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Interpretation of Uptake Kinetic of Thallium and Cadmium on Surfaces of Immobilized Green Algae as Biosorbents

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Metallic species are non-biodegradable and can only be removed physically, chemically and recently biologically from contaminated wastewater. Among the commonly found toxic heavy metals, thallium (Tl) and cadmium (Cd) are listed as priority pollutants from mostly mining and industrial wastewater effluents. In this study, 4 green algae species of *Stichococcus bacillaris, Chloroidium saccharophilum, Desmodesmus multivariabilis and Chlamydomonas reinhardtii* were used as biosorbents for Tl and Cd. Equilibrium and kinetic experiments were carried out to determine the sorption capacity (q_{max}) and rate of reaction, respectively. The possible biosorption mechanisms were determined using FTIR on the algal surface. The Langmuir model performed better than the Freundlich model with a correlation co-efficient (R^2) of ≥ 0.9 for both metals in free and immobilised algal cells. *Chlamydomonas reinhardtii* and *Chloroidium saccharophilum* showed the highest q_{max} for removal of Tl at 1000mg/g whereas removal of Cd was highest for *Chloroidium saccharophilum* at 128.21mg/g. The sorption capacity for Tl removal increased 5fold for immobilised *Chlamydomonas reinhardtii* from 1000 to 5000mg/g and 4fold for Cd removal from 23.31 to 86.21mg/g. The immobilised algae showed potential for re-usability especially for Cd with relative consistency in adsorption for the 3 cycles in the range of 88.7-92.4%. For both metals, the pseudo-second order model performed better than the first order model with R^2 of ≤ 0.99 in kinetic studies. The most active functional groups found on all tested algae for the removal of both metals were carboxyl, alkanes and amines. Generally the immobilised algae improved the sorption efficiency of Cd and Tl adsorption/desorption.

1. Introduction

The toxicity of heavy metals is known beyond reasonable doubt to cause environmental degradation and public health concerns due to their persistence in the environment and accumulation in the food chain (Gupta and Rastogi, 2008; Chojnacka, 2010). The commonly used techniques for the treatment of industrial wastewater are physical and chemical methods including ion exchange, membrane filtration, flotation, precipitation among others (Veglio, et al., 2003). These methods are associated with high cost for processing of metal concentrations, lack of specificity, production of large volumes of sludge and low performance at low metal concentrations (Kotrba, 2011). Currently biological adsorption methods are proposed as alternative technologies for removal of heavy metals and possible recovery due to their relative abundance, cost effectiveness and eco-friendliness (Kotrba, 2011). Micro algae are known to have a high binding affinity for metals due to the large surface area (Saeed and Iqbal, 2013). One of the major practical limitations of microbial algae in commercial applications is the physical characteristics of the materials. The free algal cells have a small particle size with low density, poor mechanical strength and rigidity which limits choice of suitable reactor and biomass separation difficult for re-use (Akhtar, et al., 2008). Immobilisation offers a simple and inexpensive technology to improve the robustness and stability of the biomass which could lead to development of efficient and cost effective bioremediation technology for removal/recovery of toxic metals. Immobilisation involves a cell being prevented from moving independently of its neighbours to all parts of the aqueous phase by natural or artificial means. The advantages associated with cell immobilisation include a higher cell density resulting in repeated use, greater substrate accessibility, regeneration and re-use for longer

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periods and reduced risk of contamination (Saeed and Iqbal, 2013) Among the existing methods for immobilisation, entrapment in a polymeric gels such as alginates and carrageenans are common but are limited by problems of gel stabilisation, restricted diffusion due to closed embedding structure with low mechanical strength, complex and sophisticated equipment for making gel beads on large scale which increases the cost of production. Natural immobilising agents are known to be environmentally friendly, relatively abundant and cost effective. Loofa sponge (*Luffa cylindrica*) which is abundant, cheap, rigid, bio-degradable and highly porous was used to immobilise selected micro algae species. The study aimed at using micro algal sorbents for removal/recovery of thallium and cadmium metals from simulated wastewater.

2. Materials and Methods

2.1 Microalgae Culture

Algae was collected from a freshwater dam in Hartbeespoort dam, South Africa, isolated by streak plating and molecularly identified using the Internal transcribed spacer (ITS) and 18S ribosomal RNA gene (rRNA). The species identified included *Desmodesmus multivariabilis*, *Chloroidium saccharophilum*, *Stichococcus bacillaris* and *Chlamydomonas reinhardtii*. The pure strains were then cultured using AF6 under required algal light conditions (Osram L 36W/77 Floura) at 20-23°C. The algae was harvested, centrifuged and washed at least twice in deionised water before drying in the oven for 24 hours at 50°C.

2.2 Algal Immobilisation

The loofa sponges were cut into longitudinal halves which were then cut into rectangular discs, soaked in boiling water for 30 minutes and washed thorough with tap water. The discs were then soaked in distilled water for 24 hours and changed 3 times. The sponges were autoclaved, dried in an oven at 70° C and weighed before use in biosorption experiments.

2.3 Equilibrium and Kinetic Experiments

A stock solution of 1000 mg/L of Cd^{2+} and Tl^{3+} was used in this study. Equilibrium experiments were carried out concurrently with kinetic experiments at varying initial concentrations ranging from 15-150 mg/L for Cd and 15-500 mg/L for Tl to test free and immobilised algal cells. The biomass was kept constant and the pH maintained in the range of 5.5-6 using 0.1M NaOH and HCl. The samples were taken at predetermined time intervals, centrifuged and the filtrate analysed using Inductively Coupled Plasma (ICP, Spectro Arcos FHS12, Boschstroisse, Germany).

2.4 Surface Characterisation of Functional Groups

The functional groups were characterised using the Fourier Transform Infrared (FTIR) spectrum, (Perkin Elmer 100). The algal samples before and after adsorption were each placed on the diamond stage, monitored and data processed with different peaks to represent the functional groups.

2.5 Regeneration and Re-Use

The immobilised cells were tested for their re-usability to remove and recover Tl and Cd in 3 cycles. Nitric acid was used as the eluent. The biomass filled with heavy metals from previous equilibrium experiments was rinsed twice in de-ionised water, weighed and immersed in of HNO_3 acid for 1 hour. A sample was withdrawn, centrifuged and filtrate analysed using ICP. The immobilised algae was re-used in the adsorption/desorption in the preceding cycles for upto 3 cycles.

3. Results and Discussion

3.1 Equilibrium Modelling

The Langmuir and Freundlich models are the most widely used and accepted simplistic mathematical models as they usually fit the experimental done relatively well (Volesky and Holan, 1995). The sorption capacity and affinity of the tested algal species were determined using the Langmuir Eq (1) and Freundlich Eq (2) respectively. Generally, the Langmuir model performed better than the Freundlich model with a regression coefficient (R^2) ≥ 0.9 for Cd and Tl sorption, Table 1.

$$C_e/q_e = C_e/q_{\max} + 1/bq_{\max} \tag{1}$$

$$\log\ q_e = \log\ k + 1/n \log\ C_e \tag{2}$$

The study was aimed at finding species with both a high sorption and affinity for metals. Free algal cells of *Chlamydomonas reinhardtii* and *Chloroidium saccharophilum* showed similarities in Tl adsorption with the highest q_{max} of 1000 mg/g and b of 1.667 L/g. *Stichococcus bacillaris* generally showed the lowest q_{max} of 8.33.3 mg/g for Tl adsorption, Table 1. Cadmium adsorption was highest for *Chloroidium saccharophilum* with a q_{max} of 128.21 mg/g and lowest for *Chlamydomonas reinhardtii* at 23.31 mg/g using free algal cells, Table 2.

Table 1: Equilibrium model constants for adsorption of Tl using tested algae

Algal species	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (L/g)	R^2	n	K	R^2
Chlamydomonas reinhardtii	1000	1.667	0.987	1.854	9.943	0.730
Desmodesmus multivariabilis	909.09	0.524	0.917	3.141	10.779	0.894
Chloroidium saccharophilum	1000	1.667	0.949	2.062	10.92	0.940
Stichococcus bacillaris	833.33	0.293	0.907	2.856	9.526	0.754

Table 2: Equilibrium model constants for adsorption of Cd using tested algae

Species	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (L/g)	R^2	k	n	R^2
Chlamydomonas reinhardtii	23.31	0.141	0.831	1.09	1.097	0.631
Desmodesmus multivariabilis	32.57	1.490	0.954	2.75	3.68	0.512
Chloroidium saccharophilum	128.21	0.016	0.969	1.78	1.47	0.975
Stichococcus bacillaris	125	0.049	0.967	2.95	2.02	0.923

3.2 Immobilised Algae for Adsorption of Tested Heavy Metals

Loofa sponge was used as an immobilising agent for *Chlamydomonas reinhardtii* which showed uniform attachment of algal cells in the fibrous network. The sorption capacity of free algal cells and immobilised *Chlamydomonas reinhardtii* increased from 1000 to 5000 mg/g for Tl and 23.31 to 86.21 mg/g for Cd respectively, Table 3. Immobilised micro algae also showed higher efficiency in the removal of Cd than free algal cells (Saeed and Iqbal, 2006). The R^2 was generally better for Langmuir than Freundlich model at ≤ 0.998 for immobilised algae.

Table 3: Equilibrium model constants for adsorption of Cd and Tl using immobised test algae

Heavy metal	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (L/g)	R^2	k	n	R^2
Thallium	5000	0.250	0.998	31.893	2.702	0.811
Cadmium	86.21	0.347	0.877	1.439	7.159	0.986

3.3 Surface Characterisation of Functional Groups

The algal surface wall was characterised using the FTIR to determine the active functional groups. The tested algae showed similar functional groups with minimal differences in wave length, The highest wavelength was in the range of 3258-3300 cm^{-1} indicating a medium hydroxyl bond for carboxylic acid and the lowest 1226-1247 cm^{-1} for aliphatic amines, Table 4. The active function groups give an indication of possible functional groups on the tested algae being ion exchange and adsorption.

Table 4: The FTIR frequency of adsorption in relation to the functional groups

Frequency (cm^{-1})		**Bond**	**Functional groups**
Before adsorption	**After adsorption**		
3258	3300	O-H	Carboxylic acid
2898	2941	C-H	Alkanes
1629	1649	N-H	Primary amines
1226	1247	C-N	Aliphatic amines

3.4 Kinetic Modelling

Kinetic models are a fundamental process in biosorption studies as they provide useful information on rate controlling steps such as mass transport and chemical reaction processes for optimisation purposes (Wang and Chen, 2009). Largergren's first order and Ho's pseudo-second order models used in this study were linearised as shown in Eq (3) and Eq (4) respectively. The slope and intercept were determined from plots of t/q vs. t as shown in Fig. 1 and 2. All the 3 tested algal species showed a better fit for pseudo-second order to first order model for both metals with a R^2 ≥ 0.99, Table 5 and 6. The results also showed no significant difference in sorption between experimental and calculated results for pseudo- second order model.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

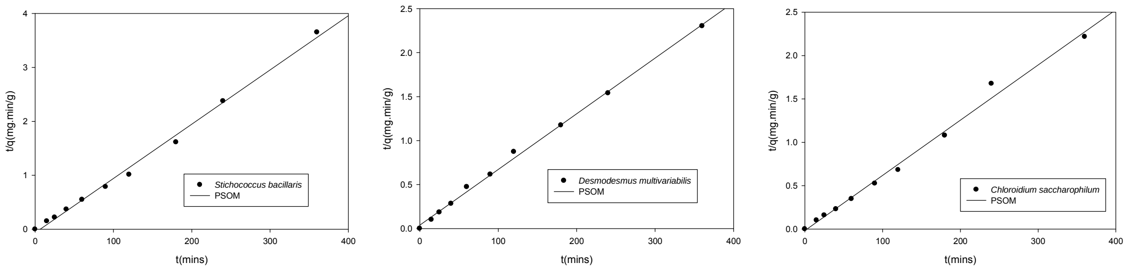


Figure 1. Linearised graphs of PSOM showing Cd adsorption for 3 algal species

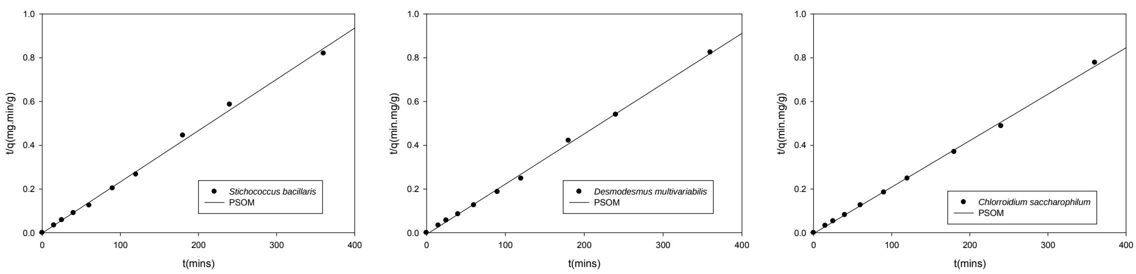


Figure 2. Linearised graphs of PSOM showing Tl adsorption for 3 algal species

Table 5: Pseudo-second order kinetic parameters for all the tested algae for adsorption of Tl

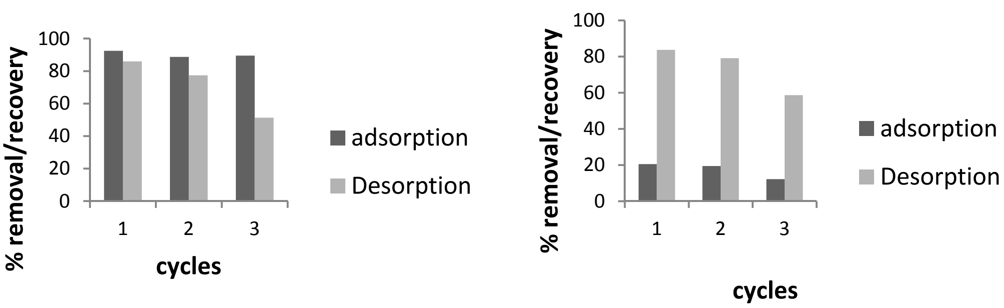
Algal species	C_i (mg/L)	$k_{2,ads}$ min^{-1}	R^2	q_{exp} (mg/g)	q_{cal} (mg/g)
Stichococcus bacillaris	250	0.00252	0.997	439.102	434.783
	500	0.00101	0.998	388.140	384.615
Desmodesmus multivariabilis	250	0.00071	0.998	436.669	434.783
	500	0.00064	0.999	912.682	909.091
Chloroidium saccharophilum	250	0.0011	0.999	462.974	476.191
	500	0.00042	0.999	918.471	909.091

Table 6: Pseudo-second order kinetic parameters for all the tested algae for Cd adsorption

		Pseudo-Second Order Model			
Species	**Initial conc. (mg/L)**	R^2	q_{exp} **mg/g**	q_{cal} **mg/g**	k_2
Stichococcus bacillaris	15	0.999	22.620	23.256	0.0164
	150	0.998	118.4	117.647	0.0041
Desmodesmus multivariabilis	15	0.999	21.25	21.186	0.288
	150	0.999	156.4	158.7	0.0005
Chloroidium saccharophilum	15	0.996	14.44	14.815	0.024
	150	0.992	162.4	156.25	0.0024

3.5 Recovery and Re-Use of Immobilised Algae

The re-use and regeneration of immobilised Chlamydomonas reinhardtii was tested for removal and recovery of Tl and Cd in 3 cycles. The adsorption of Cd in the first cycle was highest at 92.47% and removal rate at 85.91% at initial concentration of 15mg/L, Fig 3a. The removal rate remained high in the subsequent cycles with a reduction in recovery utpto 51.31% in the 3rd cycle. In other studies, the adsorption/desorption of Cd was high and maintained at relatively similar efficiency in all the cycles with immobilised algae (Akhtar, et al., 2003). At higher concentrations of 100mg/L of Cd, the removal rate was relatively low for all the cycles but performed better in recovery with the highest at 83.71% in the first cycle and 58.69 in the 3rd cycle, Fig. 3b.
The sorption efficiency for Tl removal remained relatively high in all the cycles in the range of 88.24-93.98% at initial concentration of 150 and 250 mg/L, Fig.4a and b. The recovery of Tl was generally low for all the 3 cycles ≤ 49.86%. This could be due to the time required as it there was an observable increase in the recovery of Tl with an increase in time in the 3rd cycle. In addition the experiments were carried out at higher concentration of ≤ 250mg/L with expectation of high recovery at lower concentrations.



a) 15mg/L b) 100mg/L

Figure 3: The adsorption/desorption rate of Cd using immobilised Chlamydomonas reinhardtii for 3 cycles

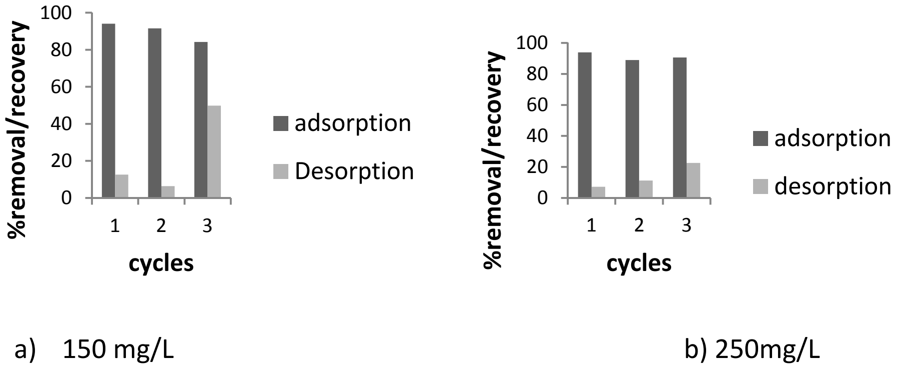


Figure 4: The adsorption/desorption rate of Tl using immobilised Chlamydomonas reinhardtii for 3 cycles

4. Conclusion

The tested free micro algal cells showed potential for removal of Cd and Tl with a high sorption capacity. The use of immobilised algae increased the efficiency of removal/recovery due to the improved mechanical strength. The equilibrium model of Langmuir and the kinetic model of Pseudo second order performed better with a higher correlation coefficient of ≤0.98. The most common functional groups found in the test algae were carboxyl, alkanes, primary and aliphatic amines.

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