

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

Na Shen\*, E.M.N. Chirwa

University of Pretoria, Department of Chemical Engineering, Lynnwood Road, Private bag X20 Hatfield, Pretoria 0002, South Africa.

## Abstract

Microalga has 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 *Tetradesmus 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<sup>-1</sup> 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<sup>-1</sup>. Furthermore, all the K<sub>d</sub> values above 5000 mL g<sup>-1</sup> 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 ( $\leq 7$  °C) or high temperature ( $\geq 60$  °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:** *T. obliquus* AS-6-1; 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 N 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.

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 their low cost, relative abundance and high binding capacity, has been considered to be promising and economical biosorbents for recovery of gold (Das N 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 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 *T. obliquus AS-6-1* and *C. 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* (the previous name is *Scenedesmus obliquus AS-6-1*) and the non-flocculating freshwater microalga *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 behaviour 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, 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 *T. obliquus AS-6-1* was initially isolated from freshwater located in southern Taiwan (Zhang et al. 2016). The non-flocculating strain *T. obliquus* (CCAP No. 276/7) was purchased from the Culture Collection of Algae and Protozoa (CCAP) for comparison purpose. These pure strains were cultured in a 12 L culture vessel containing 10L of Blue-Green (BG11) medium (Chen et al. 2016) under illumination at roughly  $60 \mu\text{mol photons m}^{-2} \text{s}^{-1}$  at  $25 \pm 1$  °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<sup>-1</sup> of chloroauric acid (HAuCl<sub>4</sub>) was used to prepare initial Au(III) concentrations between 5 and 50 mg L<sup>-1</sup>. The pH of the metal solution was adjusted with 0.1 M NaOH/ 0.1M HCl. All the reagents were of analytical grade and procured from Sigma–Aldrich.

## Batch Adsorption Equilibrium Studies

The equilibrium adsorption of Au(III) on the microalga adsorbents were conducted at different temperatures. The pre-determined 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<sup>-1</sup> 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 analysed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400). The amount of metal bound by the biosorbents at equilibrium  $q_e$  (mg g<sup>-1</sup>) was computed as follows:

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

Where,  $C_0$  and  $C_e$  are the initial and equilibrium metal concentrations (mg L<sup>-1</sup>), 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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 analysed using Atomic Absorption Spectrometer (AAS Perkin Elmer AAnalyst 400).

## Data Analysis

### Adsorption Isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour 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 Equation (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:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (2)$$

Where,  $q_e$  is the amount of metal ions absorbed at equilibrium (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of metal ions remaining in the solution (mg L<sup>-1</sup>),  $q_m$  represents the maximum adsorption capacity (mg g<sup>-1</sup>) and  $b$  is a constant related to the energy of adsorption (L mg<sup>-1</sup>).

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

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

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  $K_d$  ( $\text{mL g}^{-1}$ ) which expresses the effectiveness of the biosorbent for metal uptake (Sangvanich et al. 2010). The  $K_d$  was calculated using equation as follows:

$$K_d = \frac{C_0 - C_f}{C_f} \times \frac{V}{M} \quad (4)$$

Where,  $C_0$  is the initial concentration ( $\text{mg L}^{-1}$ ),  $C_f$  is final concentrations ( $\text{mg L}^{-1}$ ),  $V$  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 analyse the rate of adsorption uptake (Ho and McKay 1999). The expression for the Pseudo-first-order is given by the following equation:

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

which is given by the following linearized equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

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

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

which is given by the following linearized equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

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

## 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  $\leq 1.00$  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 equation (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  $\geq 151 \text{ mg g}^{-1}$  than  $q_m \leq 77 \text{ mg g}^{-1}$  at temperature of 7 °C and 60 °C. Moreover, the  $q_m$  for the tested algae had insignificant change between 30 °C 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  $\text{mg g}^{-1}$  at 30 °C, respectively, and both the tested algae expressed a higher affinity (b) of 3.69-2.95  $\text{L mg}^{-1}$  compared to the b of 1.13-1.22  $\text{L mg}^{-1}$  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  $\text{mL g}^{-1}$ , then it's considered good, and when the value is greater than 50000  $\text{mL g}^{-1}$  then its 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 42632 mL g<sup>-1</sup> at initial concentration of 20 mg L<sup>-1</sup>, 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<sup>-1</sup> at initial concentration from 20 to 50 mg L<sup>-1</sup> for *T. obliquus* AS-6-1. While at 40 °C, the  $K_d$  values were good except at initial concentration of 50 mg L<sup>-1</sup>. 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<sup>-1</sup>, but were lower than 5000 mL g<sup>-1</sup> at initial concentration of 50 mg L<sup>-1</sup>.

## 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 shown in Fig.2. With an increase in the initial Au(III) concentration from 5 to 50 mg L<sup>-1</sup>, the adsorption capacity increased with increasing time. At low concentrations of 5 and 10 mg L<sup>-1</sup>, 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<sup>-1</sup> at initial concentration of 5 and 10 mg L<sup>-1</sup>, respectively. At higher concentration of 50 mg L<sup>-1</sup>, the maximum uptake was attained within 240 min with 171 and 154 mg g<sup>-1</sup> 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<sup>-1</sup> is 1.1 times larger than that of *T. obliquus*.

### Effect of Temperature

At low ( $\leq 7$  °C) and high temperature ( $\geq 60$  °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 closed 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  $\geq 0.99$  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 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  $0.0004 \text{ g mg}^{-1} \text{ min}^{-1}$  for *T. obliquus* AS-6-1 between 30 and 40 °C, and  $0.0005 \text{ g mg}^{-1} \text{ min}^{-1}$  at 30 °C and  $0.0013 \text{ g mg}^{-1} \text{ min}^{-1}$  at 40 °C for *T. obliquus*. In addition, the rate obtained the maximum value of  $0.093 \text{ g mg}^{-1} \text{ min}^{-1}$  at pH of 2.0 for *T. obliquus* AS-6-1 and  $0.21 \text{ g mg}^{-1} \text{ min}^{-1}$  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 ( $\leq 7$  °C) and high temperatures ( $\geq 60$  °C) are unfavourable 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 °. 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 Gold (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 for recovery (Birungi and Chirwa 2015). *T. 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 potential and promising adsorbent for the recovery of gold. All the  $K_d$  values above 5000 mL g<sup>-1</sup> 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 (Alam et al. 2015, Guo et al. 2013). 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  $\leq 10$  mg L<sup>-1</sup>, the experimental data fitted the model well in the whole range of reaction. But at higher concentration of 50 mg L<sup>-1</sup>, 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 led 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<sup>-1</sup> 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 minutes due to the abundance in the available active functional groups. In this study, the abundant availability of vacant binding sites at low concentration of  $\leq 10$  mg L<sup>-1</sup> 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<sup>-1</sup> 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 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 ( $\leq 7$  °C) and high temperatures ( $\geq 60$  °C) are unfavourable in adsorption of Au(III) on algal adsorbents.

Moreover, the temperature had no significant influence on the Au(III) uptake between 30 and 40 °C, which could be 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 coefficient ( $R^2$ ) 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 Y 2008). It is more likely to predict the behaviour 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 microalga, the self-flocculating microalga *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<sup>-1</sup> estimated by Langmuir model. Pseudo second-order kinetic model agreed very well with the dynamical behaviour 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.

## Acknowledgements

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.

## References

- Aksu Z, Sag Y, Kutsal T (1992) The biosorption of copper (II) by *C. vulgaris* and *Z. ramigera*. *Environ Technol* 13:579–586.
- Arrascue ML, Garcia HM, Horna O, Guibal E (2003) Gold sorption on chitosan derivatives. *Hydrometallurgy* 71:191–200.
- Alam MA, Wan C, Zhao XQ, Chen LJ, Chang JS, Bai FW (2015) Enhanced removal of Zn<sup>2+</sup> or Cd<sup>2+</sup> 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.

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.

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.

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

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 sphagnummoss 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 and Environ Saf* 113:329-352.

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

Lawal OS, Sanni AR, Ajayi IA, Rabiou 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.

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

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

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.

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

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

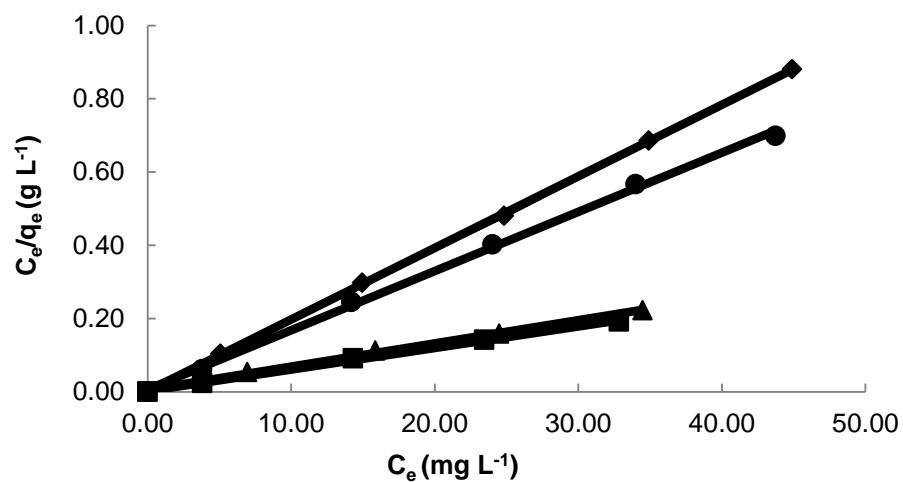


Table 2: Distribution co-efficient for adsorption of Au(III) on *T. obliquus* AS-6-1 and *T. obliquus*

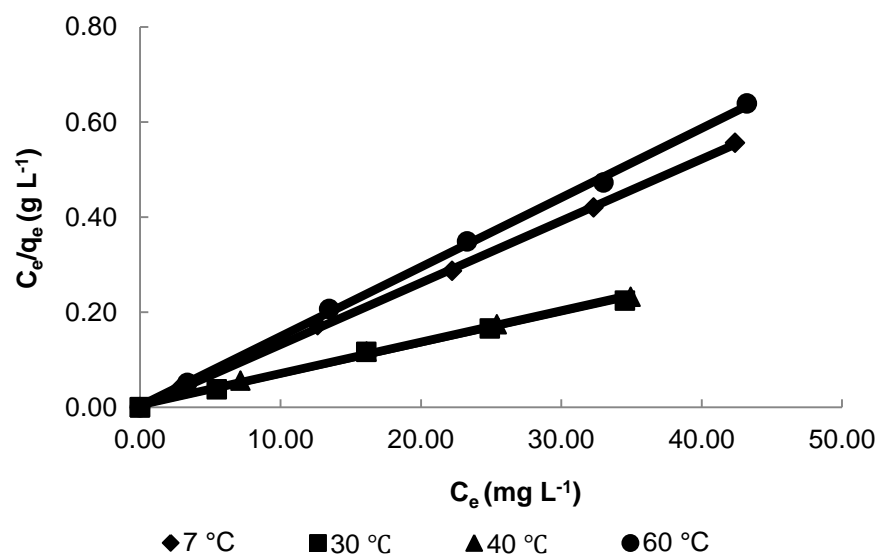
Adsorbent	$C_0$ (mg L <sup>-1</sup> )	7 °C $K_d$ (mL g <sup>-1</sup> )	30 °C $K_d$ (mL g <sup>-1</sup> )	40 °C $K_d$ (mL g <sup>-1</sup> )	60 °C $K_d$ (mL g <sup>-1</sup> )
<i>T. obliquus</i> AS-6-1	20	3366	42632	18791	4078
	30	2084	10964	8896	2486
	40	1459	7053	6324	1765
	50	1136	5225	4503	1432
<i>T. obliquus</i>	20	5814	26585	17881	4840
	30	3491	8595	8576	2868
	40	2380	6049	5738	2115
	50	1798	4469	4306	1565

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	<i>T. obliquus AS-6-1</i>				<i>T. obliquus</i>			
	$R^2$	$k_2$ ( $g\ mg^{-1}\ min^{-1}$ )	$q_{e,cal}$ ( $mg\ g^{-1}$ )	$q_{e,exp}$ ( $mg\ g^{-1}$ )	$R^2$	$k_2$ ( $g\ mg^{-1}\ min^{-1}$ )	$q_{e,cal}$ ( $mg\ g^{-1}$ )	$q_{e,exp}$ ( $mg\ g^{-1}$ )
<b>Initial Au(III) concentration (<math>mg\ L^{-1}</math>) (pH 2.0, 30 °C)</b>								
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
<b>Temperature (°C) (pH 2.0, 50 <math>mg\ L^{-1}</math>)</b>								
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
<b>pH (5 <math>mg\ L^{-1}</math>, 25 °C)</b>								
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

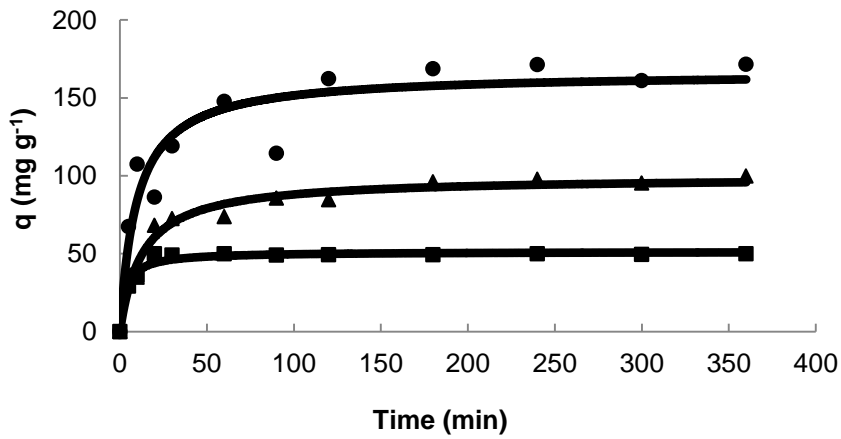


a)

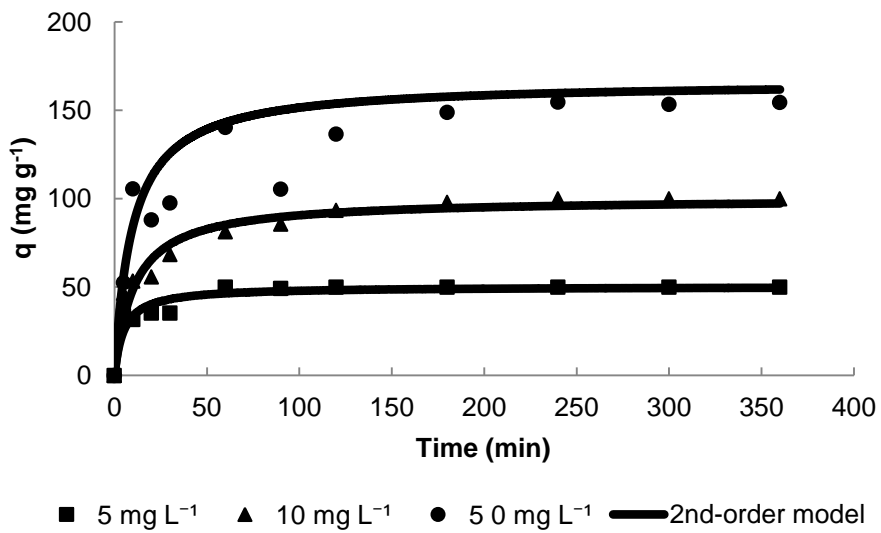


b)

Figure 1: Langmuir plot at different temperatures on *T. obliquus* AS-6-1 (a) and *T. obliquus* (b)

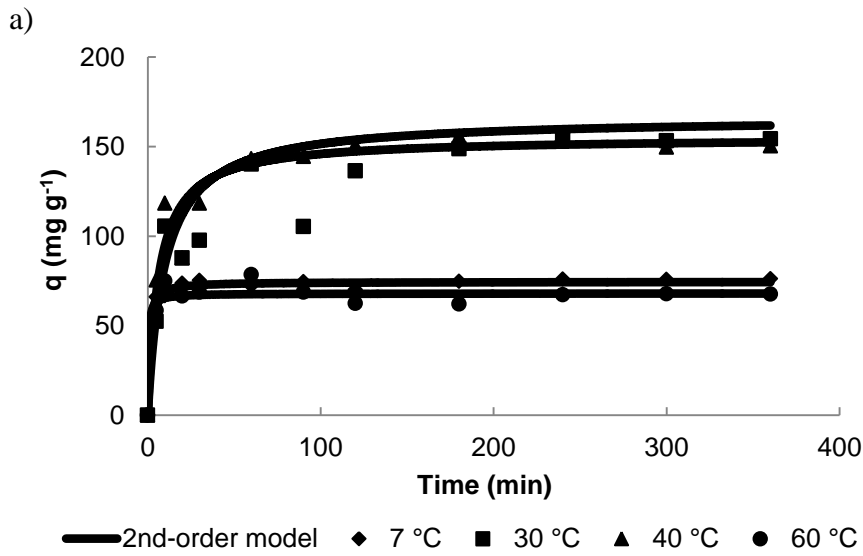
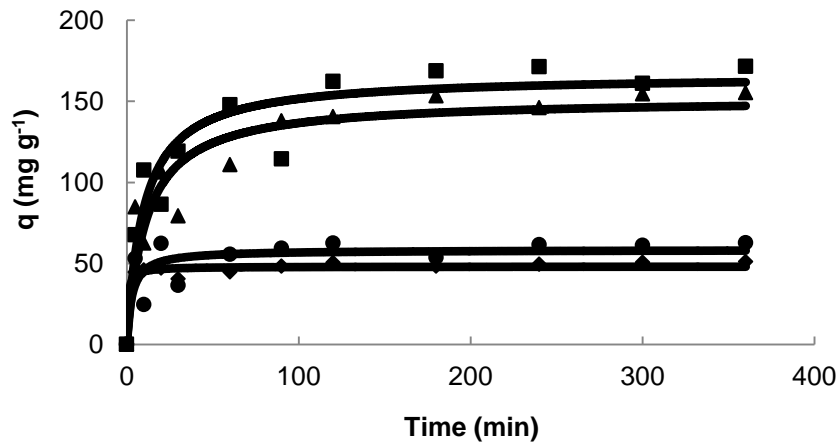


a)



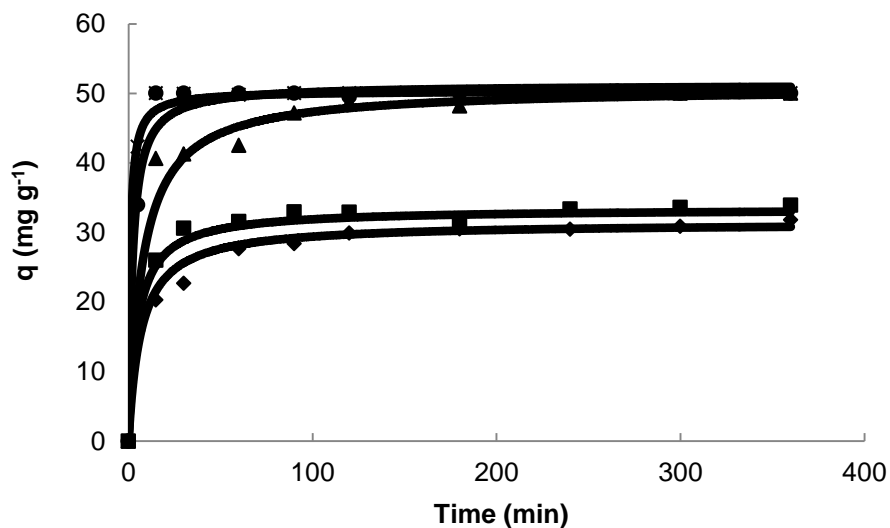
b)

Figure 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)

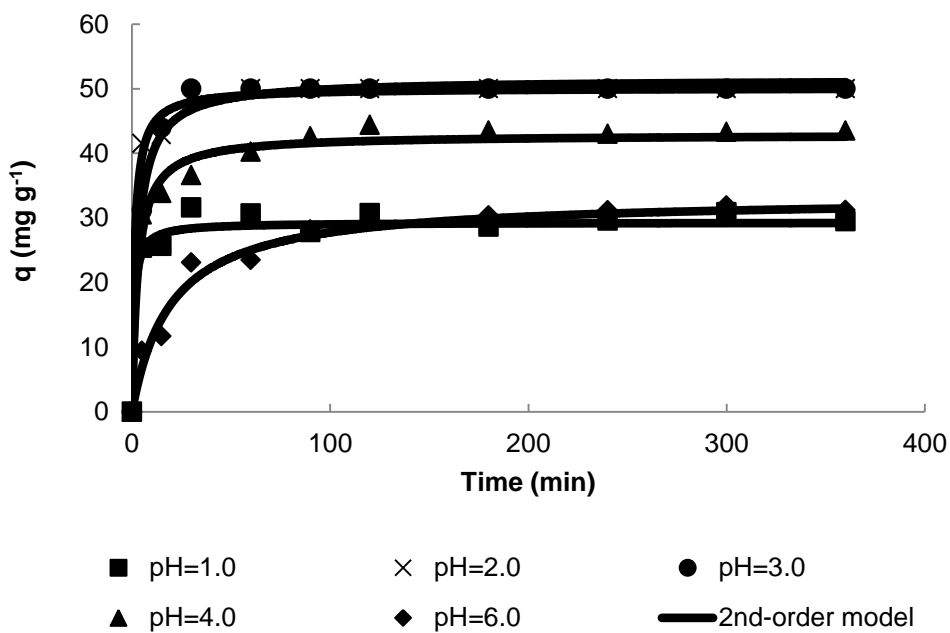


b)

Figure 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<sup>-1</sup>)

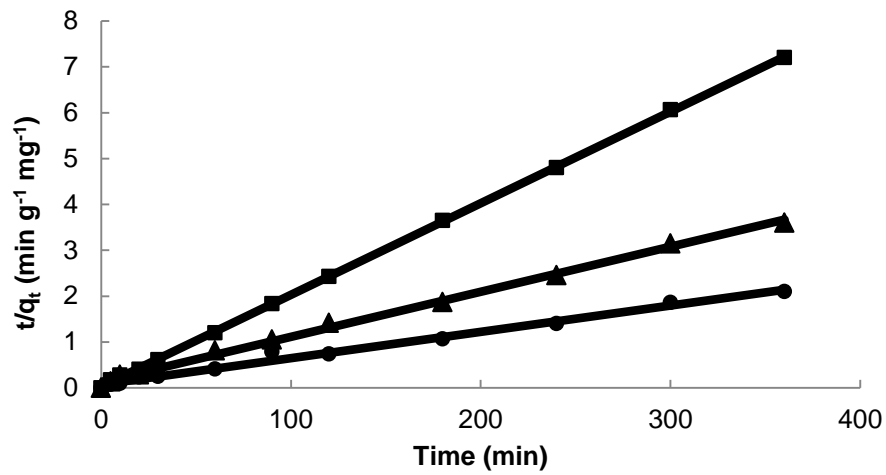


a)

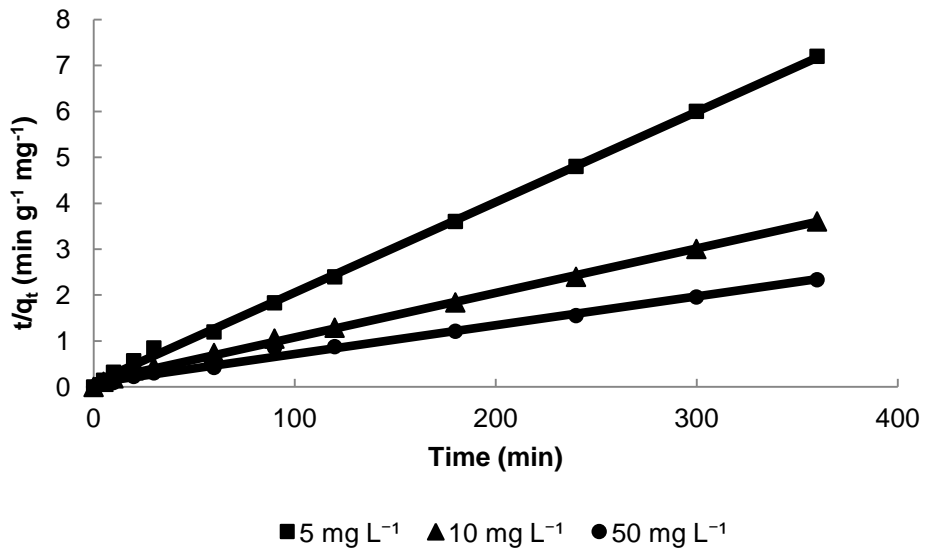


b)

Figure 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 5mg L<sup>-1</sup>)

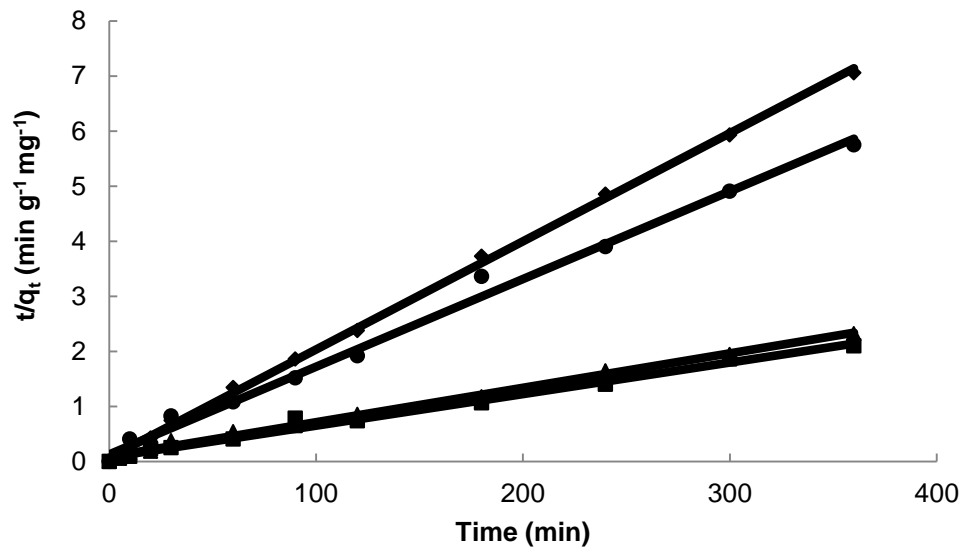


a)

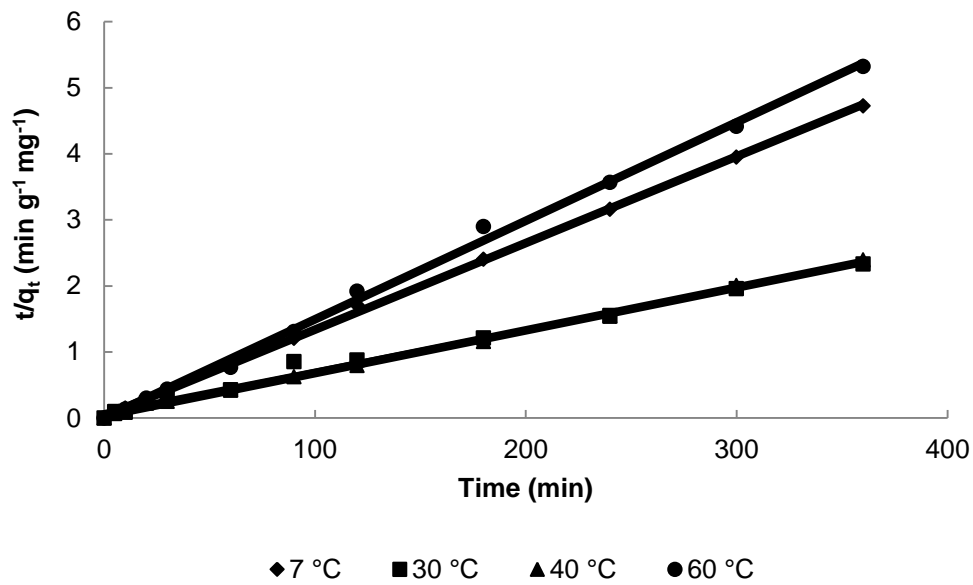


b)

Figure 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)



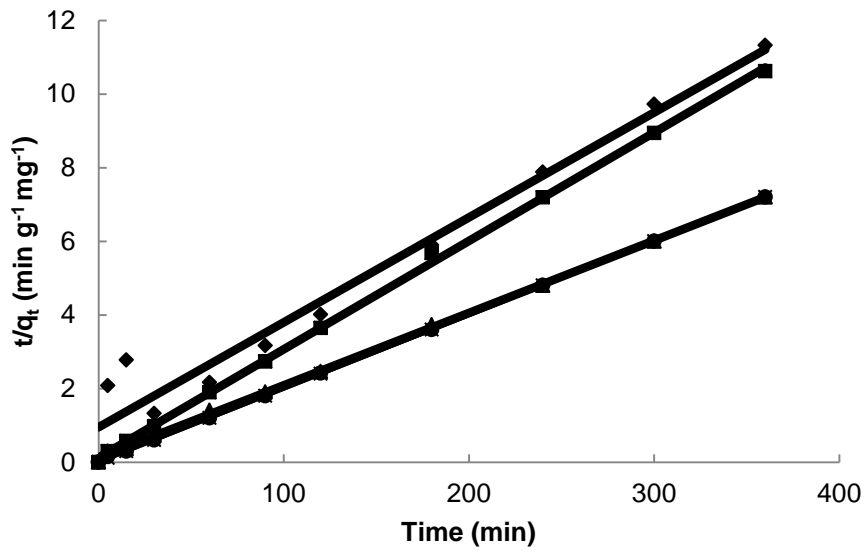
a)



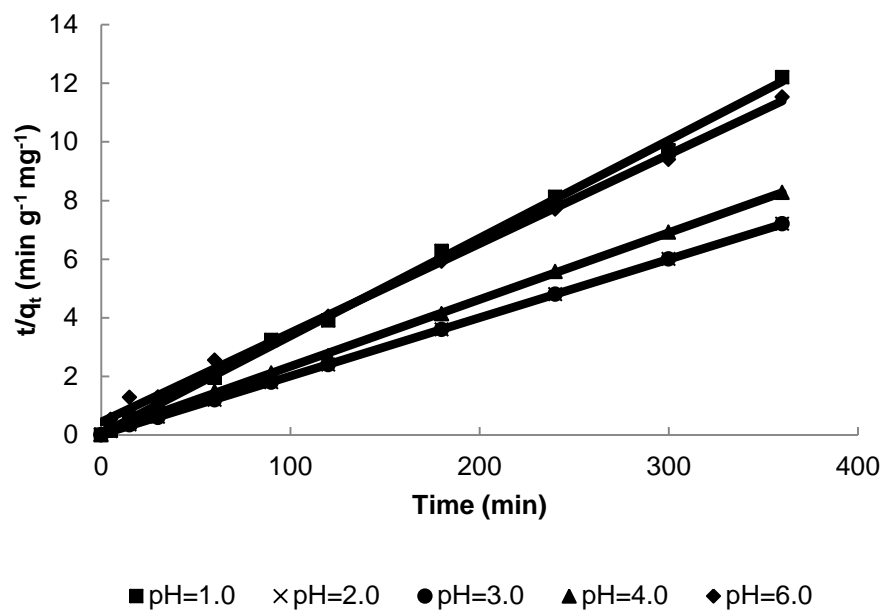
b)

Figure 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<sup>-1</sup>)





a)



b)

Figure 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 5mg L<sup>-1</sup>)