# Algal Sorbents for Treatment of Multiple Metals and Recovery of Rare Earths in Simulated and Actual Wastewater-17098

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## ABSTRACT

In this study, waste micro algae was used in adsorption/desorption of ternary system of metals including thallium (Tl), cadmium (Cd) and lanthanum (La). Equilibrium and kinetic studies were carried out con-currently in batch reactors. The effect of pH and ionic strength were tested. The Extended Langmuir model (ELM) and Combined Langmuir and Freundlich model (CLFM) were used to evaluate the data from equilibrium experiments. AQUASIM was used for kinetic modelling of a ternary system of metals. Adsorption using ternary system of metals showed a lower sorption capacity ($q_{\max}$) compared to single metallic studies due to competition for binding sites in the former. Generally, the ELM performed better than CLFM with correlation coefficient ($R^2$) of 0.99. Thallium showed the highest ($q_{\max}$) of 77.28 mg/g and ($K$) of 0.244 L/g. The affinity ($K_L$) was highest for Tl and La at 0.244 and 0.403 L/g respectively in the ELM. The experimental data from kinetic studies relatively fit well the predicted model in AQUASIM. Recovery of metals by *D. multivariabilis* was highest for La at 90.92 %. In the actual wastewater samples, all the available metal concentrations were generally reduced by tested algae. *C. vulgaris* and *D. multivariabilis* removed 100% cobalt and thallium from smelter water with an initial concentration of 0.316 and 2.302 mg/L respectively. Chromium from mine water was reduced from 78.365 to 43.47 and 38.14 mg/L using *S. acuminutus* and *D. multivariabilis* respectively. The algal species tested presented great potential for application in industrial wastewater treatment and recovery of REE.

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## INTRODUCTION

Toxic metals are directly or indirectly released into the environment mainly through anthropogenic related activities. Some of the most common sources of inorganic pollution are electroplating, mining, battery manufacturing, tanning, chemical manufacturing, coal combustion [1-4]. Unlike toxic heavy metals which are relatively abundant, some metals are scarce and unevenly distributed in the earth crust. Rare Earth Elements (REE) are ranked by as one of the most critical elements with many emerging technologies but with a diminishing supply [5]. REE are used in many applications such as green energy technologies, nuclear oil, automobile industry, electronics industry etc. Recycling using environmentally friendly technologies act as an efficient and complementary to primary mining for sustainability of critical resources [6, 7].

Conventional treatment technologies such as sand filtration, GAC adsorption, precipitation-sedimentation, flotation, ion-exchange, and electrochemical deposition systems have been used for decades for the removal of toxic heavy metals Cd, Pb, Fe, Mn, Cr, and As from wastewater [8, 9]. These technologies seem to operate relatively well for effluents containing higher metal concentrations ≥ 100 mg/L. 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 requirement especially for small-scale industries with lower metal concentration [10, 11]. Biosorption has attracted more attention as it offers the possibility of regeneration and reuse of the biosorbent [12, 13]. This is mainly attributed to the active functional groups of the cell wall which provide binding sites, e.g. carboxyl, phosphate, amines, hydroxyl, phenols among others [1, 14, 15].
Micro algae proliferate everywhere in both fresh water and marine environments including inland water bodies. In spite of their local availability, only a small percentage of the fresh water algae species that has been investigated thus far has been demonstrated to be capable of adsorbing a wide range of metallic species from water (13, 15-17).

In addition, most biosorption studies have researched on single metal pollutant systems [18-21]. Scenarios representing realistic multi-metal pollutant systems commonly encountered in the environment are limited. The use of single metal pollutant systems provides fundamental information on the adsorption potential of the various biosorbents but requires to be complimented with multi metallic studies to reflect the actual environment. Actual industrial wastewater contains different metals in varying concentrations which compete for the binding sites depending on the environmental conditions such as pH, temperature and ionic strength. This study investigated the use of freshwater micro algae for removal/recovery of multi-metals and treatment of actual wastewater.

## MATERIALS AND METHODS

### Algal Collection and Identification

The planktonic algae were collected from a fresh water dam in Hartbeespoort dam in North West province in South Africa. 30 litres of algal samples were scooped using a bucket from different sampling site and concentrated using planktonic nets of 30 and

120 µm. The algal samples were isolated using streak plating technique and analysed using molecular methods. DNA extraction from the algal samples was performed with the CTAB method of (22). The Internal transcribed spacer (ITS) and 18S ribosomal RNA gene (rRNA) were used in this study. ITS1 and ITS2 primers were used to amplify the ITS region in the forward and reverse directions, respectively. Phylogenetic analysis of sequences was checked for similarity using a basic local alignment search tool (BLAST) (http://www.ncbi.nlm.nih.gov/BLAST/).

### Algal Culture

The pure colonies were picked up by loop and allowed to grow in tubes and vials containing AF-6 media as starter cultures and stock cultures under illumination using algal lights (Osram L 36W/77 Floura) at 23°C for 12 hours day light. Starter cultures were used as back up and were maintained under illumination in static flasks. The stock cultures were further inoculated into 1000ml and 2000ml volumetric flasks to increase the volume of cultured sample and sub- cultured twice a month. The algae was harvested, centrifuged, cleaned twice with de-ioned water and dried at 50°C in the oven over night and stored for biosorption experiments.

### Equilibrium and Kinetic Experiments

For preparation of a mixture of multi metallic, initial concentration of 25-150 mg/L were used for Cd and La, and 150-800 mg/L for Tl. The varying concentrations were measured into 100 ml volumetric flask for each metal, and then mixed to make a volume of 300ml for the 3 metals. The mixture was then divided into 2 volumes of 150 ml each into Erlenmeyer flasks to make duplicates. The pH was adjusted to optimum at 6 before the start of the experiment and a constant biomass of 0.08g was used. The experimental sets were stirred on the magnetic stirrer at room temperature and a constant speed of 350 rpm. Equilibrium and kinetic studies were carried out con-currently. The first sample was taken as soon as the biomass was added into the metal concentration at time ($t_0$). The pH was adjusted occasionally using 0.1M NaOH and HCl. The preceding samples were taken at pre- determined time interval between 5-1440 minutes. The samples were centrifuged for 10 minutes at 6000 rpm and the supernatant analysed using ICP.

### Effect of pH on Ternary System

A mixture of 3 metals was used to check the effect of pH on the ternary system at initial concentration of 150 for Cd, La and 250 mg/L for Tl. The initial concentration was kept constant for all the pH values in a range of 2-8. The biomass was also kept constant at 0.05g and the experiment was run for 4 hours.

### Effect of Ionic Strength on Ternary System

Standard stock solutions of $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ were purchased from Merck, South Africa. All experiments were carried out at a constant temperature and biomass. To test for effect of ionic strength, initially experiments were carried out using Na+ at low and high molar concentration without adjusting the pH as it would bias the final results. 250mg/L of Tl, 100mg/L of Cd and La were measured using100ml volumetric flasks and then volumes of 50ml each were used for each experiment. A mixture of the 3 metals was poured into 250ml Erlenmeyer flask. All experiments were carried out in duplicates. A biomass of 0.05g was added to each flask and stirred on the magnetic stirrer at a constant speed. A sample was withdrawn from each flask, centrifuged and the filtrate analysed using ICP.

### Recovery of Metals from a Ternary System

Adsorption samples from equilibrium studies of ternary system were used in the desorption experiments. The metal loaded samples were rinsed twice in double distilled water and weighed. 0.1M nitric acid was used as the eluent and the experiments were carried out in duplicates. The biomass was added and mixture was stirred in the magnetic stirrer for 6 hrs. A sample was withdrawn, centrifuged and the filtrate analysed using ICP.

### Biosorption using Actual Industrial Samples

Industrial wastewater samples were collected from 3 industries in South Africa, namely Dilakong chrome mine, Afrisam cement industry and Manganese metal company. The industrial samples were initially analysed using ICP to determine the metal types and concentration available before biosorption experiments. 100ml of waste samples were then contacted with 0.1g of algal biomass in 250ml of Erlenmeyer flasks and stirred on the magnetic stirrer at 240 rpm for 24 hours. The samples were filtered and the filtrate analysed using ICP.

### Data Analysis

Biosorption of multiple metals using algae was done using predictive models containing parameters from single metallic systems. The extended Langmuir was used in this study and is given by the equation as follows;

$$q_{e(i)} = \frac{q_{m.i} K_{L..i}\left(C_{e.i}\right)}{1+\sum_{j=1}^{N} K_{L.j}\left(C_{e.j}\right)}$$

(Eq. 1)

where $q_{e(i)}$ is equilibrium metal uptake for I metals (mg/g), $C_{e.i}$ is equilibrium concentration (mg/L), $q_{m.i}$ is maximum adsorption capacity (mg/g) and $K_{L..i}$ is Langmuir isotherm parameters (L/g)

The Combined Langmuir-Freundlich model was also used and is given by the equation as follows;

$$q_{e.i} = \frac{q_{m.i} b_{LF.i} C_{e.i}^{1/n_{LF,i}}}{1+\sum_{a=1}^{N} b_{LF,a} C_{e.a}^{1/n_{LF.a}}} \quad \text{(Eq. 2)}$$

where $b_{LF.i}$ is the affinity constant for adsorption (L/mg), $n$ is the index of heterogeneity

The experimental data from the kinetic studies of a ternary system of La, Tl and Cd was simulated using AQUASIM (Version 2). A non-linear Langmuir-Hinshelwood (L-H) which explains kinetics of heterogeneous surfaces was used to describe the sorption behaviour of metallic ions on the adsorbent (23, 24). The L-H expression is given by the following generic equation;

$$-{}^{dc}\!/_{dt} = {}^{qC}\!/_{K+C} \qquad \text{(Eq.3)}$$

where $q$ is the rate reaction constant (1/hr), $C$ is the concentration at any time, t (mg/L), $K$ is the adsorption equilibrium constant(mg/L).

The assumption of L-H equation is that complete degradation occurs which does not seem to be the case with biosorption. When the active surface binding sites become saturated, then no further reduction occurs. Therefore, the L-H kinetics was modified to the following equation;

$$-{}^{dc}\!/_{dt} = {}^{qC}\!/_{K+C}\left[A_o - \frac{(C_o - C)}{R_c}\right] \qquad \text{(Eq.4)}$$

where $A_o$ is the initial surface area (m$^2$/g), $C_o$ is initial metal concentration and Rc is the reduction capacity (mg.g)/ (L.m$^2$).

## RESULTS AND DISCUSSION

### Empirical Modelling

The results from sorption capacity of the ELM for multi-metals was in the order of Tl> La> Cd, Table 1. Generally, the $K_L$ value for Lanthanum was highest at 0.403 L/g and lowest for Cd at -0.0013 L/g. The higher the $K_L$ value, the greater the affinity of the metal for the biosorbent and possibility of metal recovery [25-27]. Generally, from both models, it can be noted that Tl and La showed better affinity for the adsorbent compared to Cd. This could be related to the physical-chemical properties, surface properties and solution chemistry which affects biosorption preference for competing metals [28].

TABLE 1 ELM parameters for the ternary adsorption of Tl, La and Cd

| **Metals** | $q_{\max}$ **(mg/g)** | $K_{Tl}$ **(L/g)** | $K_{La}$ **(L/g)** | $K_{Cd}$ **(L/g)** |
|---|---|---|---|---|
| Thallium | 77.278 | 0.2440 | - 0.0250 | - 0.095 |
| Lanthanum | 71.307 | 0.0470 | 0.4030 | 0.2160 |
| Cadmium | 40.075 | 0.0006 | - 0.0013 | 0.0014 |

TABLE 2: CLF parameters for the ternary adsorption of Tl, La and Cd

| **Metals** | $q_{\max}$ (mg/g) | $b_{Tl}$ (L/g) | $b_{La}$ (L/g) | $b_{Cd}$ (L/g) | $n_{Tl}$ | $n_{La}$ | $n_{Cd}$ |
|---|---|---|---|---|---|---|---|
| Thallium | 5.089 | 0.445 | - 0.076 | - 0.356 | - 0.758 | 0.076 | 0.546 |
| Lanthanum | 4.300 | 0.083 | 0.005 | - 0.075 | 0.207 | 0.011 | 0.034 |
| Cadmium | 4.694 | 0.077 | - 0.005 | - 0.063 | - 0.209 | 0.017 | 0.069 |

## Kinetic Modelling

Experimental data from the ternary system was used for model optimisation and simulation with non-linear least square algorithm using Eqns. (3 and 4). The experimental data for Cd generally showed a good fit to the model with reduction occurring until a stable state was attained with no further adsorption, Fig. 1. At a concentration of 25 and 50 mg/L of Cd, most of the experimental data showed a good fit with the model especially in a period of 4 hours which had the highest data points, Fig 1. In most biosorption studies, the rate of reaction is rapid in the first 15-30 minutes due to the abundance in the available active functional groups [12, 29].
At low concentrations ≤ 50 mg/L of La, the measured data closely fit the model well in the first 5 hrs and then deviated away with an increase in time, Fig. 2. This could be due to competition of distinct ions for same site especially with Tl which showed the highest reduction in all experiments for a given period of time.

Higher concentrations in a range of 150- 250 mg/L of Tl were used to study kinetics due to the complete removal attained at lower concentrations ≤ 100 mg/L. For all the initial concentrations tested for Tl, a significant reduction was attained within a short period of time but an increase in time had an antagonistic effect on Tl as it desorbed back into the system, Fig 3.

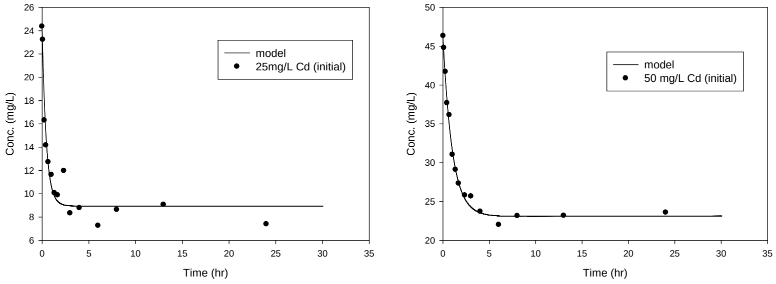

Figure 1: Experimental and model validation of Cadmium adsorption

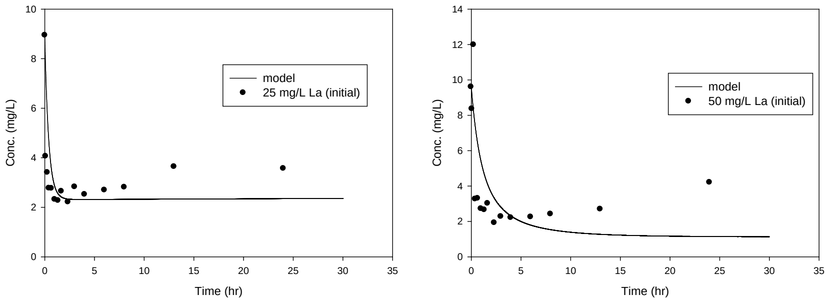

Figure 2: Experimental and model validation of lanthanum adsorption

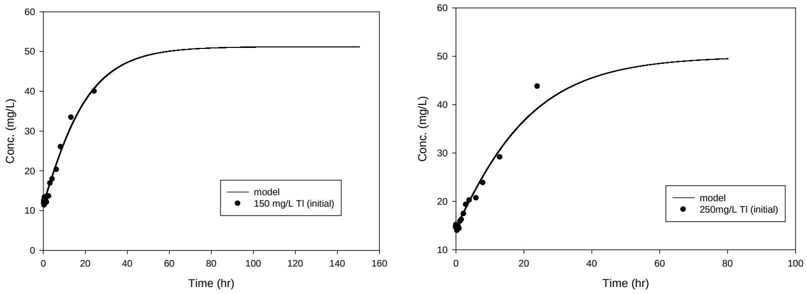

Figure 3: Experimental and model validation of Thallium adsorption

## Influence of Environmental Factors

The effect of ionic strength on the uptake of Tl, La and Cd was tested using a low and high molarity of sodium ($Na^+$) standard solution. The removal rate of Tl, La and Cd was generally low at 5.39, 47.5 and 47.995% respectively, Fig. 4. When the concentration of light ions was increased to 4.35M, $Na^+$ and $Mg^{2+}$ still showed removal efficiency of 100% with a slight reduction for $K^+$ at 90.78% and slight increase for $Ca^{2+}$ at 84.8%.

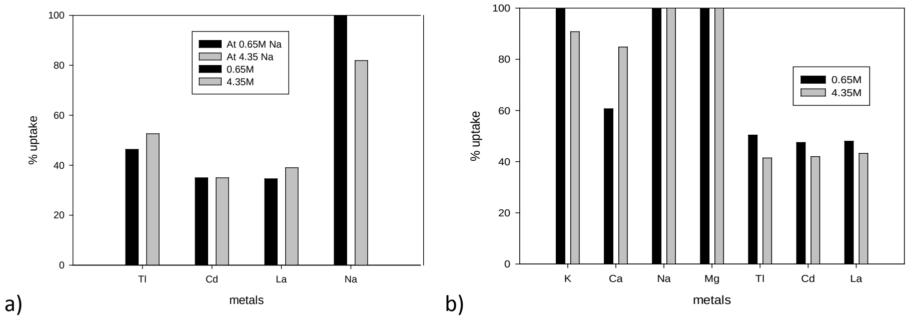

Figure.4: Effect of ionic strength on uptake of Tl, La and Cd, a) using Na+ only. b) combination of light metals

At very low pH of 2, initial uptake of Tl was attained at 83.67%, Fig.5. Sorption efficiency for Tl increased with increase in pH upto 96.42% at pH of 6. The experiment was carried out at pH ≥ 8 as precipitation tends to occur at higher pH. The uptake of Cd was generally low from pH of 2-5 then increased from pH of 5-8 with a significant rise at pH 8 of 70%. Generally the optimum pH for the 3 metals was found to be between 6 and 8.

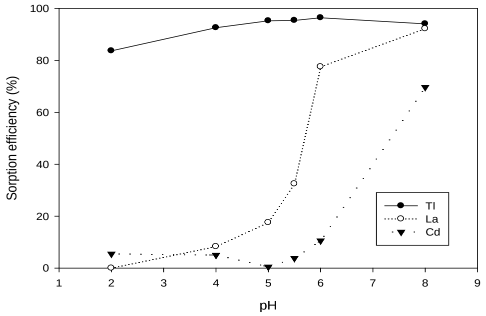

Figure 5: The effect of pH on the uptake of metals in a ternary system.

## Desorption in the Ternary System

Lanthanum showed the highest removal and recovery at 94.04 and 90.92% respectively. The removal rate for Tl was also relatively high at 83.84% but recovery was very low at 23.77%., Fig 6. The removal rate of La was higher than for Tl and this could be due to the effect of contact time. Despite the low uptake of Cd attained at 52.98%, recovery was relatively high at 90.15%, Fig. 6

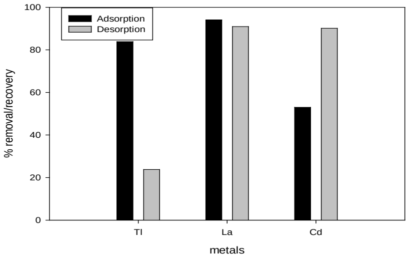

Figure. 6: Adsorption/Desorption efficiency for Tl, La and Cd using *D. multivariabilis*

## Treatment of Actual Industrial Wastewater

Wastewater from the mine beneficiary plant showed the highest heavy metal concentration in Mn which was reduced from 0.136 to 0.02mg/L by *D. multivariabilis*. Fig. 7. There was almost complete removal of Cobalt and Zinc from the industrial wastewater. The results indicate the high adsorption potential for treatment of actual wastewater using *D. multivariabilis*.

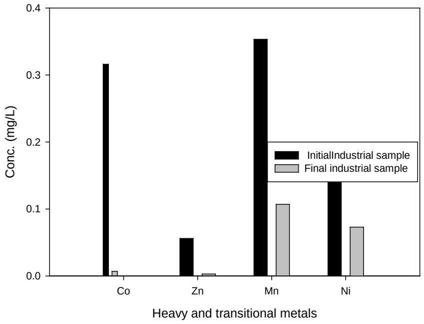

Fig.7 Treatment of industrial wastewater from mine beneficiary plant using tested algae

## CONCLUSION

The competitive adsorption models represented the ternary system well providing information of the adsorption capacity and affinity of the metals on the biosorbent. Thallium generally showed the highest $q_{\max}$ and affinity $b$ followed by lanthanum. The experimental data from the kinetic studies relatively fit well the predicted model in AQUASIM. Environmental factors were found to influence the adsorption process Recovery of the heavy metals by *D. multivariabilis* was achieved highest for La at 90.92% followed by Cd at 90.15%. The tested algal sorbents showed potential for the treatment of actual wastewater and recovery of rare earth elements for re-use.

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