

# The Adsorption Potential and Recovery of Thallium Using Green Micro-Algae from Eutrophic Water Sources

Z.S. Birungi<sup>a,1\*</sup>, E.M.N. Chirwa<sup>a</sup>

<sup>a</sup>University of Pretoria, Department of Chemical Engineering, Lynnwood Road, Private bag X20 Hatfield, Pretoria 0002, South Africa

## Abstract

Thallium (Tl) is a highly volatile and toxic heavy metal regarded to cause pollution even at very low concentrations of several parts per million. Despite the extremely high risk of Tl in the environment, limited information on removal/recovery exists. The study focussed on the use of green algae to determine the sorption potential and recovery of Tl. From the study, removal efficiency was achieved at 100% for lower concentrations of  $\geq 150$  mg/L of Tl. At higher concentrations in a range of 250-500 mg/L, the performance of algae was still higher with sorption capacity ( $q_{max}$ ) between 830 and 1000 mg/g. Generally, *Chlorella vulgaris* was the best adsorbent with a high  $q_{max}$  and lower affinity of 1000 mg/g and 1.11 L/g respectively. When compared to other studies on Tl adsorption, the tested algae showed a better  $q_{max}$  than most adsorbents. The kinetic studies showed better correlation co-efficient of  $\leq 0.99$  for Pseudo-second order model than the first order model. Recovery was achieved highest for *Chlorella vulgaris* using nitric acid at 93.3%. The strongest functional groups responsible for Tl binding on the algal cell wall were carboxyl and phenols. Green algae from freshwater bodies showed significant potential for Tl removal/recovery from industrial wastewater.

**Key words:** green algae, freshwater, cell surface, thallium, adsorption, desorption

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<sup>1\*</sup> Corresponding author. Email: zedshariff@yahoo.com; Tel: +27 12420 4338

## 1. Introduction

Thallium (Tl) is a non-essential and very toxic element often excluded from the list of priority metallic pollutants [1, 2]. Thallium is regarded to be more toxic to humans than mercury, lead and cadmium and notable for causing occupational, accidental and environmental hazards [3, 4]. Thallium appears in two oxidation states; Tl (I) which is highly soluble in aqueous environments and resembles alkali metals and Tl (III) which is more stable forming complexes with sulphates, chlorides, carbonates and nitrates [5-7]. Thallium deposits are generally scarcely distributed worldwide with many industrial applications such as catalyst for making certain alloys, molecular probes, thermometers, acusto-optical equipment, optical glass with refractive index, imitation jewellery, scintillation counters, and super-conductivity in ceramic compounds [8, 9].

One of the major concerns of Tl toxicity lies in the similar ionic radii of  $Tl^+$  and monovalent cations especially potassium ( $K^+$ ) in the crystal lattice which affects all organic ligands. In this case, the cell membrane has non-discriminatory uptake of  $Tl^+$  over  $K^+$  which alters the proper functioning of the biochemical reactions, for example pyruvate kinase, ATPase, stabilisation of ribosomes [4, 10, 11]. Thallium has been reported to cause acute and chronic poisoning with effects such as degenerative changes in the heart, liver and kidney, damage of the central nervous and cardiovascular systems, psychosis, insomnia, alopecia, peripheral neuropathy, gastroenteritis [12-14].

Previous research on removal technologies has focussed on using pre-concentration of Tl by chelating resins [15]; oxidative precipitation of thallichydroxide, reductive cementation of thallium; chemical precipitation by hydroxide compounds, solvent extraction using tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO) [16, 17]; extraction by complex forming re-agents [18]. U.S.EPA approved various treatment technologies such as activated alumina and ion exchange for removal of thallium but the methods are seemingly costly and ineffective [19].

Biosorption is an alternative and or complementary method which utilises relatively cheap waste biomass for sequestering of heavy metals. A variety of microorganisms like bacteria and algae have been utilised in biosorption of some common heavy metals with the exception of Tl [20, 21]. Information on the occurrence, mechanisms, behaviour, and bioremediation of thallium toxicity in the environment is still sketchy [18, 22]. Micro-algae especially green

algae has over 500 genera and approximately 15,000 species found mainly in freshwater of which a few were investigated for their biosorption potential [23, 24]. This study focused on the biosorption potential of 3 green algal species from eutrophic freshwater bodies. Equilibrium and kinetic models were used to estimate the sorption potential and the rate of reaction respectively.

## **2.0 Experimental**

### **2.1 Algal Isolation and Culture**

Algal samples were sourced from Hartbeespoort dam, a freshwater body in South Africa. The algae was centrifuged and washed several times with double distilled water to obtain a sterile concentrate. Agar plates were prepared from bacteriological agar and AF-6 media using standard procedures by [25]. The algae was streaked on the agar plates and left to grow for seven days. Repeated plating was done to eliminate bacteria and obtain pure colonies representing a single species. The algal species were identified using 18S ribosomal RNA gene and the species identified through BLAST search. The identified species included *Scenedesmus acuminatus*, *Chlorella vulgaris* and *Chlamydomonas reinhardtii*. The unialgal species were inoculated into AF-6 media and cultured in the laboratory as starter cultures under controlled temperature at 21- 23°C and algal light (Osram L 36 W/77 Flouora). The algae were then sub-cultured in conical flasks of 1000 and 2000 ml to increase the surface area and volume of algal growth. Harvesting was done twice every month, centrifuged and washed twice in double distilled water to remove excess nutrients. The samples were then dried in the oven at 50°C overnight and stored for sorption experiments.

### **2.2 Sample Preparation and Isotherm Experiments**

The algal samples were crushed in a mortar to form a powder and screened through a 0.3 mm sieve to obtain a uniform size and increase the surface area for adsorption. All chemicals used were of analytical grade and purchased from Merck and Laboratory consumables and chemical supplies in South Africa. Tl is very toxic especially through inhalation and contact with skin or eyes, and was therefore handled with care using the Material Safety Data Sheet (MSDS). The safety gear used in the laboratory included a lab coat, safety goggles, latex gloves and foot wear. All experiments containing Tl were carried out in fume hoods and the waste disposed in a labelled container. After handling of Tl, soap and water was used to thoroughly clean the hands. A standard stock solution of 1000 mg/L of  $Tl^{+}$  was used to

prepare initial Thallium concentrations between 15-500 mg/L. The initial Tl concentrations were measured into 100 ml Erlenmeyer volumetric flasks. The pH of the solution was kept constant at 6 using 0.1M NaOH and HCl for equilibrium experiment. The weighted biomass of 50 mg was added to the measured Tl concentrations and stirred on a magnetic stirrer at a constant speed of 350 (rpm) for 6 hours. The effect of pH was also studied under constant conditions at initial concentration of 250 mg/L and a biomass of 80 mg in the pH range of 2-8 for 4 hours. The experiment was carried out in duplicates and control set up. The pH was adjusted hourly to optimum. A sample was drawn, centrifuged and the supernatant analysed using Inductively Coupled Plasma (ICP, Spectro Arcos FHS12, oschstroisse, Germany).

### **2.3 Kinetics of Thallium Removal and Recovery**

The effect of initial concentration and contact time on Tl adsorption was tested. A constant biomass of 50 mg and initial Tl concentration in the range of 250-500 mg/L was used for all the algal species. The weighted algal samples were mixed in the Tl solution and stirred on a magnetic stirrer at room temperature and a constant speed of 350 rpm. Samples were taken at known time intervals, centrifuged at 6000 rpm for 10 minutes and the supernatant analysed using ICP. The algae logged with Tl from equilibrium experiments were used for desorption kinetics. The samples were rinsed twice in deionised water and added to 0.1M nitric acid concentration for recovery. Samples were also drawn at set time intervals and the supernatant analysed using ICP.

### **2.4 Algal Characterisation**

The algal samples were characterised using the Fourier Transform Infrared Spectroscopy (FTIR- Nicolet iS5, Thermo, South Africa) and Scanning Electron Microscopy (SEM, JOEL JSM 5800LV, Tokyo, Japan). The FTIR sample holder was first cleaned using acetone and a background spectrum collected to check the performance of the instrument. A sample was then loaded and the sample spectrum obtained. Data processing was done to transform absorbance into % transmittance showing wavelength peaks.

Sample preparation for SEM was carried out using 0.5% aqueous osmium tetroxide and phosphate buffer at a concentration of 0.05M for 1 hour. The buffer was used to protect the biological sample from becoming acidic. Water was then extracted from the sample using a range of ethanol grades from 30-100%. The final rinsing was done three times with anhydrous ethanol. Critical drying point using liquid carbon dioxide was then used for sample

drying to prevent damaging the sample. The sample was then mounted on stubs and then coated with gold. After sample preparation, SEM was used to obtain images at different magnification before and after adsorption.

### 3. Results and Discussion

#### 3.1 Isotherm Modelling

The Langmuir and Freundlich models were used to fit experimental data using linearised equation 1 and 2 respectively. These models are widely accepted and often used in biosorption studies involving single solute systems [26-28]. The linearised graph  $C_e/q_e$  vs.  $C_e$  for Langmuir model and  $\log q_e$  vs.  $\log C_e$  for Freundlich model was plotted for all the tested algae, Fig. 1 and 2. The models were compared and the Langmuir model generally exhibited a better correlation coefficient ( $R^2$ ) of  $\leq 0.99$  as compared to the Freundlich model with  $\leq 0.94$  for all the 3 tested species. The slope and intercept were calculated from the linearised equations for sorption capacity ( $q_{max}$ ) and affinity of the metal ( $b$ ). The Langmuir, 1916 [29] is expressed by the linearised equation;

$$C_e/q_e = C_e/q_{max} + 1/bq_{max} \quad (1)$$

where  $q_e$  is the adsorbed metal at equilibrium (mg/g),  $q_{max}$  is the maximum amount of metal sorbed (mg/g),  $b$  is a constant related to the energy of sorption and  $C_e$  is the equilibrium metal ion concentration (mg/L).

The Freundlich, 1906 [30] is represented by the linearised equation as follows;

$$\log q_e = \log k + 1/n \log C_e \quad (2)$$

where  $k$  is biosorption equilibrium constant, representative of the sorption capacity and  $n$  is a constant indicative of biosorption intensity

The essential characteristics of Langmuir were expressed using a dimensionless constant separation factor,  $R_L$  [31].

$$R_L = \frac{1}{1 + (b_L C_o)} \quad (3)$$

where  $R_L$  is the separation factor;  $b_L$  constant related to energy of adsorption from Langmuir model (L/g);  $C_o$  is the highest initial concentration (mg/L)

*Chlamydomonas reinhardtii* and *Chlorella vulgaris* had the highest  $q_{max}$  of 1000 mg/g but the latter expressed a lower affinity ( $b$ ) of 1.11 L/g compared to the former with 1.67 L/g, Table 1. *Scenedesmus acuminatus* had both high  $q_{max}$  and lowest  $b$  of 833.3 mg/g and 0.290 L/g respectively. Depending on the interest of the study, biosorbents with a higher  $q_{max}$  and a lower  $b$  are reported to be better adsorbents regardless of recovery levels [28, 32, 33]. Biosorbents with both a high  $q_{max}$  and a high  $b$  usually have a better efficiency for recovery [34]. The Langmuir isotherm was further evaluated using a separation factor,  $R_L$  given by the equation (Eq. 3.7). When  $R_L$  is  $>1$  then it's unfavourable and favourable if  $0 < R_L < 1$  [35].  $R_L$  was calculated for all the tested algae and found to be favourable for adsorption for all the species, Table 1.

The tested algal species were compared with some other potential adsorbents for Tl removal. All the 3 tested algal species had significant  $q_{max}$  in a range of 830-1000 mg/g compared to most adsorbents tested for thallium removal except for Prussian blue NP (PB) which had 1400 mg/g, Table 2. The high binding capacity for PB could be attributed to the physical chemical properties of the reaction medium such as particle size, moisture content and is usually used as an antidote for Tl poisoning [36].

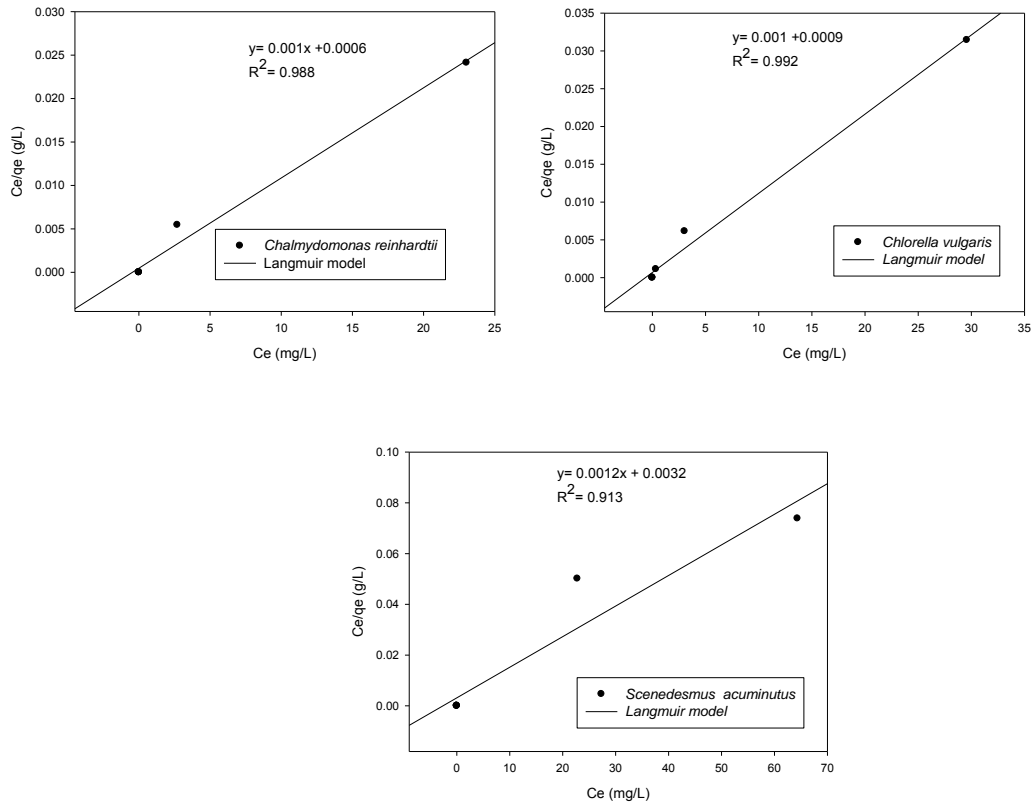


Figure 1: Linearised models of Langmuir for *C. vulgaris*, *C.reinhardtii*, *S. acuminatus*

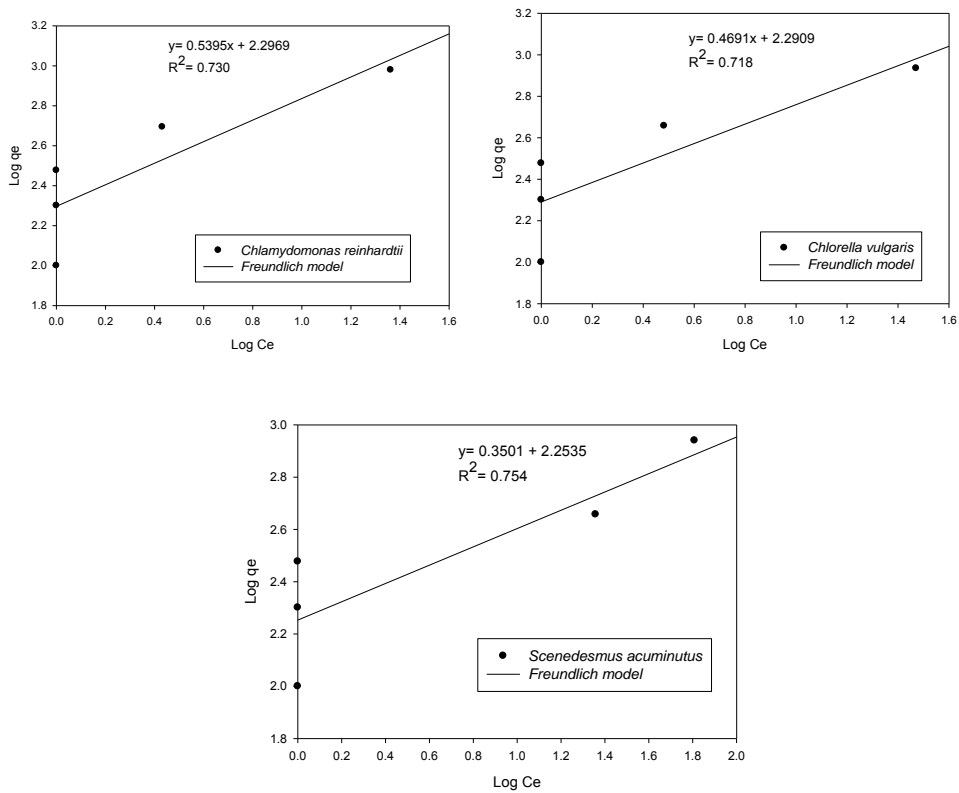


Figure 2: Linearised models of Freundlich for *C. vulgaris*, *C.reinhardtii*, *S. acuminatus*,

**Table 1:** Model constants and regression coefficients for Langmuir and Freundlich isotherms

Algal species	Langmuir constants			Freundlich constants			
	$q_{max}$ (mg/g)	$b$ (L/g)	$R_L$	$R^2$	$n$	$K$	$R^2$
<i>Chlorella vulgaris</i>	1000	1.111	0.0018	0.992	2.132	9.884	0.718
<i>Scenedesmus acuminatus</i>	833.33	0.290	0.0069	0.907	2.856	9.521	0.754
<i>Chlamydomonas reinhardtii</i>	1000	1.667	0.0012	0.987	1.854	9.943	0.730

**Table 2:** Comparison of adsorption capacity of TI using tested algae with other adsorbents

Adsorbent	$q_{max}$ (mg/g)	References
Sodium Polystyrene sulfonate	713	[37]
Modified sugar beet pulp	185.2	[38]
Pistachio hull	125	[39]
Prussian blue NP	1400	[36]
Activated coal	59.7	[38]
Modified eucalyptus	80.65	[40]
Alginate- PB	103	[41]
Saw dust	13.18	[40, 42]
Peat	24.14	[43]
Modified tree leaves	54.6	[44]
<i>Scenedesmus acuminatus</i>	833.33	Current study
<i>Chlorella vulgaris</i>	1000	Current study
<i>Chlamydomonas reinhardtii</i>	1000	Current study

### 3.2 Adsorption Affinity of TI on Tested Algae

The adsorption affinity of metals can be 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 the sorbents to sorbate. When the  $K_d$  value is more than 5000 mL/g, then it's considered good, and when the value is greater than 50000 mL/g then its excellent [45, 46]. The  $K_d$  was calculated using equation (Eq. 4) for all the tested algae. The adsorption affinity of the metal using biosorbents can be expressed using the distribution co-efficient,  $K_d$  as indicated below.



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

where  $C_o$  is the initial concentration,  $C_f$  is final concentrations (mg/L);  $V$  is the volume of solution (ml);  $M$  is the weight of algae (g).

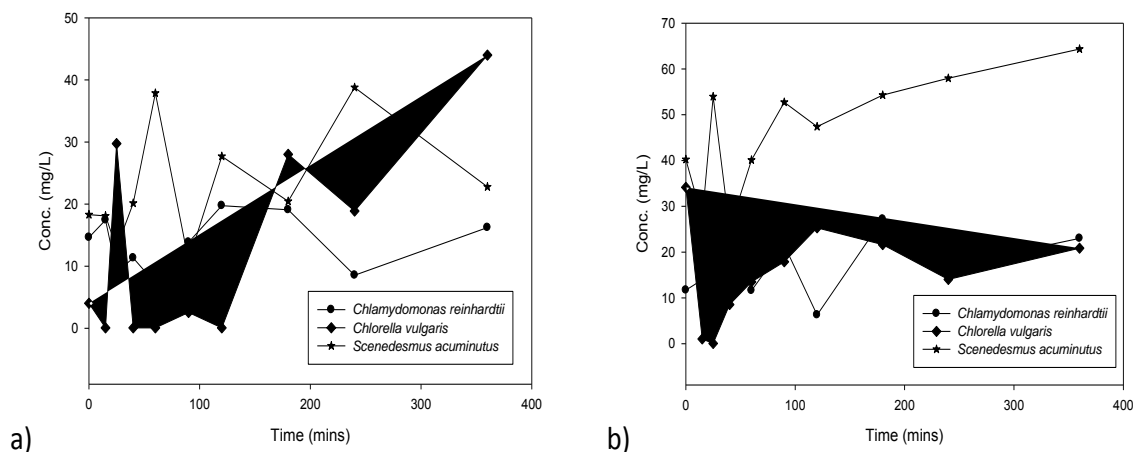
*Chlorella vulgaris* and *Chlamydomonas reinhardtii* had significantly high  $K_d$  values of 45934 and 41458 mL/g respectively at initial concentration of 500 mg/L which was very close to excellent value given, Table 3. The  $K_d$  value for *Scenedesmus acuminatus* was also good with 19945 mL/g greater than 5000. All the species confirmed to have a strong binding affinity for Tl.

**Table 3:** Distribution co-efficient for removal of Tl using 3 test algae

Species	$c_o$ (mg/L)	$c_f$ (mg/L)	$K_d$ (mL/g)
<i>Scenedesmus acuminatus</i>	250	22.784	19945.23
	500	64.350	13540.02
<i>Chlorella vulgaris</i>	250	28.043	15829.76
	500	20.862	45934.04
<i>Chlamydomonas reinhardtii</i>	250	16.221	28825.19
	500	23.011	41457.48

### 3.3 Effect of Initial Concentration on Removal of Tl

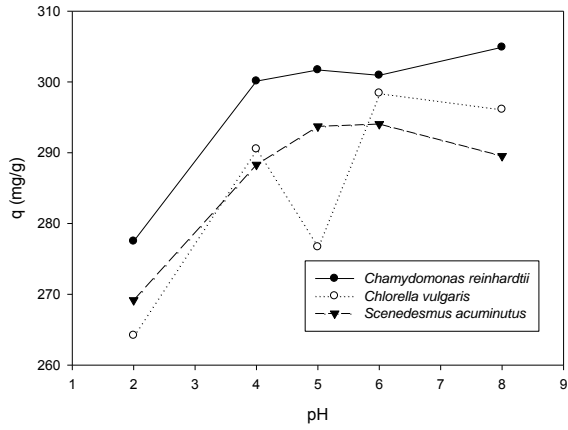
The effect of initial concentration on removal of Tl was studied in the range of 50-500 mg/L for three algal species. At very low concentration  $\leq 150$  mg/L, there was complete efficiency with 100% uptake in less than 5 minutes for all the species. At higher concentrations, maximum uptake was still attained in the first 25 minutes with initial concentration between 250- 500 mg/L reduced  $\leq 55$  mg/L, Fig. 3. Fluctuations in the removal of Tl were observed in the preceding period until equilibrium was attained which could be due to saturation of some active functional groups. *Chlorella vulgaris* showed the highest removal rate at 95.83% followed by *Chlamydomonas reinhardtii* at 95.4% in a period of 6 hours.



**Figure 3:** Dependence of high initial thallium concentration with time for the 3 algal species, a) at 250 mg/L and b) at 500 mg/L

### 3.4 Effect of pH on Removal of Tl

The variation in solution pH is an important factor which influences the binding of protons and cation for the active sites on the adsorbent [47, 48]. At low pH of 2, there was a generally low uptake of Tl for all tested species, Fig 4. At lower pH, the hydrogen ions ( $H^+$ ) are in excess and compete with  $Tl^+$  for the functional groups on the algae. When the pH was increased to 4, uptake also increased due to deprotonation of active sites. At pH of 5, uptake increased for *Chlamydomonas reinhardtii* and *Scenedesmus acuminatus* but reduction was observed for *Chlorella vulgaris*. Between pH of 5 and 6, there was no significant change in uptake except an increase was observed for *Chlorella vulgaris*, Fig. 4. The sorption of Tl in other studies was also found to increase with an increase in pH [19, 49]. The results indicated optimal pH to be between 5 and 6 for Tl adsorption. At pH above 7, there was a general reduction in removal except for *Chlamydomonas reinhardtii* which showed a minimal increase in uptake. At very high pH, precipitation usually occurs inhibiting any further uptake hence reduction in sorption.



**Figure 4:** Effect of pH on uptake of Tl for all tested algae

### 3.5 Adsorption Kinetic Model for Thallium Removal

Kinetic models assist in understanding the adsorption mechanisms caused by variation in experimental conditions. In this study, the first and Pseudo- second order kinetic models were tested on 3 algal species. The linearised equations for first and Pseudo-second order model were used to estimate the slope and intercept, Eq. 5 and 6. The first-order rate expression of Lagergren, 1898 [50] is given by the linearised equation as follows;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

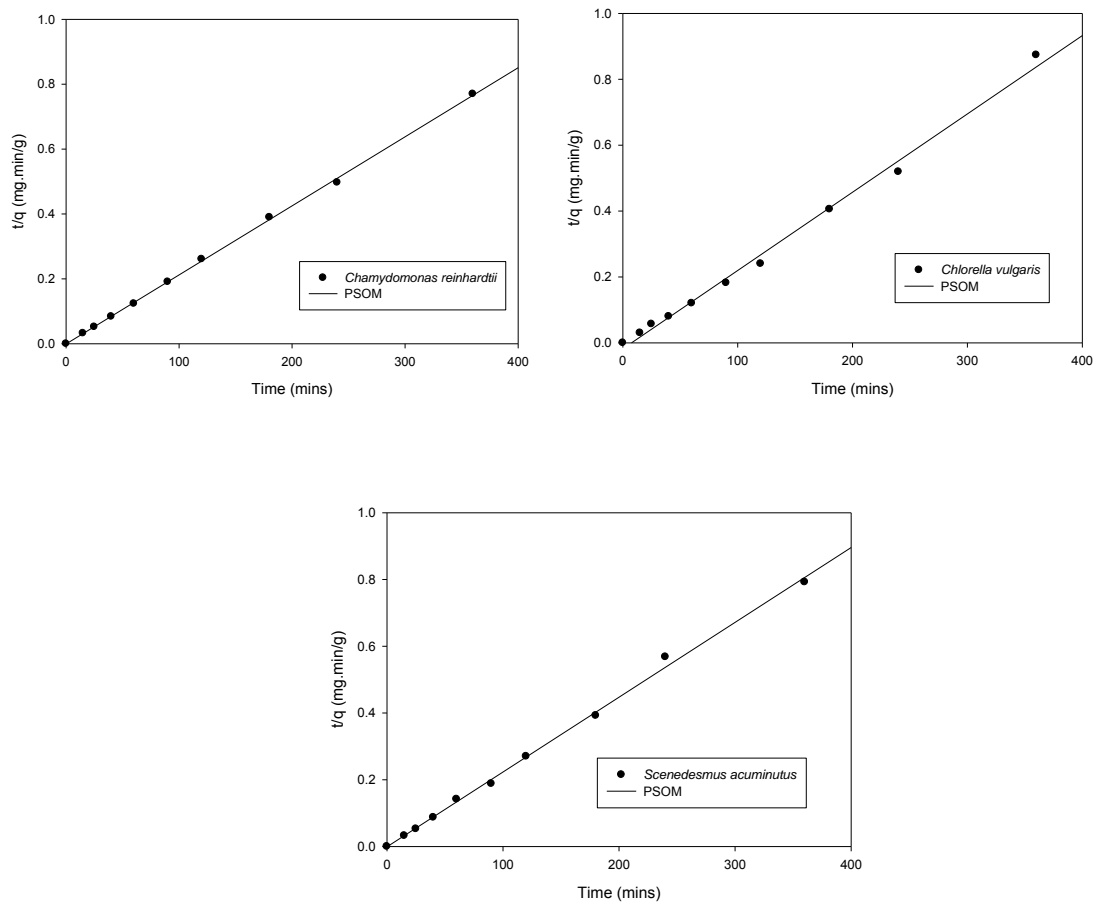
Pseudo second order equation of [51] is given by the following linearised form;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

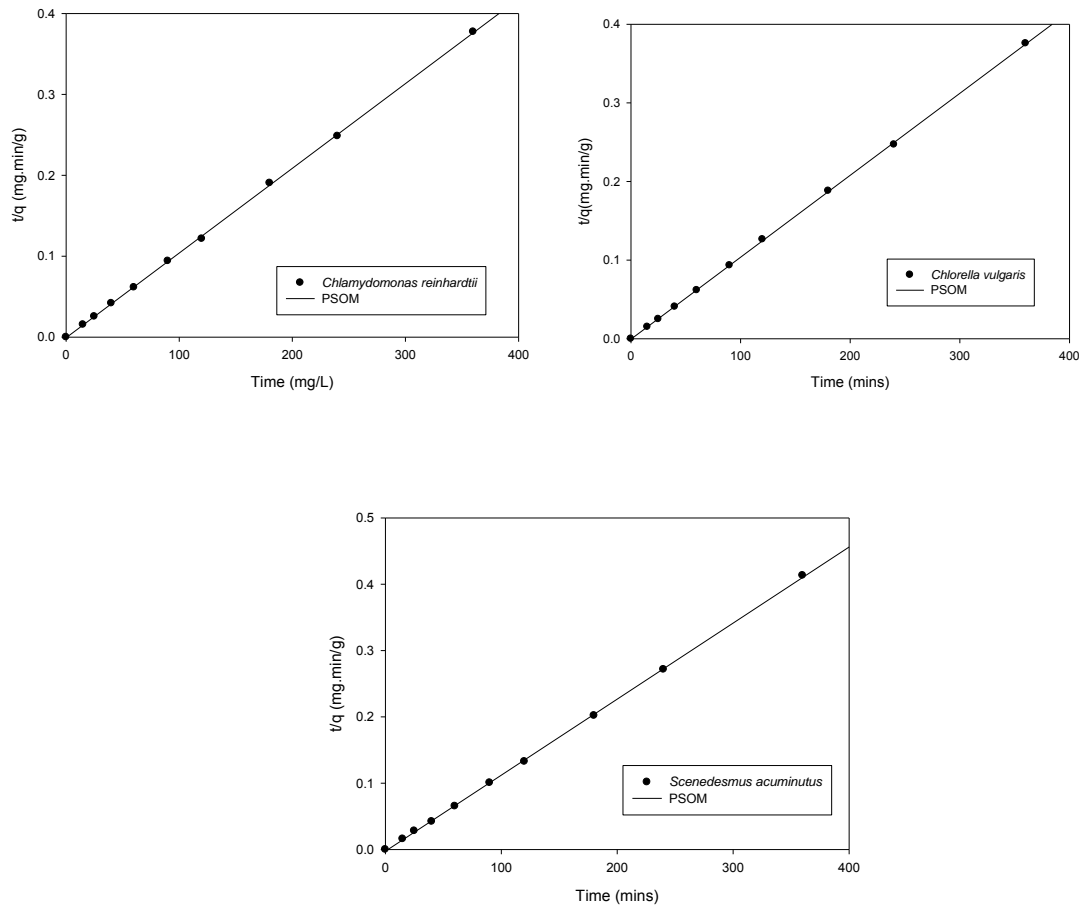
where,  $q_t$  is the amount of adsorbed metal on the algal biomass at time (t) in (mg/g);  $q_e$  is the equilibrium sorption uptake (mg/g);  $k_1$  the rate constant of Lagergren first-order adsorption ( $\text{min}^{-1}$ ) and  $k_2$  is the rate constant of second-order adsorption.

The first order model fit well with only a few data points in the first 10 minutes and then the experimental data became scattered with a very low correlation co-efficient for the rest of the period. The experimental data fit well with the Pseudo-second order model with  $R^2$  of  $\geq 0.99$  at initial concentrations of 250 and 500 mg/L of Tl, Fig. 5a and 5b. In other studies on biosorption of heavy metals the Pseudo-second order model fit better than the first order model [52-54].

Additional evidence for preference of Pseudo- second order model was provided in Table 4 with no pronounced difference between experimental  $q_{exp}$  and calculated  $q_{cal}$  data especially at initial concentration of 250 mg/L. At higher concentrations of 500 mg/L, the difference was slightly greater between  $q_{exp}$  and  $q_{cal}$ . This could be attributed to the rate of chemical reaction  $k_2$  observed to be high especially for *Chlorella vulgaris* and *Chlamydomonas reinhardtii* at 0.002 and 0.001min<sup>-1</sup> respectively.



**Figure 5a:** Linearised plots of Pseudo- second order kinetic model for 3 algal species at 250 mg/L



**Figure 5b:** Linearised plots of Pseudo- second order kinetic model for 3 algal species at 500 mg/L

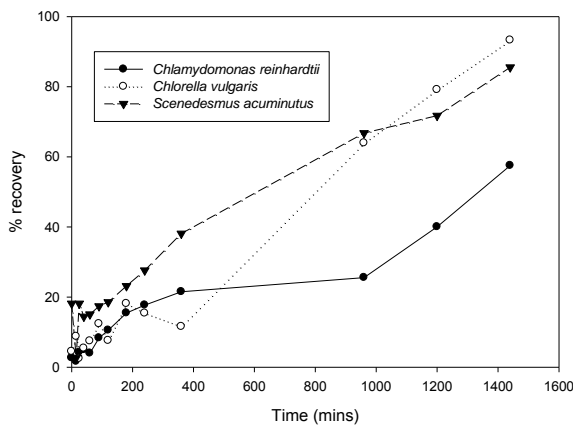
**Table 4:** Pseudo-second order adsorption kinetic parameters for all the tested algae at concentrations of 250 and 500 mg/L for Thallium

Algal species	$c_i$ (mg/L)	$k_2$ $\text{min}^{-1}$	$R^2$	$q_{\text{exp}}$ (mg/g)	$q_{\text{cal}}$ (mg/g)
<i>Scenedesmus acuminatus</i>	250	0.00084	0.998	454.432	454.546
<i>Chlorella vulgaris</i>	250	0.00032	0.994	412.005	416.67
<i>Chlamydomonas reinhardtii</i>	250	0.0074	0.9995	467.559	476.191
<i>Scenedesmus acuminatus</i>	500	0.000484	0.999	871.300	909.091
<i>Chlorella vulgaris</i>	500	0.002	0.999	958.276	1000
<i>Chlamydomonas reinhardtii</i>	500	0.00143	0.9998	953.978	1000

### 3.6 Effect of Contact Time on Thallium Recovery

The recovery of Tl was a much slower process than its uptake in the 3 tested algal species. The desorption efficiency was very low in the first 360 minutes with less than 40% recovery

for all the algal species. This could be due to the formation of very strong complexes of Tl with the active functional groups which were not easily released. After 16 hours, the percentage recovery doubled for *Scenedesmus acuminatus* and *Chlorella vulgaris* to  $\geq 66\%$  respectively. In a period of 24 hours, there was a significant recovery of Tl with 93.26% and 85.52% achieved for *Chlorella vulgaris* and *Scenedesmus acuminatus*, Fig.6. *Chlamydomonas reinhardtii* had the lowest recovery rate of 57.49% in the same period. The results implied that given more time, there is possibility of total recovery for some species. Some studies indicated that essentially all Thallium was recovered due to the cation exchange mechanism (reversible) as opposed to the precipitation or absorption [55, 56].



**Figure 6:** Efficiency of Tl recovery for *Chlorella vulgaris*, *Chlamydomonas reinhardtii* and *Scenedesmus acuminatus* at initial concentration of 250 mg/L

### 3.7 Desorption Kinetic Model for Thallium Removal

The modified desorption kinetic models of first order and Pseudo- second order model were used to estimate the rate of recovery (57). The slope and intercept were estimated from the following desorption Eqns. 7, 8 and 9.

$$\frac{dq}{dt} = -k_{1,des}q, \quad (7)$$

The modified 2<sup>nd</sup> order rate equation assumes the rate of desorption is proportional to the square of Tl filled sites and is given by differential Eq.;

$$\frac{dq}{dt} = -k_{2,des}q^2 \quad (8)$$

where  $k_1$  is the 1<sup>st</sup> order desorption rate constant;  $q$  is the remaining amount of metal bound to the biomass at time  $t$ ;  $k_2$  is 2<sup>nd</sup> order desorption rate constant. The differential equations 7 and 8 were integrated using the following Eq.;

$$q_{n+1} = q_n - \left(\frac{dq}{dt}\right)_n (t_{n+1} - t_n) \quad (9)$$

where  $q_n$  is the amount of Tl remaining in algae at time  $t_n$  and  $q_{n+1}$  is the amount of Tl at time  $t_{n+1}$  minus the rate of desorption multiplied by the incremental time step,  $k_1$  the rate constant of modified first-order desorption ( $\text{min}^{-1}$ ) and  $k_2$  is the rate constant of modified second-order desorption.

In the modified first order model the data fit only for the first 15 minutes for the 3 tested algal species. Generally the modified Pseudo-second order had a higher  $R^2 \geq 0.99$  compared to the first order model. In addition, there was no pronounced difference between the experimental ( $q_n$ ) and calculated ( $q_{n+1}$ ), Table 5. Njikam and Schiewer, 2012 [57] also found that the modified Pseudo-second order showed a better fit compared to modified first order model.

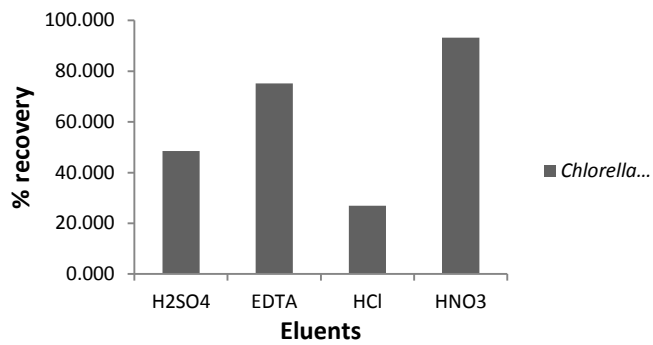
**Table 5:** Modified Pseudo-second order kinetic model parameters

Algal species	$C_i$ (mg/L)	$k_{2,des}$ ( $\text{Min}^{-1}$ )	$R^2$	$q_n$ (mg/g)	$q_{n+1}$ (mg/g)
<i>Chlamydomonas reinhardtii</i>	250	0.000002	0.9702	421.341	416.67
<i>Chlorella vulgaris</i>	250	0.0031	0.998	360.501	238.1
<i>Scenedesmus acuminatus</i>	250	0.000003	0.838	361.02	400
<i>Chlamydomonas reinhardtii</i>	500	0.0000006	0.898	926.161	909.091
<i>Chlorella vulgaris</i>	500	0.0000009	0.910	582.197	588.24
<i>Scenedesmus acuminatus</i>	500	0.000001	0.938	681.40	666.67

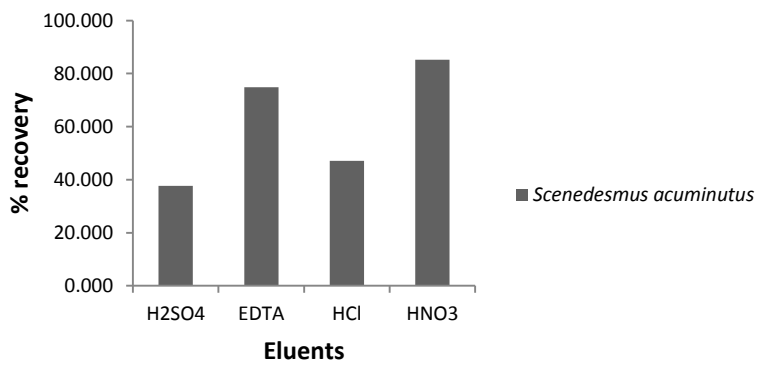
### 3.8 Comparison of Different Eluents for Tl Recovery

The recovery of Tl from biomass loaded with metal was tested using  $\text{H}_2\text{SO}_4$ , EDTA, HCl and  $\text{HNO}_3$ . Low concentration of 0.1M was used for all cases as the biomass degenerates with increase in concentration reducing the sorption efficiency [58]. For *Scenedesmus acuminatus*,  $\text{HNO}_3$  recovered the highest Tl of up to 85.2% followed by EDTA with 74.83%, Fig.7a.

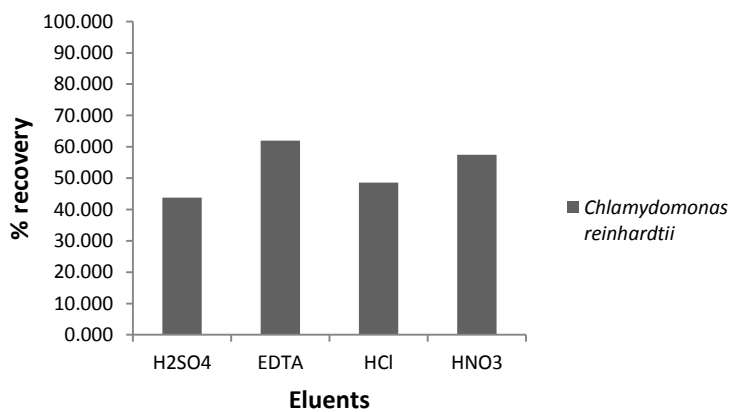
a)



b)



c)



**Figure 7:** Comparison of different eluents for recovery of T1 for all the test algae

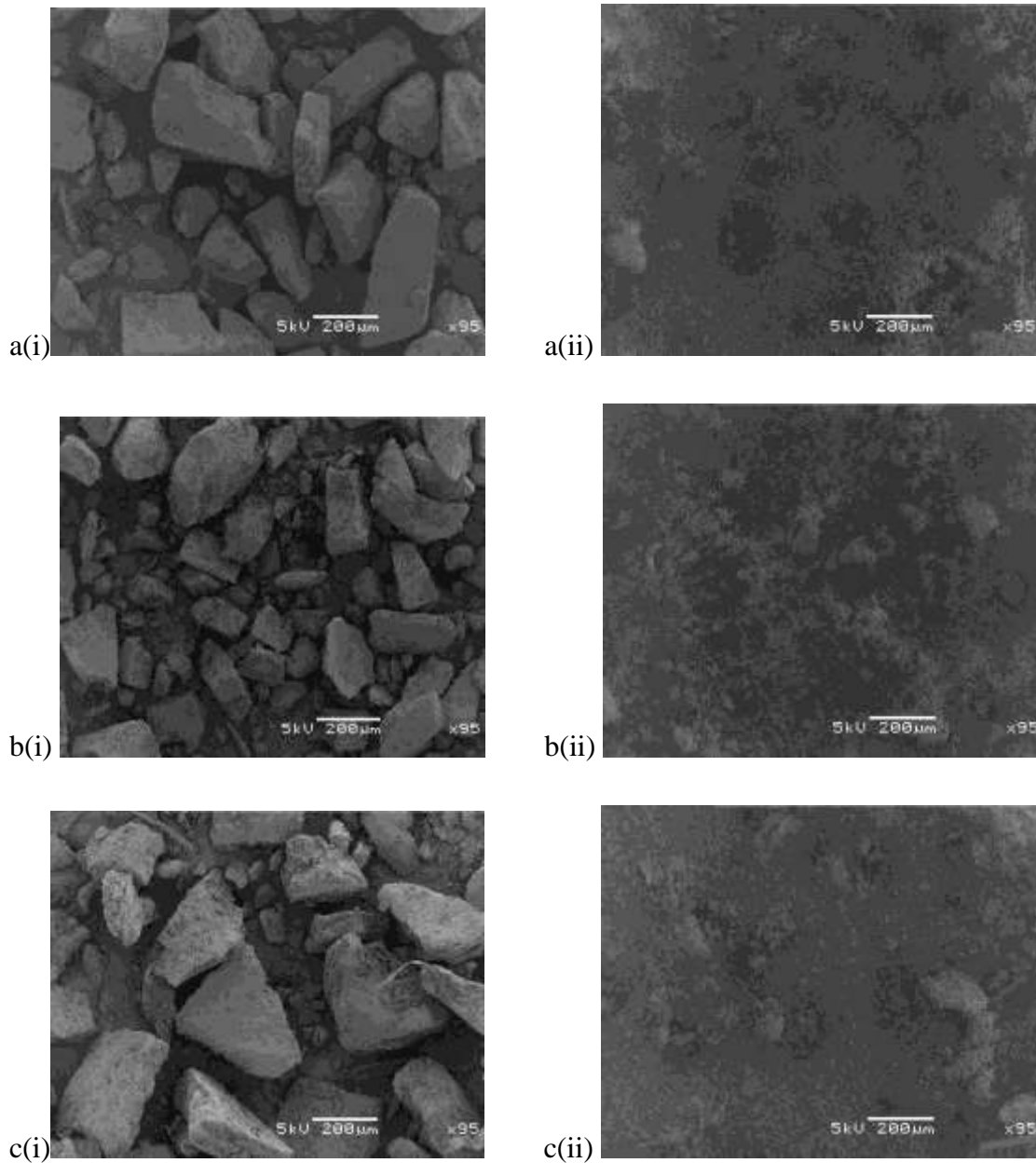
*Chlorella vulgaris* had the highest sorption efficiency at 93.26% followed by EDTA at 75.12%, Fig. 7b. In *Chlamydomonas reinhardtii*, there was a slight difference in recovery



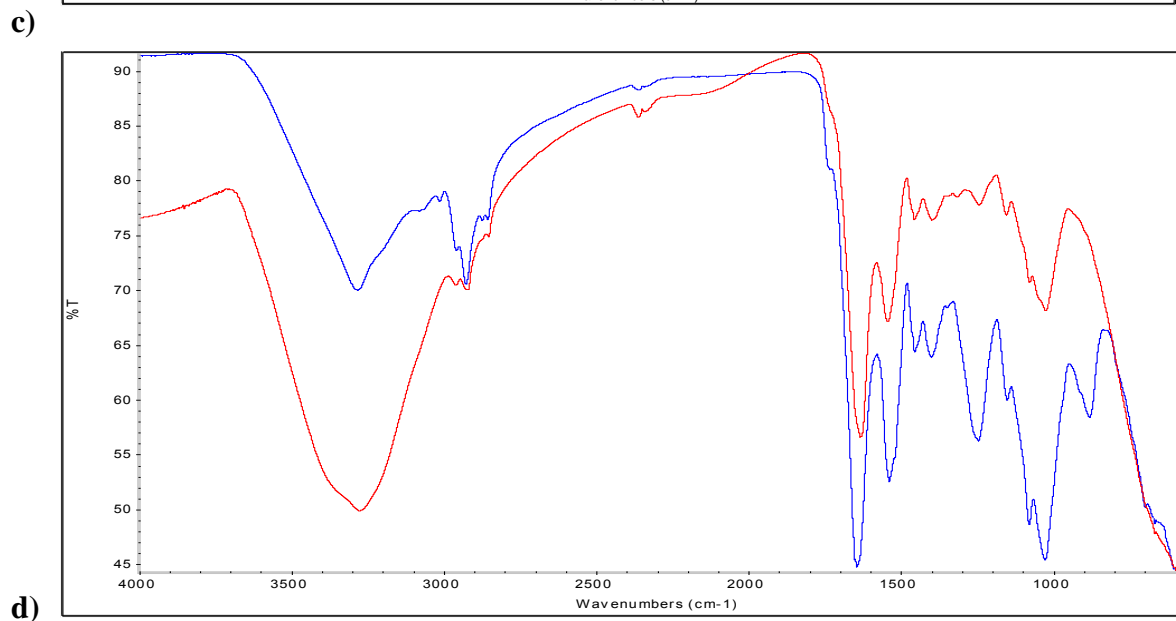
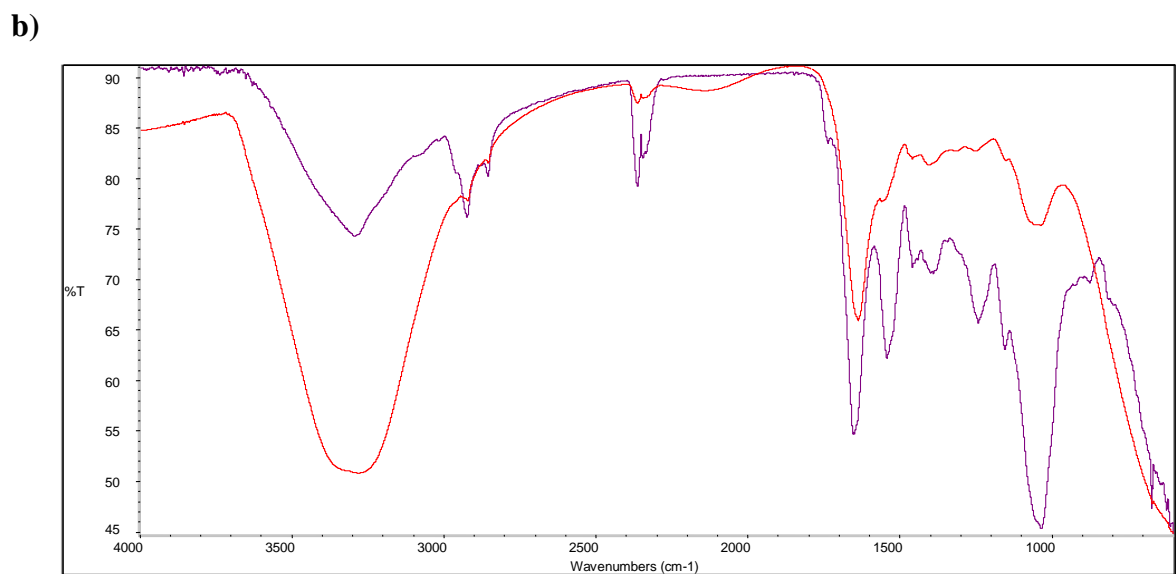
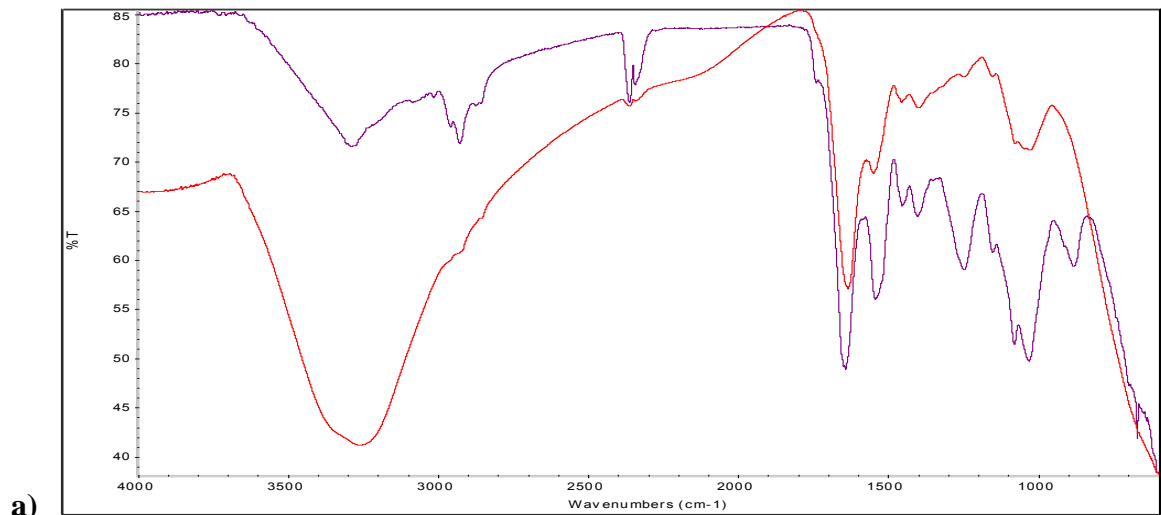
between  $\text{HNO}_3$  and EDTA at 57.49 and 61.93% respectively, Fig.7c. In general, use of HCl and  $\text{H}_2\text{SO}_4$  exhibited very low efficiencies in the recovery of Tl. The preference of eluents was in the order of  $\text{HNO}_3 > \text{EDTA} > \text{HCl} > \text{H}_2\text{SO}_4$ . Our results also coincide with [58], who also found  $\text{HNO}_3$  as a better desorbing agent for heavy metals.

### 3.9 Surface Characterisation of Test Algae

The SEM provided detailed information on surface topography through acquisition of a beam of electrons on the sample. All the algal samples before adsorption formed compact and



**Figure 8:** SEM images for a) *Chlamydomonas reinhardtii*, b) *Chlorella vulgaris* and c) *Scenedesmus acuminatus*- i) before, ii) after adsorption of Tl



**Figure 9:** FTIR peaks of transmittance of TI in a) *Chlamydomonas reinhardtii*, b) *Scenedesmus acuminatus*, c) *Chlorella vulgaris* and red representing before adsorption

irregular surface whereas after adsorption the surface was fragmented and indication of adsorption of metals on the surface wall, Fig. 8.

For FTIR analysis, *Chlamydomonas reinhardtii* showed pronounced peaks at 3273.82  $\text{cm}^{-1}$  before adsorption and 3293.45  $\text{cm}^{-1}$  after adsorption. This indicates a very strong O-H stretch which depicts phenols and alcohols. Another stretch was between 2916.56 and 2920.48  $\text{cm}^{-1}$  which is indicative of an O-H bond for carboxylic acid. Other bonds ranged from 1637-1645, 1546-1539, 1024-1039.9  $\text{cm}^{-1}$  representative of primary amines, nitro compounds and aliphatic amines respectively, Fig. 9a.

For *Scenedesmus acuminatus* and *Chlorella vulgaris*, there was no significant difference in peaks with the highest attained between 3289 and 3301  $\text{cm}^{-1}$  reflecting primary and secondary amines and amides, Fig. 9b and c. The carboxyl stretch also appeared for the 2 species in the range of 2854-2924  $\text{cm}^{-1}$ . Other similar stretches were 1629-1652, 1534-1546, 1024-1048  $\text{cm}^{-1}$  representing primary amines, nitro compounds and aliphatic amines respectively. It can be noted that there was slight difference in wavelength for all the species inferring similar functional groups. The differences in uptake levels were due to variations in wave numbers which influences the transmittance.

## **Conclusion**

The potential for green micro algae tested on Tl showed excellent sorption capacities of 100% removal at concentrations  $\geq 150$  mg/L for all the tested species. Different eluents were tested with  $\text{HNO}_3$  acid emerging as the most efficient for recovery of Tl. The recovery of Tl was also promising with  $\geq 93\%$  recovery for some species despite the longer period taken. The strongest functional groups responsible for Tl binding on the algal cell wall were carboxyl and phenols. The functional groups showed the possible mechanisms involved including ion exchange, coordination and or complexation in addition to physical adsorption. Further research is required with a combination of multi metals to reflect the actual environment before use in continuous reactors.

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