CHEMICAL ENGINEERING TRANSACTIONS
VOL. 65, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608- 62-4; **ISSN** 2283-9216

Biosorption and Desorption Potential of Gold(III) by Freshwater Microalgae Scenedesmus Obliquus AS-6-1

Na Shen*, Evans M.N. Chirwa

Water Utilization and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa
nashen2016@gmail.com

Biosorption is an eco-friendly and cost-effective way for recovering gold from high-volume and low-concentration wastewater. In this study, the freshwater microalgae Scenedesmus obliquus AS-6-1 were used as biosorbent for gold(III) in short-term batch tests. For an initial gold(III) concentration of 5 mg/L, the optimum condition of gold(III) adsorption was 0.10 g/L biomass dosage, the temperatures in the range of 20 - 25 °C, pH 2.0 within 30 min. The level of Au (III) uptake by S. obliquus AS-6-1 could approach 15 % of the organism's dry weight at the optimum conditions with an initial concentration of 20 mg/L. The gold-loaded biomass of S. obliquus AS-6-1 was able to be regenerated by 0.1 M thiourea at pH 2.0 and its desorption efficiency retained 95 %, 94 % and 88 %, respectively, in three alternating adsorption/desorption cycles. The current experiments suggest that the freshwater microalga S. obliquus AS-6-1 is a promising and efficient biosorbent for gold recovery.

1. Introduction

Gold is usually found embedded in quartz veins or placer stream gravel and is mined in South Africa, the USA (Nevada, Alaska), Russia, Australia, and Canada. Nevertheless due to the excessive exploitation in 19th century, the amount of natural gold resources cannot meet the growing demand of its industrial and medical applications. Therefore, recovery of gold from secondary sources such as electroplating wastewater has been a focus research in recent years. Several traditional methods have been used for gold recovery, including chemical precipitation, ion exchange, electrochemical methods and membrane processes (Das, 2010). However, these methods suffer from high operation cost and generation of secondary wastes. Hence a cost-effective and eco-friendly approach for the treatment of low-concentration metal wastewater (below 10 - 40 mg/L) is needed (Ju et al., 2016). Biosorption, a metabolism-independent process where metals in solution are bound by functional groups present on the dead biomass, has been considered as an effective and economical process for recovery of different metals especially from high volumes of diluted solutions (Volesky, 2007).

A great diversity of biomaterial has been used as adsorbents for gold biosorption, such as fungi (Nakajima, 2003), bacteria, yeast, algae (Ju et al., 2016), agro wastes (Maruyama et al., 2014) and biopolymers (Gao et al., 2017). Among these different biosorbents, the algae biomass is of particular interest due to their low cost (non-requirement of the specific nutrients and oxygen) (Suresh Kumar et al., 2015), relative abundance and high binding capacity (Birungi and Chirwa, 2016). Biosorption of gold has been studied with brown algae (Vijayaraghavan et al., 2011), red algae (Castro et al., 2013) and microalgae (Ting et al., 1995), but most research attention has been focused on recovery of gold nanoparticles from aqueous solutions by reducing Au(III) to Au(0).

In the current study, batch tests on optimization of parameters were conducted to attain the optimal conditions of gold biosorption by the microalgae S. obliquus AS-6-1 before Au(III) reduced to Au(0). The consecutive adsorption/desorption cycles were also carried out to determine the possibility of regeneration of the binding sites on microalga biomass as biosorbent. The work presented here shows that the microalga S. obliquus AS-6-1 has efficient biosorption and desorption potential for gold(III) recovery.

2. Materials and Methods

2.1 Preparation of Microalgae

The microalga S. obliquus AS-6-1 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 10L 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 15 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 1 M NaOH/1M HCl. Desorption of gold from biomass was done by 0.1 M thiourea. All the reagents were of analytical grade and procured from Sigma–Aldrich.

2.3 Batch Biosorption Studies

Biosorption studies were carried out in triplicates with different biosorbent dosage (0.01 - 0.12 g/L) in 100 mL Au(III) solution at an initial concentration of 5 mg/L, while maintaining at a pH of 2.36. The flasks were then shaken for 360 min at 25 °C. Effect of contact time was studied in 100 mL of 5 mg/L of Au (III) solution at optimized biomass dosage. Samples were taken at time intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90, 120, 240 and 360 min, centrifuged and the filtrate was analysed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The effect of pH on adsorption was conducted at an initial Au (III) concentration of 5 mg/L in 100 mL metal solution at 25 °C with varying pH from 1.0 to 7.0. The effect of temperature on biosorption was studied at different temperatures (20, 25, 30, 40, 50, 60 °C). Batch biosorption studies were carried out at optimized adsorption parameters in 100 mL solution of different initial Au (III) concentrations in the range of 5 - 50 mg/L to determine the variation in adsorption capacity and efficiency with different initial gold ion concentration.

2.4 Desorption and Regeneration

Reusability of the microalga biosorbent was determined by carrying out three cycles of successive adsorption/desorption experiments. Biosorption experiments were conducted in triplicates at the optimized adsorption conditions. The subsequent desorption of bound gold was carried out by dispersing the biomass in 50 mL of 0.1 M thiourea as eluent at pH of 2.0, 25°C for 30 min. The biomass was harvested by centrifugation (8000 rpm, 8 min) and washed with deionized water after desorption. The biomass was then reused as adsorbent for subsequent adsorption/desorption cycles. Each new cycle of adsorption was carried out by supplementing 5 mg/L of Au (III). The samples were collected, centrifuged and the filtrate was analysed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400).

3. Results and Discussion

3.1 Effect of Biomass Dosage

A range of biomass dosage from 0.01 to 0.12 g/L was used to obtain the best binding performance by S. obliquus AS-6-1. The maximum Au(III) adsorption efficiency achieved was 100 % using 0.04 – 0.12 g/L biomass dosage at equilibrium, while the adsorption efficiency was below 70 % at biosorbent dosage of 0.01 – 0.02 g/L (Figure 1(a)). This suggests that the dosage of S. obliquus AS-6-1 biomass ≥ 0.04 g/L was able to completely adsorb Au (III) at the initial concentration of 5 mg/L. Figure 1(a) shows that the time reaching the maximum adsorption efficiency was highly dependent on the biomass dosage. It took 10 - 30 min to reach 100 % adsorption efficiency at biosorbent dosage of 0.6 – 0.12 g/L, but 90 min was required at dosage of 0.04 g/L. At low initial Au (III) concentration of 5 mg/L, the binding capacity decreased with the increasing biomass dosage (Figure 1(b)). However, the adsorption efficiency decreased at lower biomass dosage (Figure 1(a)) which may be due to the insignificant binding sites. A shorter adsorption time along with higher adsorption efficiency using less biomass dosage is desirable in industrial application. In this study, the adsorption rate was introduced to determine the optimum biomass dosage. It is defined as the amount of adsorbed metal ions per g dry cell weight (DCW) per minute within a period of time (Zhang et al., 2016). The adsorption rates of different biosorbent dosage at the equilibrium time were shown in Figure 1(c). The maximum adsorption rate achieved was 5.0 mg/g DCW / min within 10 min at biomass dosage of 0.10 g/L for the initial Au (III) concentration of 5 mg/L.

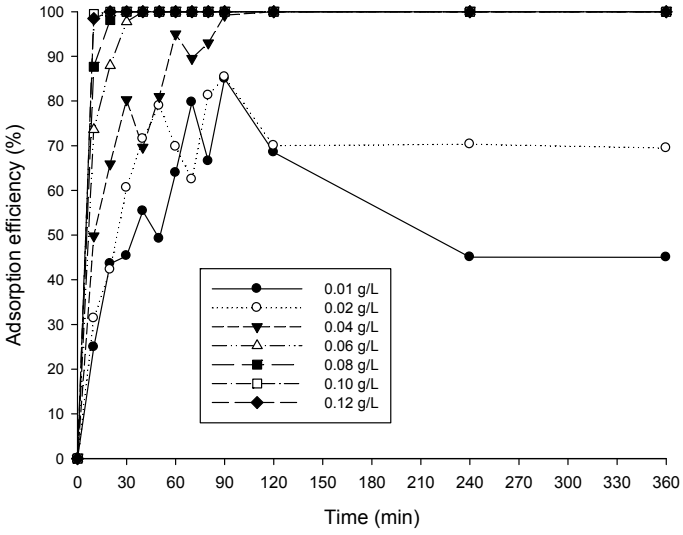
3.2 Effect of Contact Time

Figure 2(a) shows that 0.5 mg of Au (III) could be adsorbed completely by 10 mg of S. obliquus AS-6-1 within 10 min and remained at the constant adsorption capacity of 50 mg/g. The maximum amount of Au (III) uptake

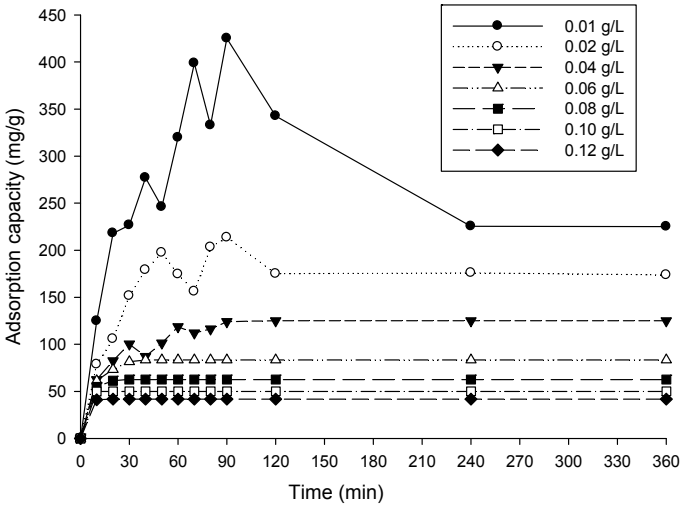
and adsorption equilibrium was achieved quickly within the first 10 min, which may be due to the abundant availability of vacant binding sites. In order to get a stable equilibrium, further adsorption experiments were carried out for 30 min, time more than required for equilibrium. It is worth noting that after 8h of agitation, the colour of algae changed to reddish purple and some purple particles attached to the flask wall. This indicates the possible bioreduction of gold and the presence of gold nanoparticles. The similar colour change was observed in the cases of biosorbents such as brown alga Turbinaria conoides (Vijayaraghavan et al., 2011) and red alga Chondrus crispus (Castro et al., 2013).

3.3 Effect of pH

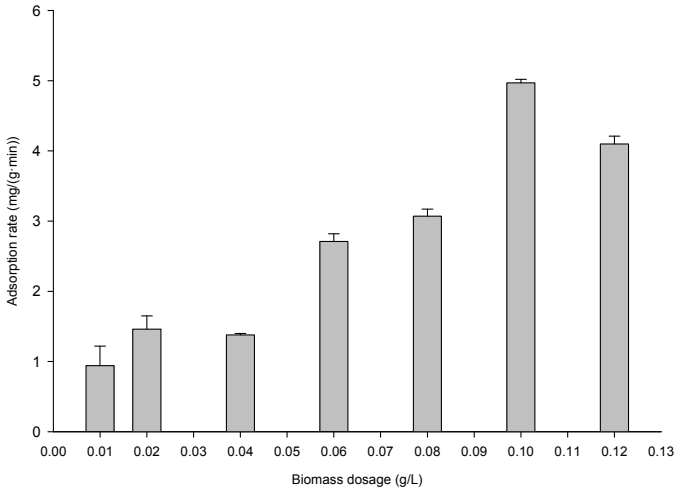
The pH of solution is one of the most important factors during the process of biosorption. Batch adsorption tests were conducted at pH ranging from 1.0 to 7.0 and the adsorption capacities were measured at 30 min (Figure 2(b)). The maximum adsorption capacity of 50 mg/g was found to be at pH 2.0. The Au (III) uptake slightly decreased at pH 3.0 and then declined drastically in further increase of pH to 7.0. The decrease in adsorption capacity as the pH increase may be due to the less availability of positively charged binding sites on biomass against the negatively charged $AuCl_4^-$ in the solution. The decline in uptake at pH 1.0 may be related to the charge reversal of biosorbent below pH 2.0 (Das, 2010). The optimum pH obtained (pH 2.0) is well in accordance with the previous studies on Au (III) adsorption by lyophilized Chlorella vulgaris (Greene et al., 1986).



(a) Adsorption efficiency of different biomass dosage

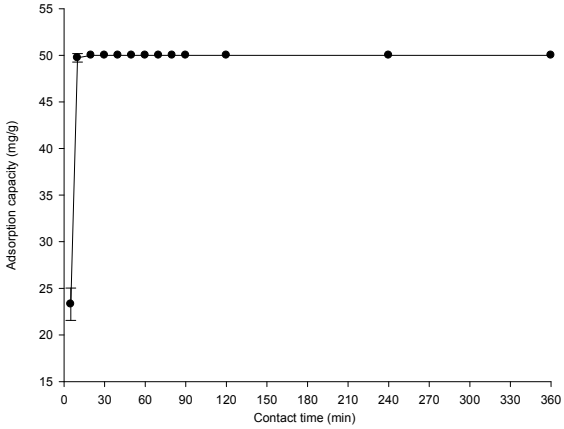


(b) Adsorption capacity of different biomass dosage

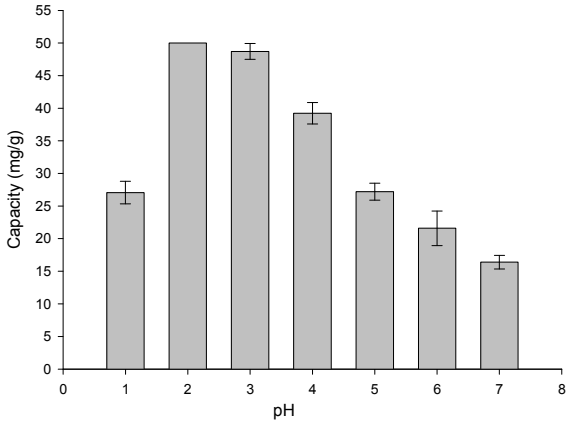


(c) Adsorption rate of different biomass dosage at the corresponding equilibrium time

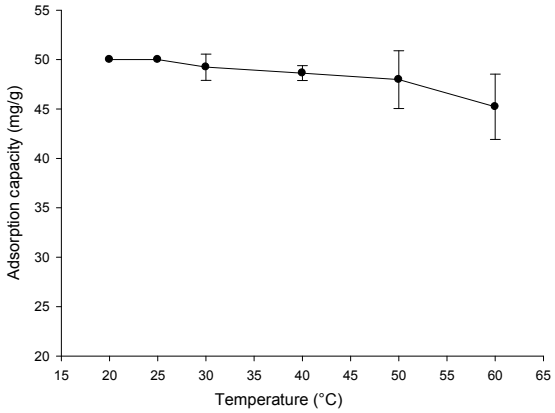
Figure 1: Effect of biomass dosage on Au (III) (a) adsorption efficiency, (b) adsorption capacity, (c) adsorption rate (pH 2.36, 25°C, 100 mL of initial conc. 5 mg/L)



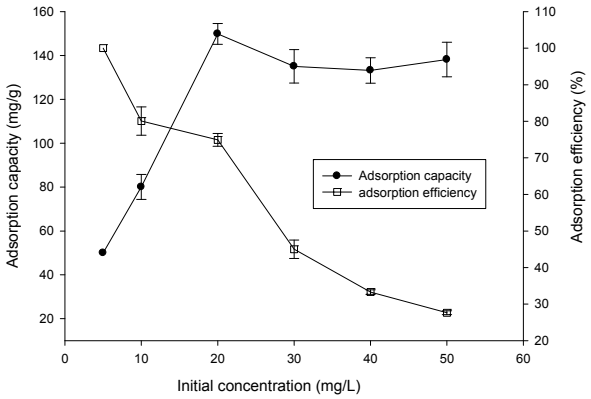
(a) Contact time (biomass dosage 0.10 g/L, pH 2.36 25°C, 100 mL of initial conc. 5 mg/L)



(b) pH ((biomass dosage 0.10 g/L, contact time 30 min 25°C, 100 mL of initial conc. 5 mg/L)



(c) Temperature (biomass dosage 0.10 g/L, pH 2, contact time 30, 25°C, 100 mL of initial conc. 5 mg/L)



(d) Initial Concentration (biomass dosage 0.10 g/L, contact time 30 min, pH 2, 25°C, 100ml)

Figure 2: Effect of (a) contact time, (b) pH, (c) temperature, (d) initial concentration on Au (III) adsorption capacity

3.4 Effect of Temperature

The adsorption capacity was not influenced by the temperatures in the range of 20 – 25 °C as shown in Figure 2(c), with retaining the maximum uptake of 50 mg/g. Therefore, further biosorption studies were conducted at room temperature 25 °C. More than 97 % of Au (III) was effectively adsorbed by S. obliquus AS-6-1 from 20 to 40 °C. However, with further increase in temperature to 60 °C, the adsorption capacity was gradually decreased. As a whole, the adsorption capacity decreased with an increase in temperature which may be due to the Au (III) adsorption process is exothermic in nature. Adsorption studies conducted by Fujiwara et al. (2007) showed a similar trend with change in the temperature.

3.5 Effect of Initial Au (III) Concentration

The effect of initial Au (III) concentration on biosorption was investigated using increasing loading of Au (III) from 5 to 50 mg/L (Figure 2(d)). The uptake capacity increased with the increase in initial concentration to 20 mg/L and no considerable change was observed from the initial concentration of 30 to 50 mg/L. The increase in adsorption capacity may be owing to the higher availability of metal ions. At higher concentration, the metal ions are needed to overcome the mass transfer resistance and diffuse to the biomass surface by intra-particle diffusion at a slower rate, which may account for the reduction in the adsorption efficiency. In this study, further biosorption studies were carried out using 5 mg/L of initial concentration in order to completely utilize the Au (III) in solution.

3.6 Adsorption/Desorption

Regeneration and reuse of biosorbent is very much necessary especially when the biomass availability and preparation is costly. Reusability of S. obliquus AS-6-1 as biosorbent was studied by three cycles of alternating adsorption/desorption experiments with the supplement of 5 mg/L of Au (III) at the beginning of each cycle (Figure 3). The adsorption efficiency of Au (III) in the first cycle was highest at 100 % and slightly reduced in the subsequent two cycles. This may due to some binding sites on the adsorbent were occupied by the cumulative gold ions from the previous cycle after desorption. The decrease of desorption efficiency from 95 % to 88 % in three alternating adsorption/desorption experiments may be owing to the irreversible Au (III) binding property of the adsorbent system or due to the reduction of Au (III) to Au (0) which cannot be recovered by the eluent thiourea. The gold-loaded biomass of S. obliquus AS-6-1 regenerated by 0.1 M thiourea at pH 2.0 retained good adsorption/desorption capability in three consecutive cycles. Further studies are still required to investigate the adsorption/desorption potential of S. obliquus AS-6-1 throughout more cycles.

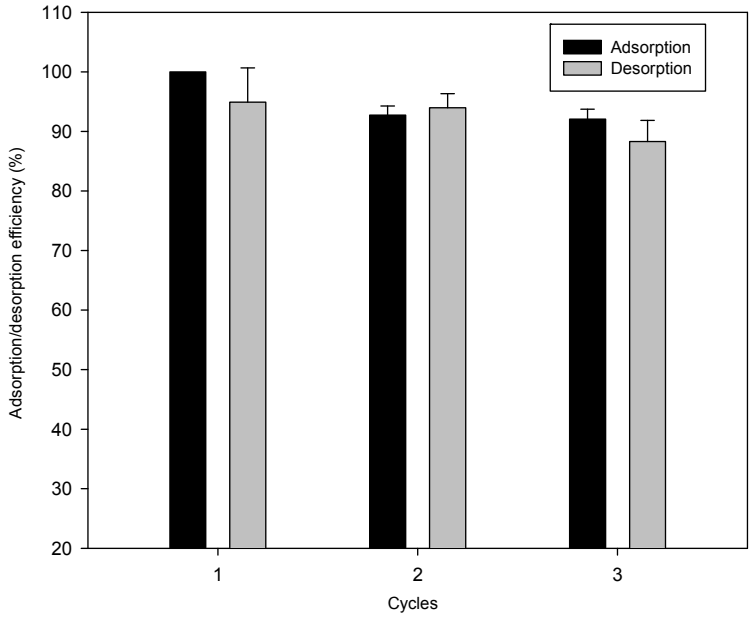


Figure 3: The adsorption and desorption efficiency in three alternating adsorption/desorption cycles by using 50ml of 0.1 M thiourea as the eluent (initial concentration in each cycle was 5 mg/L)

4. Conclusions

The optimum condition for adsorption of gold(III) by S. obliquus AS-6-1 was 0.10 g/L biomass dosage, the temperatures in the range of 20 - 25 °C, pH 2.0 within 30 min with an initial gold(III) concentration of 5 mg/L. The level of Au (III) uptake by S. obliquus AS-6-1 is approximately 15 % of the organism's dry weight at the optimum conditions with an initial concentration of 20 mg/L. The microalgae loaded with 0.5 mg gold(III) could be regenerated with 50 mL of 0.1 M thiourea at pH 2.0 and retained good adsorption and desorption performance in three alternating adsorption/desorption cycles. These results suggest the good potential of the freshwater microalga S. obliquus AS-6-1 as a promising and efficient biosorbent for Au (III) recovery.

Acknowledgments

The authors would like to thank the Sedibeng Water, South Africa and the Water Utilization and Environmental Engineering Division at the University of Pretoria for financial and logistical support during the study of gold recovery by microalgae, and appreciate the kind help of Professor Xin-Qing Zhao in Shanghai Jiao Tong University and Professor Jo-Shu Chang in National Cheng Kung University, Taiwan for providing the microalgae strains.

Reference

Birungi Z.S., Chirwa E.M.N., 2016, Interpretation of Uptake Kinetic of Thallium and Cadmium on Surfaces of Immobilized Green Algae as Biosorbents, Chemical Engineering Transactions, 49, 421-426.

Castro L., Blázquez M.L., Muñoz J.A., González F., Ballester A., 2013, Biological synthesis of metallic nanoparticles using algae, IET Nanobiotechnology, 7, 109-116.

Das N., 2010, Recovery of precious metals through biosorption - A review, Hydrometallurgy, 103, 180-189.

Fujiwara K., Ramesh A., Maki T., Hasegawa H., Ueda K., 2007, Adsorption of platinum (IV), palladium (II) and gold (III) from aqueous solutions on l-lysine modified crosslinked chitosan resin, Journal of Hazardous Materials, 146, 39-50.

Greene B., Hosea M., Mcpherson R., Henzl M., Alexander M.D., Darnai D.W., 1986 Interaction of gold (I) and gold (III) complexes with algal biomass, Environ. Sci. Technol, 20, 627-632.

Gao X., Zhang Y., Zhao Y., 2017, Biosorption and reduction of Au (III) to gold nanoparticles by thiourea modified alginate, Carbohydrate Polymers, 159, 108-115.

Ju X., Igarashi K., Miyashita S., Inagaki K., Fujii S., Sawada H., Kuwabara T., Minoda A., 2016, Effective and selective recovery of gold and palladium ions from metal wastewater using a sulfothermophilic red alga, Galdieria sulphuraria, Bioresource Technology, 211, 759-764.

Maruyama T., Terashima Y., Takeda S., Okazaki F., Goto M., 2014, Selective adsorption and recovery of precious metal ions using protein-rich biomass as efficient adsorbents, Process Biochemistry, 49, 850-857.

Nakajima A., 2003, Accumulation of gold by microorganisms, World Journal of Microbiology & Biotechnology, 19, 369-374.

Suresh Kumar K., Dahms H.U., Won E.J., Lee J.S., Shin K.H., 2015, Microalgae - A promising Tool for Heavy Metal Remediation, Ecotoxicology and Environmental Safety, 113, 329–352.

Ting Y.P., Teo W.K., Soh C.Y., 1995, Gold uptake by Chlorella vulgaris, Journal of Applied Phycology, 7, 97-100.

Volesky B., 2007, Biosorption and Me, Water Research, 41, 4017–4029.

Vijayaraghavan K., Mahadevan A., Sathishkumar M., Pavagadhi S., Balasubramanian R., 2011, Biosynthesis of Au(0) from Au(III) via biosorption and bioreduction using brown marine alga Turbinaria conoides, Chemical Engineering Journal, 167, 223-227.

Zhang X., Zhao X., Wan C., Chen B., Bai F., 2016, Efficient Biosorption of Cadmium by the Self-flocculating Microalga Scenedesmus obliquus AS-6-1, Algal Research, 16, 427–433.