number of factors could potentially affect the silver biorecovery process, but some of them do not have significant effect on it [15]. Therefore, in this study, Plackett–Burman design (PBD) was used to screen the most statistically significant factors. PBD was chosen because it can identify main factors by relatively few experiments assuming that interaction effects between factors are negligible [15]. Six factors (determined from our previous preliminary experiments [16]) were selected as independent variables and amount of silver ions reduced, $M$ (%) was chosen as the response. The factors were varied; the minimum and maximum, are specified in table 1.

| Factors                                      | Code | Minimum (-1) | Maximum (+1) |
|----------------------------------------------|------|--------------|--------------|
| Amount of palm leaves extract (%v/v)         | A    | 10           | 50           |
| Concentration of silver ions in wastewater (mg/L) | B    | 500          | 2500         |
| pH of reaction medium                        | C    | 2            | 10           |
| Reaction temperature (°C)                    | D    | 30           | 90           |
| Concentration of copper ions in wastewater (%w/w) | E    | 10           | 50           |
| Reaction time (h)                            | F    | 1            | 2            |

2.5.2. Optimization by RSM. Based on the results of PBD analysis, four significant factors were simultaneously optimized using RSM. Other insignificant factors i.e. concentration of copper ions in wastewater and reaction time were kept constant at 10% (w/w) and 2 hours respectively. Central composite design (CCD) consists of 24 full factorial designs augmented with a group of star points (axial) and six center points (cube) was chosen to design the experiments. The value of alpha ($\alpha$) was determined to be 2 from the factorial portion $2^4$ of the fractional factorial design of four variables which allows simultaneous rotatability and orthogonality [17]. Each factor in the design was studied at five different levels as shown in table 2. Thirty experiments were conducted with amount of silver ions reduced, $M$ (%) as the response.

| Factors                                      | Code | $-\alpha$ | -1 | 0 | +1 | $+\alpha$ |
|----------------------------------------------|------|-----------|----|---|----|-----------|
| Amount of palm leaves extract (%v/v)         | $X_1$| 10        | 20 | 30| 40 | 50        |
| Concentration of silver ions in wastewater (mg/L) | $X_2$| 500       | 1000 | 1500 | 2000 | 2500 |
| pH of reaction medium                        | $X_3$| 2         | 4  | 6 | 8  | 10        |
| Reaction temperature (°C)                    | $X_4$| 30        | 45 | 60| 75 | 90        |

2.6. Characterization

Solid particles recovered at optimum conditions were characterized by field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray (EDX) using FEI Quanta 450 SEM. Aside from that, palm leaves extract, residue solution and biorecovered solid particles were subjected to Fourier-transform infrared spectroscopy (FTIR) using PerkinElmer Spectrum One FTIR.

3. Results and discussion

3.1. Plackett–Burman design (PBD)

Results obtained from PBD experiments (data not shown) were analyzed using MINITAB (version 18.1, Minitab Inc., Pennsylvania, U.S.A.) statistical software. The software generates main effects plot together with Pareto chart as shown in figure 1 and 2 respectively. From figure 1, it is observed that all factors show positive effects except concentration of copper ions in wastewater because the presence of copper ions competes with silver ions and therefore lowering the yield of silver ions being reduced. The
Pareto chart in figure 2 indicates a minimum t-value limit of 2.05 at a confidence level of 95.0%. The length of each factor is proportional to the absolute values of estimated effects and t-value is included as vertical reference line. In Pareto Chart, the effects above the t-value limit are considered significant factors and effects below the t-value limit are not significant [18].

![Figure 1. Main effects plot](image1)

![Figure 2. Pareto chart](image2)

3.2. Central composite design (CCD)

Results obtained from CCD experiments (data not shown) were analyzed using MINITAB software. Regression analysis was performed to fit the response data to a second-order quadratic model.

3.2.1. Model equation. From the software, the following model equation (1) in coded factors was proposed for the silver biorecovery process:

$$M = -20.41 + 0.8852X_1 + 0.036096X_2 + 5.947X_3 + 1.0664X_4 - 0.010207X_1^2 - 0.000009X_2^2 - 0.4736X_3^2 - 0.008431X_4^2 - 0.000049X_1X_2 + 0.01441X_1X_3 + 0.001487X_1X_4 + 0.000067X_2X_3 + 0.000005X_2X_4 + 0.00506X_3X_4$$ (1)

where $M$ is amount of silver ions reduced (%), $X_1$ is amount of palm leaves extract (%v/v), $X_2$ is initial concentration of silver ions in wastewater (mg/L), $X_3$ is pH of reaction medium and $X_4$ is reaction temperature (°C).

3.2.2. Analysis of variance (ANOVA). ANOVA was performed to test the significance of the proposed model in equation (1) and the results are summarized in table 3. The model F-value (2085.12) with very low p-value (< 0.0001) indicated that the proposed model was highly significant and appeared to reasonably represent the process. Non-significant lack-of-fit (LOF) confirms the ability of the proposed model for well-fitted the experimental data (LOF p-value 0.197). This is proved by the coefficient of determination, $R^2$ (0.9993) which indicates the proposed model is best suited for predicting the performance of the silver biorecovery process and only 0.07% of the total variations were not satisfactorily explained by the model [19]. The predicted $R^2$ (0.9978) is reasonable in agreement with the adjusted $R^2$ (0.9988). High adjusted $R^2$ values indicate a good correlation and relation between the experimental data and the obtained model [20]. Figure 3 shows the 3D response surface plots.
Table 3. ANOVA for the regression coefficients of the proposed model equation (1).

| Source         | Degrees of freedom | Sum of squares | Mean sum of squares | F-value | p-value |
|----------------|--------------------|----------------|--------------------|---------|---------|
| Model          | 14                 | 1328.95        | 110.746            | 2085.12 | 0.000   |
| Linear         | 4                  | 1065.55        | 266.388            | 5015.57 | 0.000   |
| Quadratic      | 4                  | 259.92         | 64.981             | 1223.47 | 0.000   |
| Interaction    | 6                  | 3.47           | 0.867              | 16.33   | 0.000   |
| Residual error | 15                 | 0.90           | 0.053              | 16.33   | 0.000   |
| Lack-of-fit    | 10                 | 0.76           | 0.063              | 2.20    | 0.197   |
| Pure error     | 5                  | 0.14           | 0.029              |         |         |
| Total          | 29                 | 1329.85        |                    |         |         |

*Probability (corresponding level of significance, p < 0.05 was considered as significant).

Figure 3. Response surface plot showing the effect of: (a) amount of palm leaves extract (%v/v) and concentration of silver ions (mg/L); (b) amount of palm leaves extract (%v/v) and pH of reaction medium; (c) amount of palm leaves extract (%v/v) and reaction temperature (°C); (d) concentration of silver ions (mg/L) and pH of reaction medium; (e) concentration of silver ions (mg/L) and reaction temperature (°C); and (f) pH of reaction medium and reaction temperature (°C), on amount of silver ions reduced (%).

3.2.3. Optimum conditions. Figure 4 shows the optimization plot generated by the software.

Figure 4. Optimization plot
3.2.4. Validation. Validation experiment was conducted at the predicted optimum conditions. From the experiment, the measured $M$ was 93.30%, which is 3.98% lower than the predicted value. Therefore, the proposed mathematical model is acceptable and the predicted optimum conditions were valid.

3.3. Characterizations

Figure 5 shows the captured SEM image of the biorecovered solid particles at 200000 x magnification. It is observed that the solid particles were polydispersed with mostly spherical and irregular in shapes, and homogeneously distributed. The particles sizes were ranging from 20 to 60 nm. Figure 6 shows EDX spectrum of the biorecovered solid particles together with their assigned peaks. Strong peaks observed around 2.96 keV (Lα) confirms the biorecovered solid particles to be elemental silver.

![Figure 5. SEM of the biorecovered solid particles](image1)

![Figure 6. EDX of the biorecovered solid particles](image2)

The shifting of peak 3351 cm\(^{-1}\) to 3265 cm\(^{-1}\) and significant increase of peak 1668 cm\(^{-1}\) from 1667 cm\(^{-1}\) in figure 7 suggests that hydroxyl groups reduced silver ions and are oxidized to carbonyl groups [21], [22]. Besides that, the shifting peak at 2923 cm\(^{-1}\) to 2921 cm\(^{-1}\) and appearance of another three peaks at 3073, 972 and 904 cm\(^{-1}\) reveals that alkane groups are oxidize to alkenes. The presence of phenolic compounds lead to the oxidation-reduction reactions which in turn induced reduction of silver ions (Ag\(^{+}\)) to zero-valence silver atoms (Ag\(^{0}\)) [23]. The phenolic compounds released hydrogen ions (H\(^{+}\)) and were simultaneously get oxidized in the redox reaction.

![Figure 7. FTIR spectra](image3)
The biorecovered solids contain hydroxyl, alkane, carbonyl, amines and ether functional groups which representing compounds such as polysaccharides, carboxylic acids and proteins. Similar compounds have been reported to act as stabilizing agents using different extract of plants [24], [25]. It is thought that oxygen in the hydroxyl group of polysaccharides and carboxylic acids, and nitrogen in the amine group of proteins are negatively charged [26]. Likewise, the surfaces of silver solid particles are positively charged [27]. Therefore, the oxygen and nitrogen atoms herein might facilitate the adsorption onto the silver solid particle surfaces [28], [29].

4. Conclusion
Palm leaves extract was able to reduce and recover silver from simulated silver electroplating wastewater. Four out of six factors were found to significantly affect the silver biorecovery process, determined by PBD. The silver biorecovery process was successfully optimized by RSM. Optimum conditions for the process were 50\% (v/v) of palm leaves extract, 1975 mg/L of initial silver ions concentration, pH 7.5 of reaction medium and 70 °C of reaction temperature to yield 93.30\% of silver being recovered. Characterization of the biorecovered solid particles proved that silver was successfully reduced and recovered in its elemental form and nano-sized. In addition, hydroxyl and carboxyl compounds act as reducing agents to reduce silver ions while polysaccharides, carboxylic acids and proteins act as stabilizing agents to cap and stabilize the silver solid particles formed.

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