CrossMark

Equilibrium and kinetic modeling for biosorption of Au(III) on freshwater microalgae

Na Shen[1] · E. M. N. Chirwa[1]

Abstract

Microalgae have been considered as a promising biosorbent for recovery of precious metal ions from diluted aqueous solutions; especially the self-flocculating microalga has the potential for cost-effective harvesting of tiny microalgae. In this study, the adsorption of Au(III) by the self-flocculating microalgae *Tetradesmus obliquus* and non-flocculating *T. obliquus* as a control was studied in different initial Au(III) concentrations, temperatures, and pH. The adsorption equilibrium by the tested microalgae fitted well to the Langmuir model at different temperatures. The maximum adsorption capacity from the Langmuir model for *T. obliquus AS-6-1* was 169.49 mg g^{-1} obtained at pH 2.0 and 30 °C, which was higher than that observed by the non-flocculating *T. obliquus* with 153.85 mg g^{-1}. Furthermore, all the K_d values above 5000 mL g^{-1} at 30 °C for *T. obliquus AS-6-1* showed that the flocculating microalgae had a stronger adsorption affinity to Au(III). The initial Au(III) concentration and solution pH significantly affected the adsorption capacity of Au(III) on algal species. While, their adsorption of Au(III) was slightly influenced at temperature from 30 to 40 °C but significantly influenced and decreased at low (≤ 7 °C) or high temperature (≥ 60 °C). The experimental data fitted well to the second-order kinetic model, which indicated that the adsorption reaction on the surface of adsorbent was the rate-limiting step, instead of mass transfer.

Keywords *Tetradesmus* · Chlorophyta · Gold · Biosorption · Equilibrium model, kinetic model

Introduction

With the rising cost of gold production and its limiting source in natural ores, recovery of gold ions from industrial effluents containing low-concentration metals, is extremely important from economical and environmental points of view. Various methods, such as, co-precipitation, ion exchange, solvent extraction, and adsorption onto solid-phase materials have been used for separation, pre-concentration, and removal of gold ions from aqueous solutions (Al-Saidi 2016). Among these technologies, biosorption has been considered as a promising technology to remove or recover precious metals from aqueous solutions with its advantage of low cost, high efficiency, minimal generation of chemical or biological sludge, regenerability, and possible recovery of metals by desorption (Won et al. 2014).

Many factors influencing biosorption of precious metals include: solution pH, temperature, biomass dosage, ionic strength, initial solute concentration, agitation rate, and contact time (Das 2010). Several authors have reported that the solution pH is one of the most important variables which affect the speciation of metals in solution through hydrolysis, complexation, and redox reactions (Esposito et al. 2002; Fiol et al. 2006). Temperature of the solution is also a significant factor during the process of biosorption, which was presented in different scenario by many workers. Aksu et al. (1992) reported that temperature seemed not to influence the biosorption performances in the range of 20–35 °C. But a significant effect of temperature on gold(III) uptake by the egg shell membrane material was observed at 65 °C by Ishikawa et al. (2002). Initial metal ion concentration is another important impact on biosorption, generally with a higher concentration resulting in a higher adsorption capacity (Ho and McKay 2000). This is because at lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low. However, at higher concentrations, the sites available for adsorption become fewer compared to moles of solute present. Hence, the adsorption efficiency is strongly dependent upon the initial concentration.

✉ Na Shen
nashen2016@gmail.com

[1] Department of Chemical Engineering, University of Pretoria, Lynnwood Road, Hatfield, Private Bag X20, Pretoria 0002, South Africa

Various types of inactive biological materials such as bacteria, fungi, algae, agricultural and industrial by-products are used as adsorbents in biosorption process (Park et al. 2010). Algal biomass, due to its low cost, relative abundance and high binding capacity, has been considered to be promising and economical biosorbents for recovery of gold (Das 2010). *Chlorella vulgaris*, a green alga, was capable of removing more than 90% of the gold from very dilute solution (Ting et al. 1995). Au(III) was successfully recovered as metallic gold nanoparticle using dead brown alga, *Turbinaria conoides* (Vijayaraghavan et al. 2011). The red alga *Galdieria sulphuraria* was found to be selective for the recovery of gold from metal wastewater (Ju et al. 2016).

However, one of the major challenges for metal biosorption by microalgae cultures is high cost associated with the harvest of tiny microalgal cells from diluted wastewater. A cost-effective strategy is using gravity sedimentation facilitated by flocculation, especially using the self-flocculation of microalgal cells. Nowadays, several flocculating microalgae, such as *Tetradesmus obliquus AS-6-1* and *Chlorella vulgaris JSC-7* have been reported to have higher efficiency for cadmium removal than their non-flocculating microalgae (Alam et al. 2015; Zhang et al. 2016). However, so far still no report is available for using self-flocculating microalgae in recovering gold ions.

In this study, the self-flocculating microalga *T. obliquus AS-6-1* (previous name *Scenedesmus obliquus AS-6-1*) and the non-flocculating *T. obliquus* as the control were used as biosorbents for Au(III) in batch tests. The aim of this paper was to study the adsorption behavior of gold ions using the self-flocculating microalga at different initial gold concentrations, temperatures and pH. The equilibrium and kinetics of Au(III) adsorption by the tested microalgae were investigated. The adsorption rates were measured and determined quantitatively in correlation with initial gold concentration, temperature, and solution pH value. The results will be useful for further studies in the identification of microalga with the highest adsorption capacity and in the design of adsorption system.

Materials and methods

Preparation of adsorbent

The self-flocculating microalga *Tetradesmus obliquus AS-6-1* was initially isolated from freshwater located in southern Taiwan (Zhang et al. 2016). The non-flocculating strain *Tetradesmus obliquus* (CCAP No. 276/7) was from the Culture Collection of Algae and Protozoa (CCAP) for comparison purpose. These pure strains were cultured in a 12 L culture vessel containing 10 L of BG11 medium (Chen et al.

2016) under illumination of ~ 60 μmol photons m^{-2} s^{-1} at 25 ± 1 °C. The strains were then harvested from the growth media after 15 days and washed thoroughly with deionized water before freeze-drying.

Chemicals

A standard stock solution of 1000 mg L^{-1} of chloroauric acid (HAuCl$_4$) was used to prepare initial Au(III) concentrations between 5 and 50 mg L^{-1}. The pH of the metal solution was adjusted with 0.1 M NaOH/0.1 M HCl. All the reagents were of analytical grade and from Sigma–Aldrich.

Batch adsorption equilibrium studies

The equilibrium adsorption of Au(III) on the microalga adsorbents were conducted at different temperatures. The predetermined initial Au(III) concentrations were measured into 250-mL Erlenmeyer volumetric flasks. The pH of the solution was kept constant at 2.0 using 0.1 M NaOH and HCl for equilibrium experiment. The weighed biomass of 100 mg L^{-1} was added to the measured Au(III) concentrations and shaken at a constant speed of 150 rpm for 6 h. The temperature was controlled at 7, 30, 40, and 60 °C. The experiment was carried out in triplicates. A sample (1.5 mL) was drawn, centrifuged, and the supernatant was analyzed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The amount of metal bound by the biosorbents at equilibrium q_e (mg g^{-1}) was computed as follows:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{1}$$

Where, C_0 and C_e are the initial and equilibrium metal concentrations (mg L^{-1}), respectively, V is the volume of solution (L) and M is the amount of biomass (g).

Batch adsorption kinetic studies

The effect of initial concentration, temperature, and pH on Au(III) adsorption kinetics was tested. A constant biomass of 10 mg in 100 mL Au(III) solution containing initial concentration in the range of 5–50 mg L^{-1} was used for *T. obliquus AS-6-1* and *T. obliquus*. The pH of solutions were maintained at 2.0 and then shaken for 360 min at 30 °C. Effect of temperature was studied in 100 mL of 50 mg L^{-1} of Au(III) solution at different temperatures (7, 30, 40, 60 °C). The 10 mg of algal samples were mixed in the gold solution of pH 2.0 and shaken by a shaker at different predetermined temperatures. Effect of pH on adsorption kinetics was conducted at an initial Au(III) concentration of 5 mg L^{-1} in 100 mL metal solution at 25 °C with varying pH from 1.0 to

6.0. Samples were taken at time intervals of 5, 15, 30, 60, 90, 120, 180, 240, 300, and 360 min and then centrifuged at 8000 rpm for 8 min. The supernatant was analyzed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400).

Data analysis

Adsorption isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, and is of importance in the design of adsorption system. The Langmuir and Freundlich models (Birungi and Chirwa 2015) were used to fit experimental data using linearized Eqs. (2) and (3), respectively. These models are widely accepted and often used in biosorption studies involving single solute systems. The Langmuir isotherm is expressed by the following linearized equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{2}$$

where q_e is the amount of metal ions absorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of metal ions remaining in the solution (mg L^{-1}), q_m represents the maximum adsorption capacity (mg g^{-1}) and b is a constant related to the energy of adsorption (L mg^{-1}).

The Freundlich isotherm is represented by the linearized equation as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

where K_f is the Freundlich constant related to adsorption capacity of biomass, and n is a constant indicative of biosorption intensity.

Adsorption affinity of Au(III) on tested algae

The adsorption affinity of Au(III) on algal adsorbents can be determined using the distribution co-efficient K_d (mL g^{-1}) which expresses the effectiveness of the biosorbent for metal uptake (Sangvanich et al. 2010). The K_d was calculated using equation as follows:

$$K_d = \frac{C_0 - C_f}{C_f} \times \frac{V}{M} \tag{4}$$

where C_0 is the initial concentration (mg L^{-1}), C_f is final concentrations (mg L^{-1}), V is the volume of solution (mL), M is the weight of algae (g).

Adsorption kinetics

The time-series data from the kinetic studies of a single-metal system containing Au were simulated using the Computer Program for the Identification and Simulation of Aquatic Systems AQUASIM 2.01 (AQUASIM, EAWAG, Dübendorf, Switzerland). The non-linear Pseudo-first-order and Pseudo-second-order models were applied to analyze the rate of adsorption uptake (Ho and McKay 1999). The expression for the Pseudo-first-order is given by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

which is given by the following linearized equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

The expression for the Pseudo-second-order is given by the differential rate law:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

which is given by the following linearized equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

where q_t is the amount of adsorbed metal on the algal biomass at time (t) in (mg g^{-1}); q_e is the equilibrium adsorption capacity (mg g^{-1}); k_1 is the rate constant of Lagergren first-order adsorption (min^{-1}) and k_2 is the rate constant of second-order adsorption (g mg^{-1} min^{-1}).

Results

Adsorption isotherm

Langmuir and Freundlich isotherm models were used in this study to evaluate the experimental data for adsorption of gold(III) on *T. obliquus AS-6-1* and *T. obliquus* at different temperatures. The isotherm constants from Langmuir and Freundlich models at 7, 30, 40, and 60 °C were listed in Table 1. The Langmuir model exhibited a better correlation co-efficient (R^2) of ≤ 1.00 as compared to the Freundlich model with $R^2 \leq 0.91$ for the tested algae. The slope and intercept were calculated from the linearized Eqs. (2) and (3) for maximum adsorption capacity (q_m) and affinity of the metal (b). The linearized graph C_e/q_e vs. C_e for Langmuir model was plotted in Fig. 1. At temperature of 30 and 40 °C, both of *T. obliquus AS-6-1* and *T. obliquus* had higher q_m of $\geq$ 151 mg g^{-1} than $q_m \leq 77$ mg g^{-1} at temperature of 7 and

Table 1 Langmuir and Freundlich isotherm constants at different temperature (pH = 2.0)

Temperature	Langmuir			Freundlich		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_f	n	R^2
7 °C						
T. obliquus AS-6-1	51.28	13	1.00	47.94	54.35	0.72
T. obliquus	76.92	7.22	1.00	69.74	37.04	0.78
30 °C						
T. obliquus AS-6-1	169.49	3.69	1.00	111.92	7.53	0.74
T. obliquus	153.85	2.95	1.00	105.75	8.88	0.83
40 °C						
T. obliquus AS-6-1	158.73	1.13	1.00	55.54	3.06	0.92
T. obliquus	151.52	1.22	1.00	55.48	3.19	0.91
60 °C						
T. obliquus AS-6-1	61.73	2.57	1.00	52.88	23.70	0.57
T. obliquus	68.49	4.87	1.00	54.14	14.27	0.71

60 °C. Moreover, the q_m for the tested algae had insignificant change between 30 and 40 °C.

It is worth noting that the q_m for *T. obliquus AS-6-1* is higher than q_m for *T. obliquus* at 30 and 40 °C, but the results were reversed at 7 and 60 °C, with the q_m for *T. obliquus* higher than that for *T. obliquus AS-6-1*, Table 1. In addition, *T. obliquus AS-6-1* and *T. obliquus* had the highest q_m of 169.49 and 153.85 mg g^{-1} at 30 °C, respectively, and both the tested algae expressed a higher affinity (b) of 3.69–2.95 L mg^{-1} compared to the b of 1.13–1.22 L mg^{-1} at 40 °C, Table 1.

Adsorption affinity of Au(III) on tested algae

The adsorption affinity of Au(III) on algal adsorbents can be further determined using the distribution co-efficient (K_d) which expresses the effectiveness of the biosorbent for metal uptake. The higher the K_d, the stronger the binding affinity of adsorbent to adsorbate. When the K_d value is more than 5000 mL g^{-1}, then it is considered good, and when the value is greater than 50,000 mL g^{-1} then it is excellent (Sangvanich et al. 2010).

As shown in Table 2, the K_d values were decreased with an increasing initial Au(III) concentration at different temperatures. At 30 and 40 °C, the K_d values for *T. obliquus AS-6-1* and *T. obliquus* were higher than those at 7 and 60 °C. *T. obliquus AS-6-1* had significantly high K_d values of 42,632 mL g^{-1} at initial concentration of 20 mg L^{-1}, 30 °C, which was very close to excellent value given Table 2. All the K_d values of 30 °C were above 5000 mL g^{-1} at initial concentration from 20 to 50 mg L^{-1} for *T. obliquus AS-6-1*. While at 40 °C, the K_d values were good except at initial concentration of 50 mg L^{-1}. In the case of *T. obliquus*, the K_d values at 30 and 40 °C were good from initial concentration of 20 to 40 mg L^{-1}, but were lower than 5000 mL g^{-1} at initial concentration of 50 mg L^{-1}.

Adsorption kinetics

Effect of initial concentration

The effect of initial concentration on adsorption of Au(III) on *T. obliquus AS-6-1* and *T. obliquus* at pH 2.0, 30 °C was
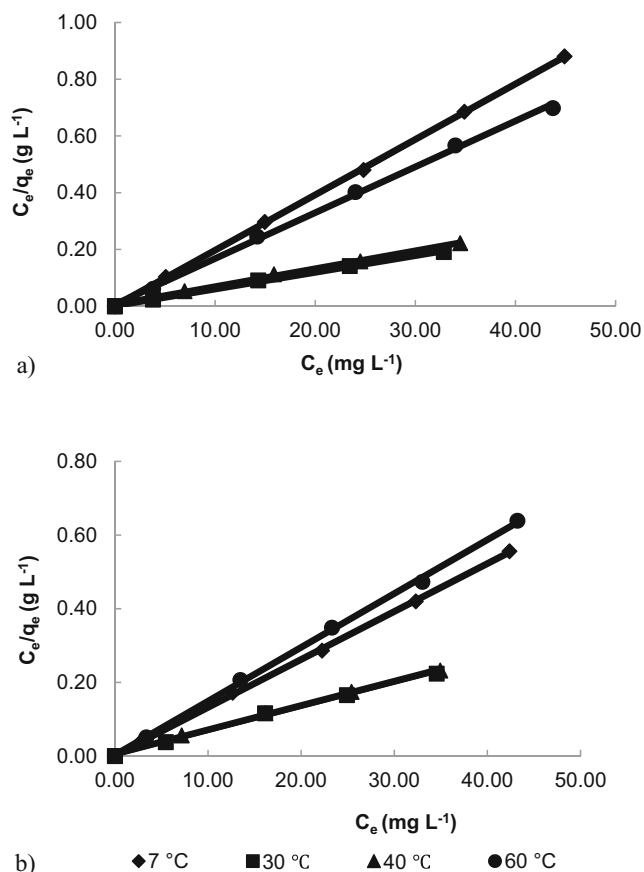
Fig. 1 Langmuir plot at different temperatures on *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**)

Table 2 Distribution co-efficient for adsorption of Au(III) on *T. obliquus AS-6-1* and *T. obliquus*

Adsorbent	C_0 (mg L^{-1})	7 °C K_d (mL g^{-1})	30 °C K_d (mL g^{-1})	40 °C K_d (mL g^{-1})	60 °C K_d (mL g^{-1})
T. obliquus AS-6-1	20	3366	42,632	18,791	4078
	30	2084	10,964	8896	2486
	40	1459	7053	6324	1765
	50	1136	5225	4503	1432
T. obliquus	20	5814	26,585	17,881	4840
	30	3491	8595	8576	2868
	40	2380	6049	5738	2115
	50	1798	4469	4306	1565

shown in Fig. 2. With an increase in the initial Au(III) concentration from 5 to 50 mg L^{-1}, the adsorption capacity increased with increasing time. At low concentrations of 5 and 10 mg L^{-1}, there was complete efficiency with 100% uptake in less than 60 and 180 min for both of the tested algae, respectively. The equilibrium uptake for *T. obliquus AS-6-1* and *T. obliquus* were almost the same of 50 and 100 mg g^{-1} at initial concentration of 5 and 10 mg L^{-1}, respectively. At higher concentration of 50 mg L^{-1}, the maximum uptake was attained within 240 min with 171 and 154 mg g^{-1} for *T. obliquus AS-6-1* and *T. obliquus,* respectively. The adsorption capacity of *T. obliquus AS-6-1* at an initial Au(III) concentration of 50 mg L^{-1} is 1.1 times larger than that of *T. obliquus*.

Effect of temperature

At low (≤ 7 °C) and high temperature (≥ 60 °C), the adsorption capacities for the tested algae were much lower than that at temperature of 30 and 40 °C with an increase in time (Fig. 3). Interestingly, a slight decrease of adsorption capacity for *T. obliquus AS-6-1* was observed with an increase in temperature from 30 to 40 °C. But it is reversed for *T. obliquus* with Au(III) uptake at 40 °C higher than that at 30 °C. Generally, the Au(III) uptake on *T. obliquus AS-6-1* and *T. obliquus* at 30 °C was close to that at 40 °C.

Effect of pH

Between pH of 2.0 and 3.0, there was complete efficiency with 100% uptake in less than 15 min for *T. obliquus AS-6-1* and 30 min for *T. obliquus,* Fig. 4. With the pH increased to 6.0, the adsorption capacity was reduced drastically. However, when the pH dropped to 1.0, the decline in uptake was also observed. In addition, at pH of 4.0, there was a decrease in adsorption capacity for *T. obliquus AS-6-1* at first 90 min but the equilibrium uptake was closed to that at pH of 2.0 and 3.0. In the case of *T. obliquus*, the adsorption capacity at pH of 4.0 is moderate.

Rate constant studies

In this study, the pseudo-first-order and pseudo-second-order models were used to determine reaction rate constant and equilibrium capacity at different initial concentrations, temperatures, and pH. The correlation coefficients (R^2) for the first-order kinetic model were low and the calculated equilibrium capacity ($q_{e,cal}$) obtained did not give reasonable values. The experimental data fit very well with the pseudo-second-order model with almost all R^2 of ≥ 0.99 for different initial Au(III) concentrations, temperatures and pH (Table 3). The slopes and intercepts of plots of t/q_t versus t were used to calculate the second-order rate constant k_2 and q_e. The reaction

■ 5 mg L^{-1} ▲ 10 mg L^{-1} ● 5 0 mg L^{-1} ━━ 2nd-order model
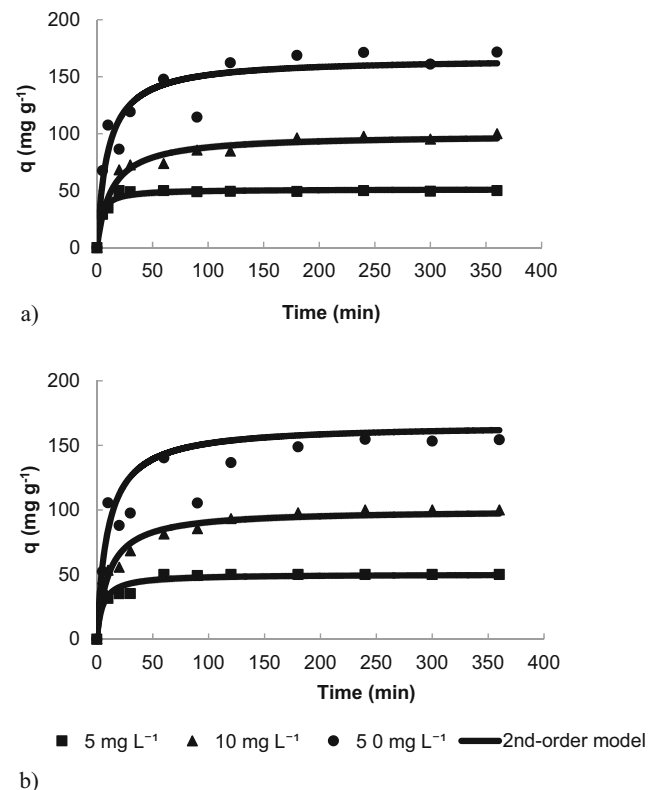
Fig. 2 Adsorption kinetics of Au(III) on *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different initial gold concentrations (pH = 2.0, 30 °C)
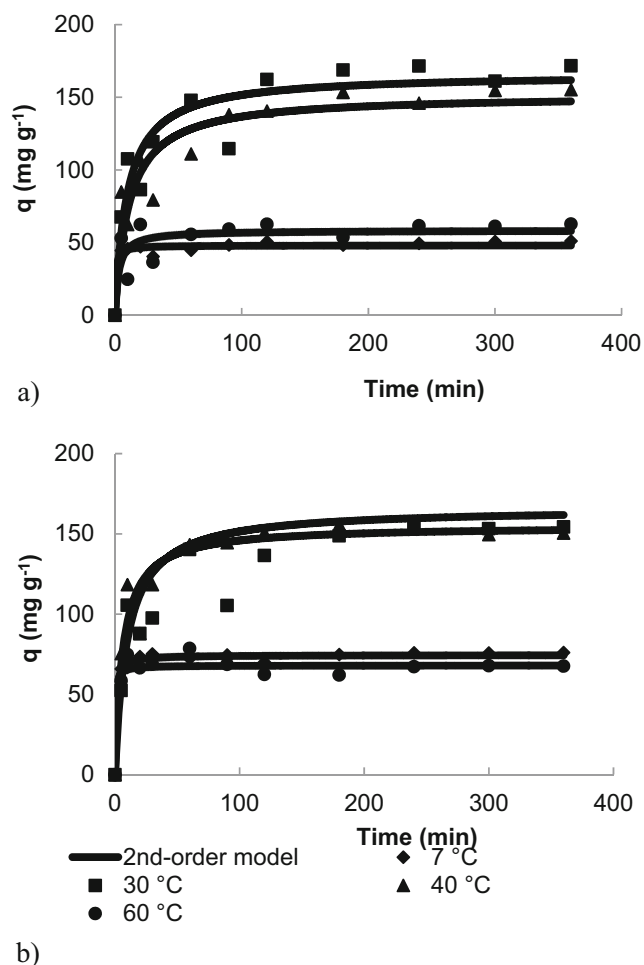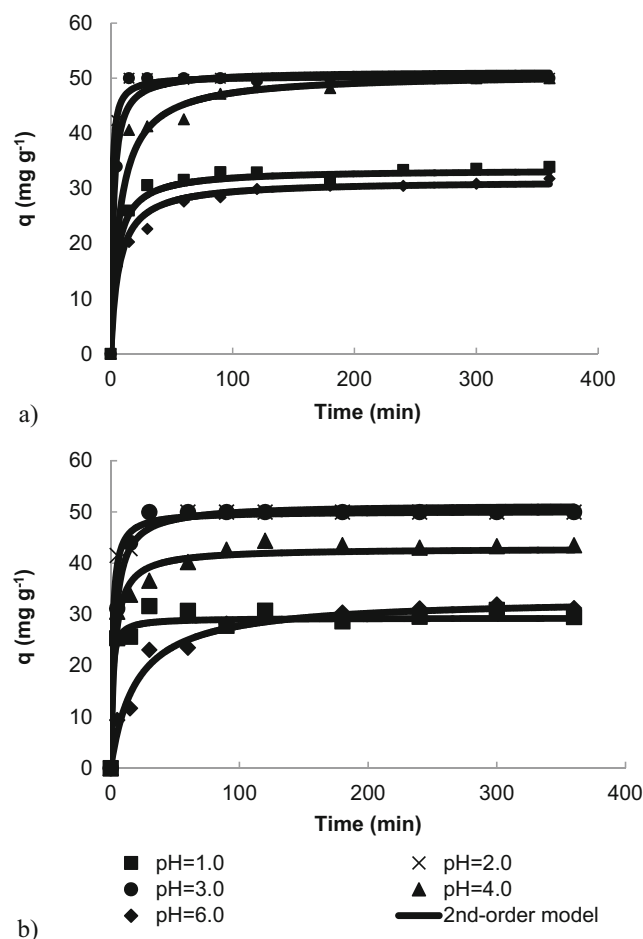
Fig. 3 Adsorption kinetics of Au(III) on *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different temperatures (pH = 2.0, initial gold concentration 50 mg L^{-1})

Fig. 4 Adsorption kinetics of Au(III) on *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different pH (25 °C, initial gold concentration 5 mg L^{-1})

rate (k_2) was decreased with an increase in initial concentration of Au(III) for *T. obliquus AS-6-1* and *T. obliquus*. The rate retained the same of 0.0004 g mg^{-1} min^{-1} for *T. obliquus AS-6-1* between 30 and 40 °C, and 0.0005 g mg^{-1} min^{-1} at 30 °C and 0.0013 g mg^{-1} min^{-1} at 40 °C for *T. obliquus*. In addition, the rate obtained the maximum value of 0.093 g mg^{-1} min^{-1} at pH of 2.0 for *T. obliquus AS-6-1* and 0.21 g mg^{-1} min^{-1} at pH of 3.0 for *T. obliquus*. The straight lines in plot of t/q_t versus t showed a good line in experimental data with the second-order kinetic model for different initial Au(III) concentration (Fig. 5). The similar straight-line agreements were also observed for data at different temperature (Fig. 6) and pH (Fig. 7).

Discussion

The Langmuir adsorption model is valid for single-layer adsorption and assumes that all the binding sites are free sites (Njikam and Schiewer 2012). The Freundlich model is also an empirical
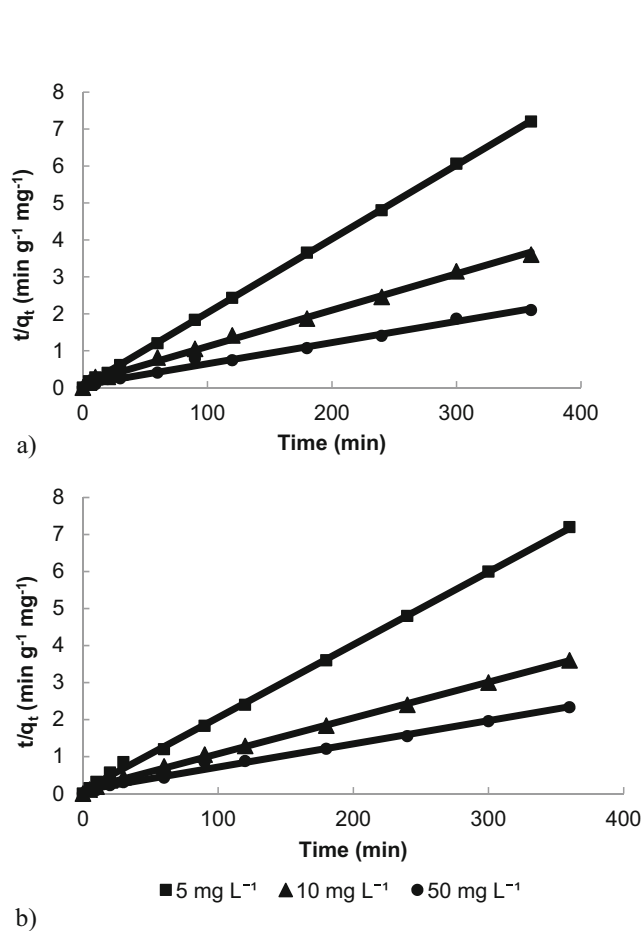
equation, which is often used to estimate the adsorption intensity of the adsorbent towards the adsorbate (Lawal et al. 2010). From the results, the Langmuir model performed better than the Freundlich model with the former exhibiting a higher correlation co-efficient (R^2) at temperature ranging from 7 to 60 °C.

The q_m obtained from Langmuir model at 30 or 40 °C was much higher than that at 7 or 60 °C. It may imply that the low (≤ 7 °C) and high temperatures (≥ 60 °C) are unfavorable in adsorption of Au(III) on algal adsorbents, which can be further demonstrated by the higher K_d at 30 or 40 °C and lower K_d at 7 or 60 °C. But the maximum adsorption capacities for *T. obliquus AS-6-1* and *T. obliquus* at 30 °C were insignificantly changed with an increase in temperature to 40 °C, thereby implying a temperature-independent adsorption of Au(III) from 30 to 40 °C. Previous study conducted by Ishikawa et al. (2002) showed the effect of temperature on the maximum uptakes was seldom of importance from 5 to 45 °C using the egg shell membrane material. However, a significant increase on Au(III) uptake was observed at 65 °C.

Depending on the interest of the study, biosorbents with both a high q_m and a high b usually have a better efficiency

Table 3 Comparison of second-order adsorption rate constants, and calculated $q_{e,cal}$ and experimental $q_{e,exp}$ values for different initial Au(III) concentrations, temperatures, and pH

Parameters	T. obliquus AS-6-1				T. obliquus			
	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	$q_{e,exp}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	$q_{e,exp}$ (mg g^{-1})
Initial Au(III) concentration (mg L^{-1}) (pH 2.0, 30 °C)								
5	1.00	0.0132	50	50	1.00	0.0043	50.76	50
10	1.00	0.0007	102.04	100	1.00	0.0009	103.09	100
50	0.99	0.0004	175.44	171.6	0.99	0.0005	158.73	154.43
Temperature (°C) (pH 2.0, 50 mg L^{-1})								
7	1.00	0.0054	51.02	51	1.00	0.0065	76.34	76.2
30	0.99	0.0004	175.44	171.6	1.00	0.0005	158.73	154.43
40	0.99	0.0004	158.73	155.23	1.00	0.0013	153.85	150.53
60	0.99	0.0019	62.89	62.63	1.00	0.0541	67.11	67.67
pH (5 mg L^{-1}, 25 °C)								
1	0.99	0.0071	33.9	33.9	1.00	0.0336	29.94	29.5
2	1.00	0.093	50	50	1.00	0.0254	50.25	50
3	1.00	0.036	50	50	1.00	0.0210	50.25	50
4	1.00	0.003	51.02	50	1.00	0.0082	43.86	43.5
6	1.00	0.004	31.95	31.8	1.00	0.0021	32.89	31.23

Fig. 5 Plot of the pseudo-second-order model for *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different initial Au(III) concentrations (30 °C, pH 2.0)
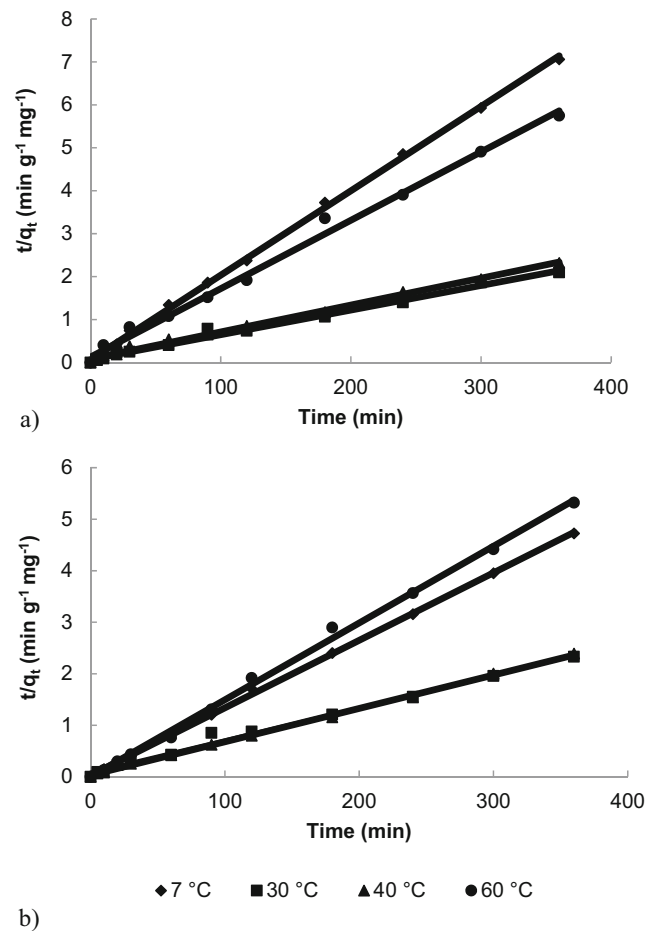
Fig. 6 Plot of the pseudo-second-order model for *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different temperatures (pH = 2.0, initial gold concentration 50 mg L^{-1})

a)

■ pH=1.0　　× pH=2.0　　● pH=3.0　　▲ pH=4.0　　◆ pH=6.0

b)
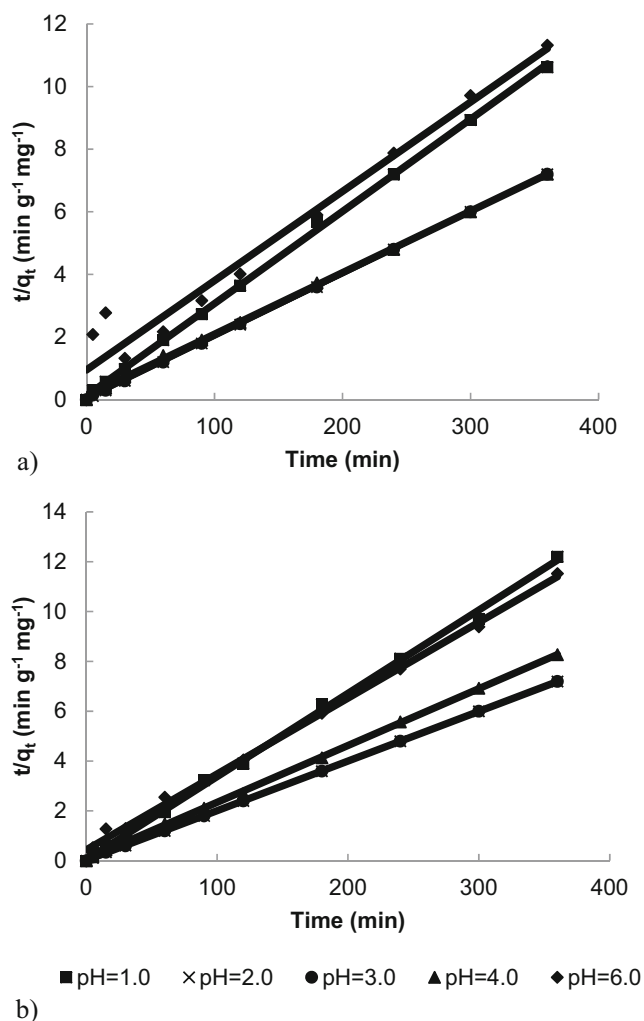
Fig. 7 Plot of the Pseudo second-order model for *T. obliquus AS-6-1* (**a**) and *T. obliquus* (**b**) at different pH (25 °C, initial gold concentration 5 mg L^{-1})

for recovery (Birungi and Chirwa 2015). *Tetradesmus obliquus AS-6-1* and *T. obliquus* had higher q_m and b at 30 °C than that at 40 °C, which implied the preference of temperature at 30 °C to gold(III) adsorption on the tested algal species for gold recovery.

A comparison of maximum uptakes (q_m) and affinity (b) between *T. obliquus AS-6-1* and *T. obliquus* at 30 °C showed a higher adsorption capacity and affinity for former than latter. This shows that *T. obliquus AS-6-1* is a more promising adsorbent for the recovery of gold. All the K_d values above 5000 mL g^{-1} at 30 °C for *T. obliquus AS-6-1* further showed that *T. obliquus AS-6-1* had a stronger adsorption affinity to Au(III) than *T. obliquus* at 30 °C. The extracellular biopolymers excreted from the self-flocculating microalga could possess more binding sites involved in gold adsorption (Guo et al. 2013; Alam et al. 2015). This might contribute to the difference on adsorption performance between the self-flocculating *T. obliquus AS-6-1* and non-flocculating *T. obliquus.*

At low concentration of ≤ 10 mg L^{-1}, the experimental data fitted the model well in the whole range of reaction. But at higher concentration of 50 mg L^{-1}, some measured data slightly scattered away from the model with an increase in time (Fig. 2). This could be due to the complete saturation of some active binding groups on algal cell wall. Birungi and Chirwa (2017) also reported the same trend due to saturation of binding sites. An increase in the initial Au(III) concentration leaded to an increase in the adsorption capacity of Au(III) on the tested algae. This may be due to the increase in the driving force of the concentration gradient, as an increase in the initial Au(III) concentration. Similar effect on the adsorption trend by initial concentration ranging from 20 to 200 mg L^{-1} has also been shown in the case of adsorption of Pt(IV), Pd(II), and Au(III) onto modified crosslinked chitosan resin (Fujiwara et al. 2007).

According to Chojnacka (2010) and Oliveira et al. (2012), the rate of reaction in most biosorption studies is rapid in the first 15–30 min due to the abundance in the available active functional groups. In this study, the abundant availability of vacant binding sites at low concentration of ≤ 10 mg L^{-1} of Au(III) may account for the complete efficiency with 100% uptake within 180 min for *T. obliquus AS-6-1* and *T. obliquus*. But at concentration of 50 mg L^{-1} of Au(III), less than 35% of Au(III) adsorbed on the algal adsorbents. The decrease in rate constant (k_2) with an increase in initial concentrations of Au(III) could probably imply that some binding sites became saturated.

Previous studies reported that adsorption is temperature-independent or exothermic reactions (Arrascue et al. 2003; Mack et al. 2007; Das 2010; Kumar et al. 2015). In the temperature ranging from 7 to 60 °C, a significant effect of temperature on Au(III) uptake by the tested algae was observed. The adsorption performance at 30 or 40 °C was much better than that at 7 or 60 °C, which demonstrated again that the low (≤ 7 °C) and high temperatures (≥ 60 °C) are unfavorable in adsorption of Au(III) on algal adsorbents.

Moreover, temperature had no significant influence on the Au(III) uptake between 30 and 40 °C, which was further demonstrated by the insignificant change in rate (k_2) between 30 and 40 °C. Although there was slight change in adsorption capacity with an increase in temperature from 30 to 40 °C for *T. obliquus AS-6-1* and *T. obliquus*, more studies are required to understand the adsorption of Au(III) on microalgal adsorbents is exothermic or endothermic or independent-temperature during a certain temperature range.

The experiment was carried out at pH ranging from 1.0 to 6.0 in this study. At low pH of 2.0 and 3.0, presence of excess H$^+$ on the cell surface enhanced the uptake of anionic gold in solution (Das 2010). With the pH increased to 6.0, the uptake was reduced drastically which may be due to the less availability of positively charged binding sites on biomass against the negatively charged AuCl$_4^-$ in the solution. Ting and Mittal (2002) proposed the formation of

hydroxide chloride complexes of gold above pH 4.0 appeared to be responsible for reduced uptake using a fungal biosorbent. Moreover, charge reversal of the biosorbent which occurred at pH 1.0 may account for the decline in uptake below pH 2.0 (Das 2010).

Complete adsorption at equilibrium was obtained at pH of 4.0 for *T. obliquus AS-6-1*, but the adsorption rate (k_2) was much lower than that at pH of 2.0 and 3.0. Additionally, the adsorption capacity at pH 4.0 for *T. obliquus* was lower than that at pH 2.0 or 3.0 within the whole range of reaction time. The results indicated that the optimal pH for Au(III) adsorption on *T. obliquus AS-6-1* and *T. obliquus* is between 2.0 and 3.0.

Kinetic models assist in understanding the adsorption mechanisms caused by variation in experimental conditions. The experimental data fit better with Pseudo second-order model than Pseudo first-order model, with the former exhibiting a higher correlation co-efficient (R^2) at different initial Au(III) concentrations, temperatures, and pH (Table 3). This suggests that the adsorption of Au(III) on *T. obliquus AS-6-1* and *T. obliquus* is not a first-order reaction. Additional evidence for preference of pseudo-second-order model was provided with no pronounced difference between experimental $q_{e,exp}$ and calculated $q_{e,cal}$ data in Table 3. The equilibrium adsorption capacity q_e is required to fit the data, but in many cases q_e remains unknown due to slow adsorption processes (Chiou and Li 2002). In this study, the second-order kinetics is applicable with the basic assumption that adsorption reaction on the surface of adsorbent is rate-controlling step (Liu 2008). It is more likely to predict the behavior over the whole range of adsorption and is in agreement with adsorption reaction on the surface of adsorbent being the rate-controlling step, instead of mass transfer.

Conclusion

Compared to the non-flocculating strain, the self-flocculating *T. obliquus AS-6-1* is a more efficient and potential adsorbent for gold recovery, probably due to its excreted extracellular biopolymers possessing more binding sites involved in gold adsorption. The Au(III) adsorption capacity by *T. obliquus AS-6-1* increased with an increase in initial concentration. The maximum adsorption capacity achieved at pH 2.0 and 30 °C was 169.49 mg g^{-1} estimated by Langmuir model. Pseudo-second-order kinetic model agreed very well with the dynamical behavior for the Au(III) adsorption by *T. obliquus AS-6-1*, which suggests that its adsorption reaction on the surface of adsorbent was the rate-limiting step but not the mass transport. More studies are required to find out the adsorption of Au(III) by the self-flocculating microalga is exothermic or endothermic or independent temperature during a certain temperature range.

References

Aksu Z, Sag Y, Kutsal T (1992) The biosorption of copper (II) by *C. vulgaris* and *Z. ramigera*. Environ Technol 13:579–586

Alam MA, Wan C, Zhao XQ, Chen LJ, Chang JS, Bai FW (2015) Enhanced removal of Zn^{2+} or Cd^{2+} by the flocculating *Chlorella vulgaris JSC-7*. J Hazard Mater 289:38–45

Al-Saidi HM (2016) The fast recovery of Au(III) ions from aqueous solutions using raw date pits: kinetic, thermodynamic and equilibrium studies. J Saudi Chem Soc 20:615–624

Arrascue ML, Garcia HM, Horna O, Guibal E (2003) Gold sorption on chitosan derivatives. Hydrometallurgy 71:191–200

Birungi ZS, Chirwa EMN (2015) The adsorption potential and recovery of thallium using green microalgae from eutrophic water sources. J Hazard Mater 299:67–77

Birungi ZS, Chirwa EMN (2017) Competitive adsorption in a ternary system of toxic metals and rare earth elements using *Desmodesmus multivariabilis*: empirical and kinetic modelling. J Appl Phycol 29:2899–2910

Chen CY, Kao AL, Tsai ZC, Chow TJ, Chang HY, Zhao XQ, Chen PT, Su HY, Chang JS (2016) Expression of type 2 diacylglycerol acyltransferse gene DGTT1 from *Chlamydomonas reinhardtii* enhances lipid production in *Scenedesmus obliquus*. Biotechnol J 11: 336–344

Chiou MS, Li HY (2002) Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. J Hazard Mater 93: 233–248

Chojnacka K (2010) Biosorption and bioaccumulation–the prospects for practical applications. Environ Int 36:299–307

Das N (2010) Recovery of precious metals through biosorption—a review. Hydrometallurgy 103:180–189

Esposito A, Pagnanelli F, Veglio F (2002) pH related equilibria models for biosorption in single metal system. Chem Eng Sci 57:307–313

Fiol N, Villaescusa I, Martinez M, Miralles N, Poch J, Serarols J (2006) Sorption of Pb (II), Ni (II), Cu (II) and Cd (II) from aqueous solution by olive stone waste. Sep Purif Technol 50:132–140

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. J Hazard Mater 146:39–50

Guo SL, Zhao XQ, Wan C, Huang ZY, Yang YL, Alam MA, Ho SH, Bai FW, Chang JS (2013) Characterization of flocculating agent from the self-flocculating microalga *Scenedesmus obliquus AS-6-1* for efficient biomass harvest. Bioresour Technol 145:285–289

Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochem 34:451–465

Ho YS, McKay G (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res 34:735–742

Ishikawa SI, Suyama K, Arihara K, Itoh M (2002) Uptake and recovery of gold ions from electroplating wastes using eggshell membrane. Bioresour Technol 81:201–206

Ju XH, Igarashi KI, Miyashita S, Mitsuhashi H, Fujii S, Sawada H, Minoda A (2016) Effective and selective recovery of gold and palladium ions from metal wastewater using a sulfothermophilic red alga, *Galdieria sulphuraria*. Bioresour Technol 211:759–764

Kumar KS, Dahms HU, Won EJ, Lee JS, Shin KH (2015) Microalgae—a promising tool for heavy metal remediation. Ecotoxicol Environ Saf 113:329–352

Lawal OS, Sanni AR, Ajayi IA, Rabiu OO (2010) Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. J Hazard Mater 177:829–835

Liu Y (2008) New insights into pseudo-second-order kinetic equation for adsorption. Colloids Surf A Physicochem Eng Asp 320:275–278

Mack C, Wilhelmi B, Duncan JR, Burgess JE (2007) Biosorption of precious metals. Biotechnol Adv 25:264–271

Njikam E, Schiewer S (2012) Optimization and kinetic modeling of cadmium desorption from citrus peels: a process for biosorbent regeneration. J Hazard Mater 214:242–248

Oliveira RC, Guibal E, Garcia O Jr (2012) Biosorption and desorption of lanthanum (III) and neodymium (III) in fixed-bed columns with *Sargassum* sp.: perspectives for separation of rare earth metals. Biotechnol Prog 28:715–722

Park D, Yun YS, Park JM (2010) The past, present, and future trends of biosorption. Biotechnol Bioprocess Eng 15:86–102

Sangvanich V, Sukwarotwat RJ, Wiacek RM, Grudzien GE, Fryxell RS, Addleman et al (2010) Selective capture of cesium and thallium from natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica. J Hazard Mater 182:225–231

Ting YP, Mittal AK (2002) Effect of pH on the biosorption of gold by a fungal biosorbent. Resour Environ Biotechnol 3:229–239

Ting YP, Teo WK, Soh CY (1995) Gold uptake by *Chlorella vulgaris*. J Appl Phycol 7:97–100

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*. Chem Eng J 167:223–227

Won SW, Kotte P, Wei W, Lim A, Yun YS (2014) Biosorbents for recovery of precious metals. Bioresour Technol 160:203–212

Zhang XY, Zhao XQ, Wan C, Chen B, Bai FW (2016) Efficient biosorption of cadmium by the self-flocculating microalga *Scenedesmus obliquus AS-6-1*. Algal Res 16:427–433