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Bioreduction of Thallium and Cadmium Toxicity from Industrial Wastewater using Microalgae

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Thallium (Tl) and Cadmium (Cd) are listed among priority metallic pollutants known to cause irreversible health effects and easily magnify in the higher trophic levels of the food chain. Micro algae has a diversity of species found in freshwater bodies but only a few have been explored for their biosorption potential as compared to macro algae. The study sourced microalgae from eutrophic freshwater body (Hartbeespoort dam) in South Africa and isolated using streak plating technique. The pure strains were identified using molecular methods of 18S ribosomal RNA gene (rRNA) as *Chlorella vulgaris* and *Scenedesmus acuminutus*. The pure strains were then cultured in the laboratory and used to determine the adsorption potential and recovery of Tl and Cd. Equilibrium and kinetic experiments were used to estimate sorption capacity and rate of reaction respectively. The effect of initial concentration on Cd and Tl adsorption was also studied. The algae was characterized to determine the active functional groups on the algal surface wall using Fourier Transform Infra-red spectroscopy (FTIR). From the study, removal efficiency was achieved at 100% for lower concentrations of ≥ 150 mg/L of Tl. At higher concentrations in a range of 250-500 mg/L Tl, the performance of *Chlorella vulgaris* and *Scenedesmus acuminutus* was still high with sorption capacity (q_{max}) of 1000 and 833.33 mg/g respectively. Cd removal was highest for *Chlorella vulgaris* at q_{max} of 175.44 mg/g and affinity (b) of 0.011 L/g. When compared to other studies on Tl and Cd adsorption, the tested algae showed a relatively better q_{max} than most adsorbents. The kinetic studies showed better correlation co-efficient of ≤ 0.99 for Pseudo-second order model (PSOM) than the first order model. Recovery of Tl was achieved highest for *Chlorella vulgaris* at 93.26% and Cd was highest for *Scenedesmus acuminutus* at 91.92% using nitric acid. The strongest functional groups responsible for Tl and Cd binding on the algal cell wall were carboxyl and amines. Microalgae from freshwater bodies showed significant potential for Tl and Cd removal/recovery from industrial wastewater.

1. Introduction

Toxic metals are directly or indirectly released into the environment mainly through anthropogenic related activities. Metallic species are non-biodegradable and can only be removed physically or chemically from contaminated wastewater (Ahluwalia and Goyal, 2007). Cadmium is one of the critical metals with a very high demand in industrial applications. Cadmium is usually released as a by-product in wastewater causing pollution even at very low concentration along the food chain. Acute and Chronic effects of Cd poisoning include bronchitis, pneumonitis, toxemia in the liver, vertigo, diarrhoea, abdominal pain, kidney damage. Thallium is another highly toxic element comparable to mercury, cadmium and lead but with limited information on dispersion in the environment. Thallium easily replaces potassium in the biological functioning of the cell membrane due to similar ionic charge and radii (Peter and Viraraghavan, 2005). The negative effects of exposure include encephalopathy, tachycardia, mild gastro intestinal disturbances, degenerative changes in kidney, liver, heart, alteration of nervous system and eventually death. Conventional treatment technologies have been used for decades for the removal of toxic heavy metals but these technologies seem to operate relatively well for effluents containing higher metal concentrations ≥ 100 mg/L (Aziz, et al., 2008). The common failure of adsorption processes is the lack of selectivity for the target metals and the high cost of operation due to high energy requirements. The use of biological material is an emerging and environmentally friendly technology with great prospects to effectively clean up toxic metals at low concentrations and possible recovery for re-use in industry (Volesky, 2007). Various living and dead organisms have been investigated for metal removal. The living biomass accumulates high levels of metals but possible recovery without cell disruption seems almost impossible. Biosorption is a term often used to refer to the treatment of wastewater containing heavy metals using dead biomass. The use of dead biomass has attracted more attention as it offers the possibility of regeneration and reuse of the biosorbent. Among the biosorbents tested, micro algae have proven to be better sorbents in certain cases mainly due to the constituents of their cell wall with a higher uptake capacity for metals compared to fungi, bacteria and yeast (Mehta and Gaur, 2005). A variety of microalgae exist but only a few have been investigated for their sorption capacity. This study investigated the potential removal/recovery of Cd and Tl from wastewater using waste micro algae.

2. Materials and Methods

2.1 Algal Identification and Culture

The planktonic algae were collected from a eutrophic dam in Hartbeespoort dam, South Africa and the pure strains isolated using streak plating technique and identified using the Internal transcribed spacer (ITS) and 18S ribosomal RNA gene (rRNA). Phylogenetic analysis of sequences was checked for similarity using a basic local alignment search tool (BLAST). The samples identified as *Chlorella vulgaris* and *Scenedesmus acuminutus*. The pure strains were cultured in AF6 medium under controlled condition using algal light (Osram L 36W/77 Floura) at a temperature of 20-23°C. The algae was harvested every two weeks, centrifuged and washed twice in deionised water before drying in the oven for 24 hours at 50°C.

2.2 Equilibrium and Kinetic Experiments

A standard stock solution of 1000 mg/L of Cd^{2+} and Tl^{+} was used to prepare initial metal concentrations. The metal concentrations used were in the range of 15-150 mg/L for Cd and 15-500 mg/L for Tl. Equilibrium experiments were carried out concurrently with kinetic experiments. The samples were stirred on a magnetic stirrer at a constant speed of 350 rpm. Samples were withdrawn at pre-determined time intervals for kinetic experiments and after 6 hours for equilibrium experiments. The samples were centrifuged for 10 minutes at 6000 rpm and the filtrate analysed using the Inductively Coupled Plasma (ICP, Spectro Arcos FHS12, Boschstroisse, Germany).

2.3 Characterisation of Functional Groups

The functional groups on the algal cell wall were identified using the Fourier Transform Infrared (FTIR) spectrum, (Perkin Elmer 100). The algal samples before and after adsorption were each placed on the diamond stage to obtain the spectrum. Data was processed with different peaks attained to represent the functional groups.

2.4 Adsorption/Desorption Experiments for Re-use

The algae was tested for their re-usability for the removal and recovery of tested metals using nitric acid (HNO3). The metal laden biomass was rinsed twice in deionised water to remove residual solution and weighed. The weighed biomass was added to 50ml of 0.1M of eluent (HNO3) and stirred on a magnetic stirrer for a period of 4-6 hours. The experiment was carried out in duplicates. The sample was drawn at the end of the experiment, centrifuged and the supernatant analysed for metal analysis.

3. Results and Discussion

3.1 Empirical Models for Single Metal Systems

Empirical models for single metal systems are used to represent equilibrium data from biosorption experiments. These models determine the potential adsorption efficiency of different biosorbents (Mehta and Gaur, 2005; Kotrba, 2011). The most commonly used models are the Langmuir isotherm which determines the sorption capacity and affinity, the other is the Freundlich model which determines the biosorption equilibrium constant (k) and biosorption intensity (n). In this study, the Langmuir and Freundlich equations (Eq) are represented in linearised form as Eq(1 and 2) respectively.

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

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

The results from the study showed that *Chlorella vulgaris* and *Scenedesmus acuminutus* had a better fit for Langmuir model than Freundlich model with a correlation coefficient (R^2) ≥ 0.9, Figure1. *Chlorella vulgaris* showed a higher q_{max} for both Cd and Tl adsorption of 175.44 and 1000 mg/g respectively, Tables 1&2. The affinity for binding metals to the algal sorbents was highest for *Chlorella vulgaris* in Tl adsorption at 1.429 L/g. Some adsorbents from literature were compared with tested algal species for sorption capacity, the latter showed a significantly higher q_{max} than former for Tl adsorption but only *Chlorella vulgaris* showed highest q_{max} for Cd adsorption, Table 3.

a)

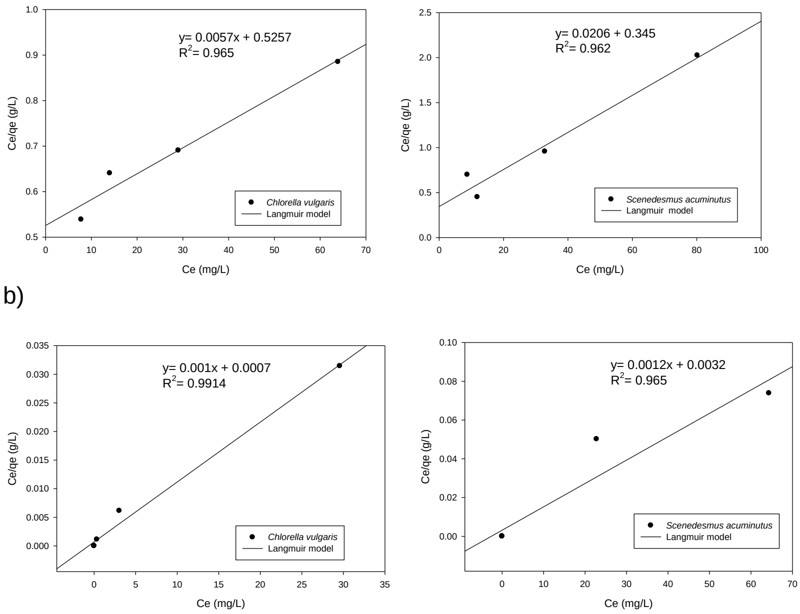


Figure 1: Graphical representation of the Langmuir model for, a) Cd adsorption, b) Tl adsorption

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

Algal species	**Langmuir constants**			**Freundlich constants**		
	q_{max} (mg/g)	b (L/g)	R^2	n	K	R^2
Chlorella vulgaris	175.44	0.011	0.965	1.286	1.59	0.97
Scenedesmus acuminutus	48.54	0.06	0.962	2.309	2.28	0.894

Table 2: 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
Chlorella vulgaris	1000	1.429	0.9914	0.0002	8.22	0.7085
Scenedesmus acuminutus	833.33	0.375	0.913	2.132	7.856	0.7673

Table 3: Comparison of sorption capacity with other adsorbents

Adsorbent	Cd q_{max} **(mg/g)**	Tl q_{max} **(mg/g)**	**References**
Sargassum sp.	85.43	-	(Sheng, et al., 2004)
Oedogonium sp.	88.2	-	(Gupta and Rastogi, 2008)
Lactic acid bacteria	54.7	-	(Halttunen, et al., 2007)
Modified sugar beet pulp	-	185.2	(Zolgharnein, et al., 2011)
Activated coal	-	59.7	(Zolgharnein, et al., 2011)
Modified eucalyptus	-	80.65	(Khavidaki, et al., 2013)
Chlorella vulgaris	**175.44**	**1000**	**Current study**
Scenedesmus acuminutus	**48.54**	**833.33**	**Current study**

3.2 Effect of Initial Concentration

The effect of initial concentration on the adsorption of Cd and Tl was tested. At a known initial concentration of 50mg/L, Cd was high for the first 15 minutes with 10.3 and 10.1 mg/L removed for *Chlorella vulgaris* and *Scenedesmus acuminutus* respectively, Figure 2a. An increase in time showed a relatively slow Cd removal of about 1mg/L removed every 2 hours with 29 mg/L left after 360 minutes. Removal of Tl was significantly removed by both test algae from initial concentration of 250 mg/L to 4.038 and 18.30 mg/L for *Chlorella vulgaris* and *Scenedesmus acuminutus* respectively in the first 15 minutes. In the preceding 120 minutes, removal was slower but then showed an increase to 43.99 and 22.78 mg/L for *Chlorella vulgaris* and *Scenedesmus acuminutus* respectively, Figure 2b.

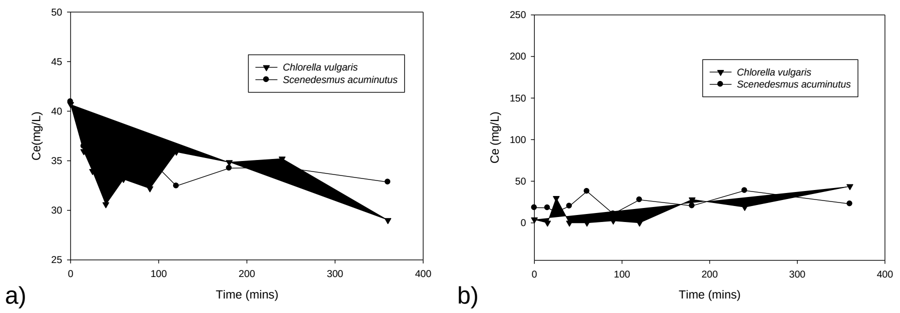


Figure 2: Effect of initial concentration on; a) Cd adsorption and b) Tl adsorption using selected algae

3.3 Characterisation of Functional Groups for Adsorption

The results from FTIR indicated a relatively similar trend for the transmittance for both the tested algae with minimal differences wavelength. *Chlorella vulgaris* showed a higher shift from 3258 to 3300 cm^{-}1 implying a medium O-H stretch of carboxylic bond and a lower frequency of 1600cm^{-}1 for amines. *Scenedesmus acuminutus* also showed a higher frequency of 3373 cm^{-}1 indicating primary and secondary amines Figure 3.

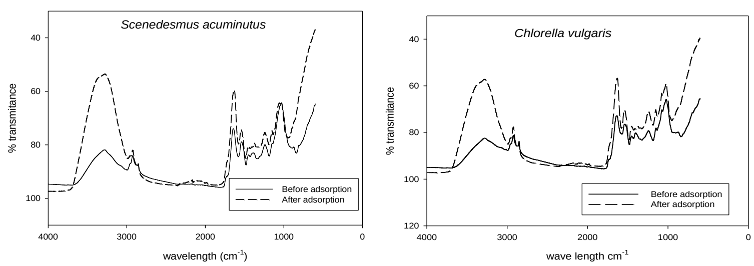


Figure 3: FTIR transmittance before and after adsorption for the tested algae

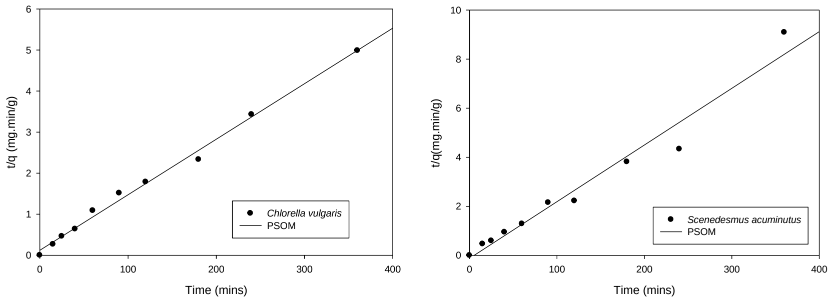
3.4 Kinetic Modelling of Single Metallic Systems

Kinetic models provide information that can be utilised in the design and optimisation of operation systems. The first order model and Pseudo second order model (PSOM) used in this study were linearized as shown in Eq(3 and 4) respectively. The PSOM generally showed a higher correlation coefficient ≥ 0.9 than first order model, Figure 4.

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

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

a)



b)

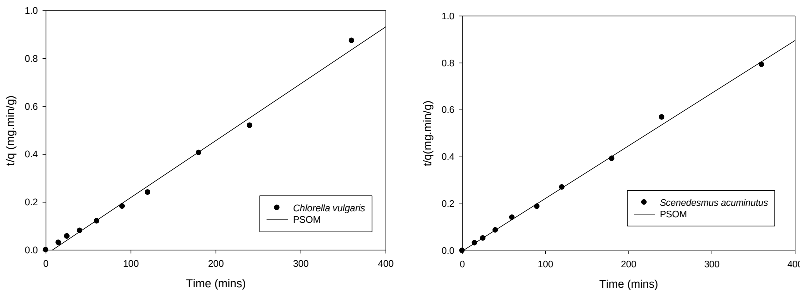
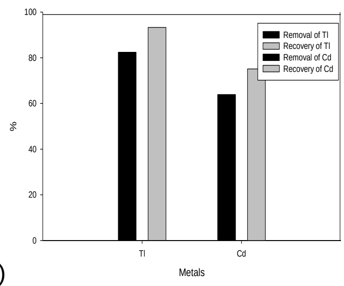


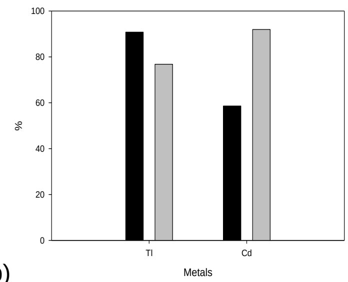
Figure 4: Pseudo second order kinetic model for, a) Cd at 100mg/L and b) Tl at 250 mg/L

3.5 Adsorption/Desorption efficiency for Tested Algae

The rate of Cd removal at an initial concentration of 50 mg/L for *Chlorella vulgaris* and *Scenedesmus acuminutus* was 63.9% and 58.6% respectively, Figure 5. Generally recovery of Cd was higher than removal with the highest rate attained by *Scenedesmus acuminutus* at 91.92%. The removal of Tl was highest for *Scenedesmus acuminutus* at 90.8% but Tl recovery highest for *Chlorella vulgaris* at 93.26%, Figure 5.



a)



b)

Figure 5: Rate of Removal/Recovery of Cd and Tl for, a) Chlorella vulgaris and b) Scenedesmus acuminutus

4. Conclusion

Chlorella vulgaris showed the highest potential for both removal and recovery of thallium and cadmium with a higher sorption capacity and higher affinity for metals. Both species showed highest removal of thallium with over 100% removed for lower concentrations ≥ 150 mg/L. The study indicated that an increase in initial concentration leads to reduction in adsorption due to saturation of binding sites. The most common functional groups influencing adsorption were carboxyl and amines. The Langmuir model performed better than the Freundlich model with a higher correlation coefficient ≥ 0.9.

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