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Preliminary Study on Desorption of Gold Ions on Self-Flocculating Microalga and its Regeneration Potential

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Microalga, possessing high binding affinity to different metals, has been considered as a promising biosorbent. Precious metals recovery and adsorbent regeneration are important for the financial competitiveness of biosorption with other processes. In this study, the desorbing agent thiourea was studied at different concentrations, contact time, pH and temperatures to optimize gold elution from the self-flocculating microalgae Scenedesmus obliquus AS-6-1. The variation in desorption performance with the adsorption time was also investigated. The gold-loaded biomass of S. obliquus AS-6-1 was regenerated efficiently by 0.2 M of thiourea at 25 ℃ and pH of 1.0 within 15 minutes. The adsorption time had significant effect on subsequent desorption, with a decrease in desorption efficiency with an increase in adsorption time. S. obliquus AS-6-1 as biosorbent remained efficient biosorption and desorption potential for gold(III) recovery in the first two adsorption/desorption cycles. The microalga cells could be harvested/separated from solutions by their gravity sedimentation. However, more studies are still required to enhance the regeneration of S. obliquus AS-6-1 by improving its flocculating property.

1. Introduction

Gold is used extensively in jewellery, electronics, electroplating and medicine, and thus creating large volume of gold-containing wastewater. With its increasing demand and limited resources, more technology have been encouraged to recovery gold from the secondary sources, especially when the gold is dissolved in large volumes of solution at relatively low concentrations (Won et al., 2014). Biosorption is considered as a promising technology to recover precious metals from aqueous solutions and wastewaters. Precious metals recovery and adsorbent regeneration are important for the financial competitiveness of biosorption with other processes (Das, 2010). In last decades, most researches were focused on enhancement of biosorption capacity and biosorption performance using various adsorbents (Won et al., 2014). But less attention was paid to recycling of used adsorbents and recovery of precious metal ions by the desorbing agents (Lata et al., 2015）. In the desorption process, metals are eluted from the biosorbent by an appropriate solution (desorbing agent) to produce a small volume of concentrated metal-containing solution in order to increase the energetic efficiency in the next stage, the electrolysis (Njikam and Schiewer, 2012). Studies have shown that thiourea in acidic solution can complex with Au (III) and Au (I) in the desorption stage, forming a relatively stable complex $Au[CS(NH_2)_2]^+$, which is then released into the solution (Ju et al., 2016).
Microalga, possessing high binding affinity to different metals, has been considered as a promising biosorbent (Monteiro and Carlos, 2012). However, the difficulty of separating metal-laden microalgal cells from diluted solutions restricts their practical application. Shen and Chirwa (2017) proposed that bio-flocculation was a feasible method to harvest/separate microalgae from diluted solutions. Recently, self-flocculating microalgae (Guo et al. 2013) have been demonstrated to possess the bio-flocculating property with the ability to aggregate together and form flocs, which can facilitate their gravity sedimentation for separation from aqueous solutions.
In the current study, batch tests on optimization of parameters in the desorption process were conducted to attain the optimal conditions of gold recovery from the self-flocculating microalgae S. obliquus AS-6-1. The consecutive adsorption/desorption cycles in separating funnel were carried out to determine the possibility of

regeneration of algal biosorbent using its bioflocculation. The work presented here shows that the self-flocculating microalga S. obliquus AS-6-1 as biosorbent has efficient biosorption and desorption potential for gold(III) recovery using its bioflocculation property. But more studies are still required to enhance the recycling of used adsorbents of S. obliquus AS-6-1 by improving its flocculating property.

2. Materials and methods

2.1 Preparation of biosorbent

The microalga S. obliquus AS-6-1 used as biosorbent was initially isolated from freshwater located in southern Taiwan (Zhang et al., 2016). The pure strain was cultured in a 12 L culture vessel containing 10 L of Blue-Green (BG 11) medium under algal light conditions (Osram L 36 W/77 Floura) at 25±1 °C. The S. obliquus AS-6-1 was then harvested from the growth media after 25 days and washed twice with deionized water before freeze-drying.

2.2 Preparation of chemicals

The standard stock solution of 1000 mg/L of chloroauric acid ($HAuCl_4$) was used as Au(III) source in this study. The pH of the metal solution was adjusted with 0.1 M NaOH/0.1 M HCl. Different concentrations of thiourea were used as eluent for desorption of gold from biomass. All the reagents were of analytical grade and procured from Sigma–Aldrich.

2.3 Batch desorption studies

Biosorption experiments were conducted in triplicates in 250 mL Erlenmeyer volumetric flasks. 10 mg of dried S. obliquus AS-6-1 was suspended in 100 mL of Au(III) solution, with an initial concentration of 5 mg/L, while maintaining at a pH of 2.0. The flasks were then shaken for 30 min at 25 °C. The microalga cells harvested by centrifugation (8000 rpm, 8 min) and washed twice with deionized water before desorption. The harvested biomass was then re-suspended in 100 mL Erlenmeyer flasks containing 50 mL of different concentrations of thiourea (0.005 – 0.5 M) at pH of 2.0, 25°C. At different desorption times (5 – 300 min), the samples were immediately centrifuged using a 2 mL Eppendorf tube at 8,000 rpm for 8 min in a Minispin® Microcentrifuge (Eppendorf, Hambury, Germany) and the supernatant was analysed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The effect of pH on desorption was conducted in 50 mL of optimum concentration of thiourea at 25 °C, with varying pH from 1.0 to 6.0. The effect of temperature on desorption was studied at different temperatures (7, 25, 35, 40, 50 °C). Batches of desorption studies were carried out at optimized desorption parameters in 50 mL of thiourea and the gold-loaded biomass after different adsorption time were harvested by centrifugation for subsequent desorption stages to determine the variation in desorption performance with the adsorption time.

2.4 Adsorption/desorption cycles

In order to test the flocculating property of microalga S. obliquus AS-6-1 and its regeneration potential, three cycles of successive adsorption/desorption experiments were conducted in 100 mL separating funnels. Preliminary experiments were conducted to determine the biomass dosage required for complete adsorption of 10 mg/L Au(III) within 30 min which was found to be at least 0.6 g/L. Thereby, the weighed 60 mg of dried S. obliquus AS-6-1 was added into 100 mL of Au(III) solution with an initial concentration of 10 mg/L, pH 2.0 for 30 min under 25 °C. The microalga cells were harvested by their gravity sedimentation for 20 min and the supernatant was analysed for gold adsorption using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The harvested cells were then rinsed twice with deionized water before desorption. The subsequent desorption experiment was carried out by dispersing the biomass in the separating funnel at the optimal desorption conditions. Microalgal cells were harvested/separated from solutions by its gravity sedimentation and the supernatant was analysed for gold recovery using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The harvested cells were washed twice with deionized water after desorption and then reused as adsorbent for subsequent adsorption/desorption cycles. Each new cycle of adsorption/desorption was carried out by supplementing 10 mg/L of Au (III).

3. Results and discussion

3.1 Effect of thiourea dosage

After adsorption procedure, 100 mL of an initial Au(III) concentration of 5 mg/L was completely bound by 10 mg biomass at pH 2.0 for 30 min under 25 °C. A range of thiourea concentration from 0.005 to 0.05 M was used to obtain the optimum dosage of desorbing agent for 0.5 mg Au (III) bound on 10 mg of S. obliquus AS-6-1 (Figure 1). 0.005 M of thiourea was not enough to strip the algal-bound Au (III) into the solution with less than 60% desorption efficiency. At thiourea dosage of 0.01 M, the maximum desorption efficiency achieved was 82 % at 30 min. At dosage of 0.05 – 0.1 M, the maximum desorption efficiency was above 90 % at 60 min. The desorption efficiency was stable and retained more than 90 % within the first 120 min at thiourea dosage from 0.2 to 0.5 M. Fluctuations in desorption efficiency in the preceding period was observed at thiourea dosage from 0.005 to 0.5 M, which could be duo to competition of gold ions bound by between functional groups on algal cell surface and thiourea. At higher concentration of thiourea (≥ 0.2 M), the strength of gold ions bound by thiourea seemed to be stronger, which is shown in the stable high desorption efficiency (> 90%) within the first 120 min. In this study, 0.2 M of thiourea was selected as the optimal dosage of desorbing agent, and higher thiourea loading was unnecessary.

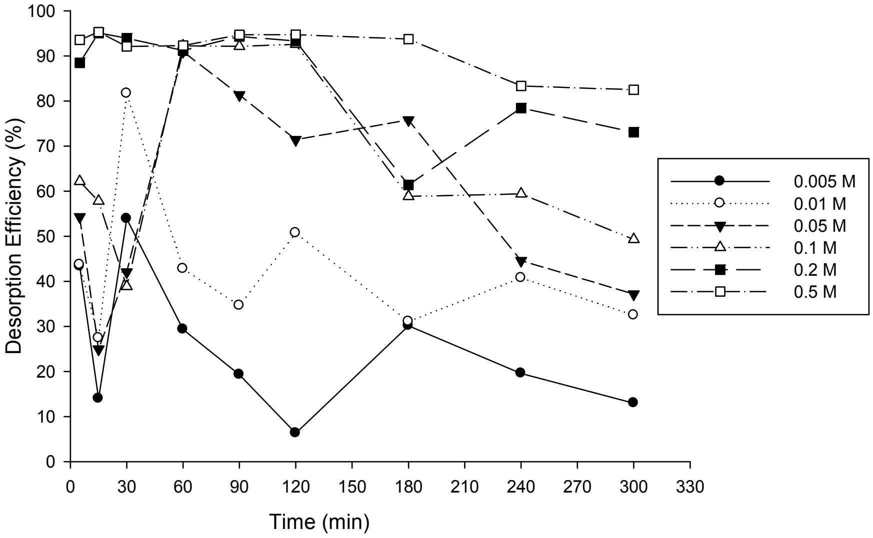

Figure 1: Effect of thiourea dosage on desorption efficiency (pH 2.0, 25°C, 50 mL of thiourea)

3.2 Effect of desorption time

It can be noticed from Figure 1 that the contact time affected significantly the desorption efficiency. At the optimal thiourea dosage of 0.2 M, desorption efficiency was almost higher than 90 % within the first 120 min and the maximum desorption efficiency achieved was 95 % at 15 min. From 15 to 120 min, desorption efficiency was slightly decreased but still retained higher than 90%. With the time increased from 120 to 300 min, there was a sharp decrease in desorption efficiency from 93 % to 73 %. On the whole, desorption efficiency was decreased with increasing time, which may be attributed to involve the adsorption of gold–thiourea complex $Au[CS(NH_2)_2]^+$ by the cell-wall binding groups. This has been observed in the recovery of gold–thiourea solutions using bacteria and yeast (Savvaidis 1998). Further desorption experiments were carried out for 15 min, the short time essential for industrial application.

3.3 Effect of pH

Batch desorption tests were conducted at pH ranging from 1.0 to 6.0 and desorption efficiency was measured at predetermined time in Figure 2. Desorption efficiencies at different pH were generally decreased with an increase in time. The maximum desorption efficiency achieved was also at contact time of 15 min at different pH from 2.0 to 5.0. In the first 30 min, desorption efficiency was decreased with an increase in pH. At pH of 1.0 and 2.0, the desorption performance was good, with maximum desorption efficiency of 95 % and 92 % at 15 min, respectively. When the pH increased from 3.0 to 6.0, the desorption efficiency drastically dropped from 63 % to 22 %. This showed that the pH of thiourea significantly influenced the desorption performance. In further experiments, the optimum pH selected as 1.0, which was observed in the case of biosorbent like alginate capsules (Kotte and Yun, 2014) and sulfothermophilic red alga, Galdieria sulphuraria (Ju et al., 2016).

3.4 Effect of temperature

The effect of temperature on desorption efficiency of gold on S. obliquus AS-6-1 was shown in Figure 3. There was a slight decrease in the desorption efficiency with an increase in temperature from 7 °C to 25 °C. With further increase to 35 °C, the desorption efficiency slightly increased to 94.77 %. When temperature increased to 55 °C, the desorption efficiency had a slight decrease from 94.77 % to 92.57 %. The results showed that temperature has little influence on the desorption efficiency in the range of 7 – 50 °C, with retaining the good desorption performance between 92.57 % and 95.97 %. Further experiments were conducted at ambient temperature 25 °C, which is easy to manipulate.

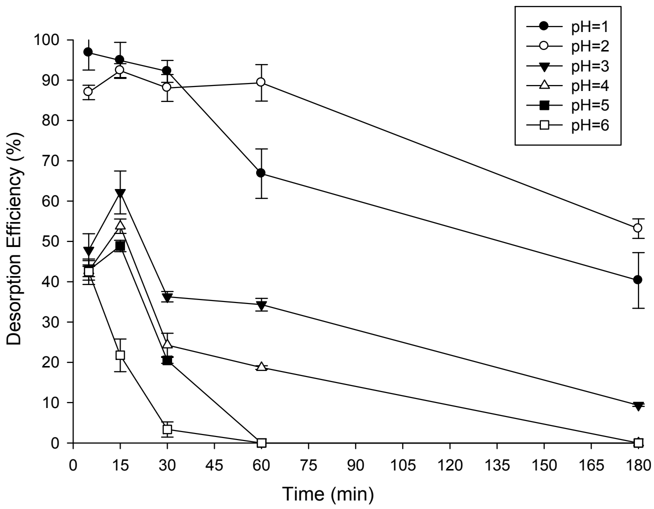

Figure 2: Effect of pH on desorption efficiency (0.2 M of thiourea, 25 °C, contact tome 15 min)

3.5 Effect of adsorption time

The short adsorption time in biosorption process is preferable in its commercial application. Few publications have reported the effect of adsorption time on the subsequent desorption. From the results in Figure 4, the adsorption time had significant influence on desorption efficiency for Au (III) bound on S. obliquus AS-6-1. As the adsorption time increased from 30 min to 60 min, the desorption efficiency slightly decreased from 92.37 % to 89.77 %. With the adsorption time increased to 24 h, the desorption efficiency drastically decreased to 55.4 %. After 1 week of agitation, the desorption efficiency further decreased to 36.77 %. The reduce in desorption efficiency with an increase in adsorption time may be due to the reduction of Au (III) to Au (0), which cannot be eluted by thiourea. In addition, the desorption efficiency decreased by 60 % within 168 h, indicating the gold ions were slowly reduced to Au (0) by the functional groups on the cell surface of biosorbent, which is in well accordance with (Greene at al., 1986).

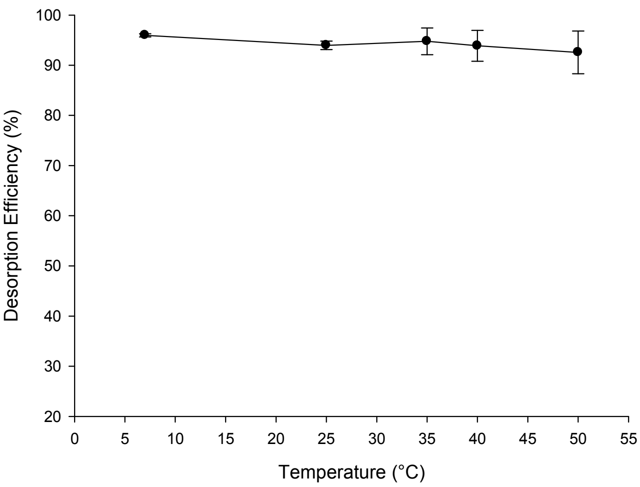

Figure 3: Effect of temperature on desorption efficiency (pH 1.0, contact time 15 min, 0.2 M of thiourea)

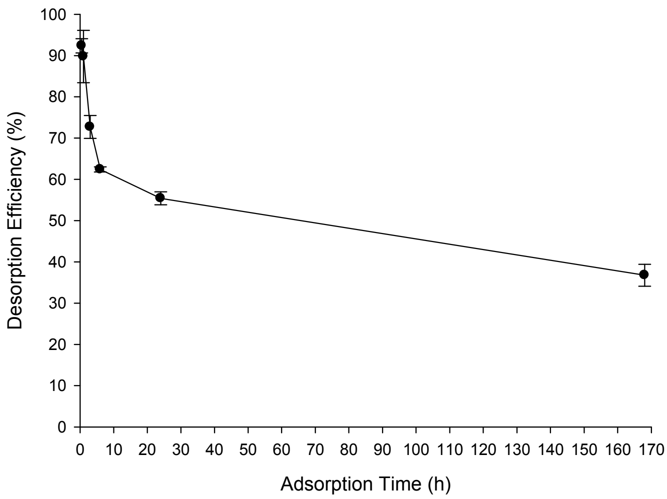

Figure 4: Effect of adsorption time on desorption efficiency (pH 1.0, contact time 15 min, 0.2 M of thiourea)

3.6 Adsorption/desorption cycles

Regeneration and reuse of biosorbent is very much necessary especially when the biomass availability and preparation is costly. In this study, reusability of S. obliquus AS-6-1 as biosorbent was studied by three cycles of alternating adsorption/desorption experiments with the supplement of 10 mg/L of Au (III) at the beginning of each cycle (Figure 5). The adsorption efficiency of Au (III) was highest with 100 % in the first cycle and remained high in the subsequent cycle. There was a reduction in adsorption upto 82.6 % in the 3rd cycle, which may be due to some binding sites on the adsorbent were occupied by the cumulative gold ions from the previous cycle after desorption. The desorption performance was also highest with 96 % in the first cycle and gradually dropped to around 70 % in the 3rd cycle. The adsorption and desorption efficiency remained high in the first two cycles but reduced with a further increase in cycles, which may be related to the loss of microalgae through each sedimentation/separation step. In order to reuse the adsorbents more times, it is required to reduce the algal loss by improving its flocculating property.

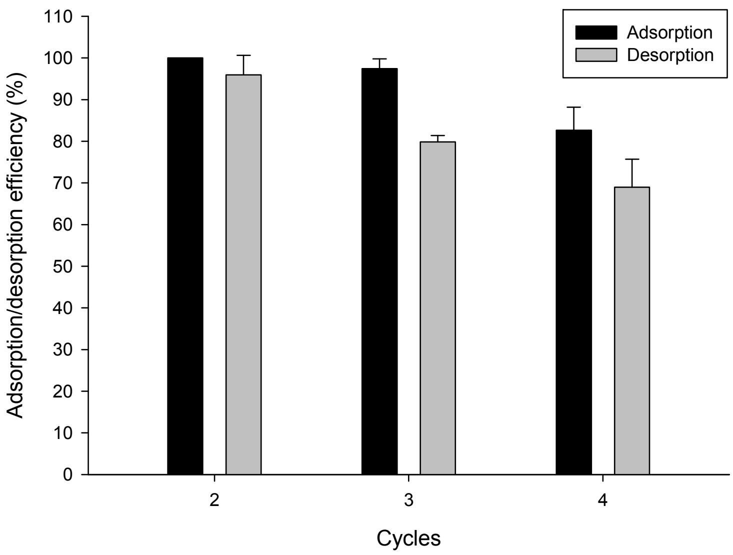

Figure 5: The adsorption and desorption efficiency in three alternating adsorption/desorption cycles by using 50 ml of 0.2 M thiourea as the eluent (initial Au (III) concentration in each cycle was 10 mg/L)

4. Conclusions

Desorption efficiency of gold(III) on S. obliquus AS-6-1 was significantly affected by the thiourea dosage and pH. The temperature had little influence on desorption efficiency in the range of 7 to 50 °C. In addition, there was a significant effect on desorption efficiency by the adsorption time, with a decrease in desorption efficiency with an increase in adsorption time. The gold-loaded biomass of Scenedesmus obliquus could be regenerated efficiently by 0.2 M of thiourea at 25 ℃ and pH of 1.0 within 15 minutes. S. obliquus AS-6-1 as biosorbent remained efficient biosorption and desorption potential for gold(III) recovery in the first two adsorption/desorption cycles. The microalga cells could be harvested/separated from solutions by their gravity sedimentation. However, more studies are still required to enhance the regeneration of S. obliquus AS-6-1 by improving its flocculating property.

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