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Competitive adsorption in a ternary system of toxic metals and rare earth elements using *Desmodesmus multivariabilis*: empirical and kinetic modelling

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Abstract The presence of competing metals in industrial wastewater creates problems of selectivity for binding sites during biosorption of cationic metallic species on microbial cell surfaces. For this reason, modelling of adsorption and uptake of multimetal solutions based on observation of performance of single metal species since this neglects the competition for reactive sites typical in multimetal solutions. In this study, a culture of the green alga *Desmodesmus multivariabilis* previously isolated from eutrophic freshwater was used as a biosorbent for adsorption/desorption of different metals in a mixed metal solution under varying environmental conditions. The Extended Langmuir Model (ELM) and Combined Langmuir and Freundlich Model (CLFM) were used to evaluate the data from a ternary metallic system. AQUASIM was used for optimization and simulation of kinetic data in ternary systems. The ELM performed better than CLFM with correlation coefficient of approximately 0.99. The highest uptake was observed for thallium with q_{max} = 909.09 mg g in single metal solution. This value was reduced to q_{max} = 77.278 mg g^{-1} in the presence of other metals which demonstrated the competitive effects of other metal ions in solution. The q_{max} value of lanthanum (La) decreased from 100 in single metals to 71.3 mg g^{-1} in multimetal solution; whereas, the q_{max} = of cadmium (Cd) decreased from 48.5 to 40.1 mg g^{-1}. Recovery of metals by *D. multivariabilis* was the highest for La at 90.92% followed by Cd at 90.15%. Competitive inhibition models provided a better insight on the potential for treatment of actual industrial wastewater with varying environmental factors.

Keywords *Desmodesmus multivariabilis* · Thallium · Cadmium · Lanthanum · Biosorption · Adsorption models

Introduction

Industrial wastewater contains a mixture of different heavy metals, metalloids, radionuclides and organic pollutants under varying environmental conditions. New research has been fuelled by the need to find sustainable ways to treat and manage metal accumulation in the environment since metals are never degraded but are rather converted from one form to another (Peakall and Burger 2003; Kotrba 2011). Metallic pollutants can be treated using physical and/or chemical methods. Recently, biological methods have been used due to the need to apply environmentally friendly technologies in the treatment of toxic waste (Hashim and Chu 2004; Ahluwalia and Goyal 2007; Gadd 2009). Conventional treatment technologies such as ion-exchange, solvent extraction, precipitation and membrane technologies have been used in the extraction of metallic ion species from wastewater. Membrane technologies employed in this process such as electrodialysis and reverse osmosis are usually expensive and produce waste brine that is difficult to dispose (Volesky 2001; Ahalya et al. 2003).

Biological treatment can be used as an alternative or complementary process to conventional treatment processes during the detoxification and metal recovery from industrial wastewater (Gorgievski et al. 2013). The advantages

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attributed to biological processes such as biosorption include, among others, relative abundance of the microbial biosorbent, low operational and maintenance cost, environmental compatibility of the process and ease of recovery due to ion exchange capacity of the biosorbent (Ahalya et al. 2003). Metallic species can be easily sequestered using wet or dry microbial biomass. However, only the biomass with high sorption capacity and selectivity for metals is considered worth pursuing for further development as industrial biosorbent. One such category of organisms is algae.

Although a wide range of studies have been conducted on the ion-exchange and biosorption capability of marine algae, fewer studies have been conducted on the biosorption capability of freshwater algae. The emphasis has been on marine algae in spite of the increasing incidence of freshwater algae due to the eutrophic inland water bodies. Additionally, very limited studies have been conducted on the biosorptive efficiency of metal ions in the presence of multiple metallic species in a single solution. Most of the studies on the biosorption of metallic ions by algal species have been conducted using marine algae with single metal ions in solution (Bakatula et al. 2014; Tabaraki and Nateghi 2014).

The use of more than one metal in biosorption studies is a more representative system as it reflects the actual wastewater with varying environmental conditions like pH, metal concentration, ionic strength and temperature (Sağ et al. 2001; Vijayaraghavan and Yun 2008a; Acheampong et al. 2010). The presence of competing ions was earlier researched to show selectivity and affinity of metals due to competition or formation of complexes that could be easily adsorbed (Mukhopadhyay et al. 2011; Fomina and Gadd 2014). Borderline metals such as Cd^{2+}, Ni^{2+} and Zn^{2+} have a tendency to effect inhibition on one another, whereas the heavy metals such as Pb^2+ and Cd^{2+} do not typically inhibit each other's adsorption on biomass (Tsezos et al. 1996; Arief et al. 2008).

Mechanistic mathematical representation of multimetal systems is complicated by the multivariance nature of both the kinetic and adsorptive functions and complex interactions among the different species as they react with each other or compete for binding sites on cell surfaces (Pagnanelli et al. 2001; Pradhan and Rai 2001; Lu et al. 2008). Several competitive adsorption models have been proposed which are based on studies on single metal and single microbial species data. The latter models are not suitable for application in multimetal systems since they do not represent the other interactions, e.g. reaction, coprecipitation and competitive inhibition of biosorption, that are expected in a multimetal solution. In this study, predictive modelling using Combined Langmuir and Freundlich Model (CLFM), semi-predictive model of Extended Langmuir Model (ELM) and kinetic models were utilised to investigate the adsorption efficiency of the green alga *Desmodesmus multivariabilis* in a ternary system of heavy metals and rare earth elements.

The algal species *D. multivariabilis* was screened and purified by Birungi and Chirwa (2014) for use in the biosorption heavy metals (Cd, Pb, Zn) and rare earth metals (La, Tl, Rd). *D. multivariabilis* was thus selected for further investigation following the good performance achieved on the biosorption of rare earth metals as reported earlier (Birungi and Chirwa 2014).

Materials and methods

Molecular identification and algal culture

Algal samples were collected from a freshwater body in Hartbeespoort Dam, North West Province in South Africa. The samples were isolated using the streak plating method and pure colonies of interest were identified with the internal transcribed spacer (ITS) and 18S ribosomal RNA (rRNA) gene. ITS1 and ITS2 primers were used to amplify the ITS region in the forward and reverse directions, respectively. To amplify the 18S rRNA gene, the specific forward primer and the conserved reverse primer were used. Polymerase chain reaction (PCR) amplification was carried out in a DNA Thermal Cycler (Gene Amp PCR System 2400—Perkin Elmer). The conditions for the ITS1/ITS2 primer pair were 5 min at 95 °C, 35 cycles of 1 min at 90 °C, 2 min at 50 °C, 1 min at 72 °C and a final elongation step of 10 min at 72 °C. All PCR amplifications were performed in 50 μL master mix solution containing 10 mM Tris HCl, 50 mM KCl, 0.1% Triton X-100, 1.5 mM $MgSO_4$, 200 μM dNTP, 0.4 μM of each primer, 1.0 u Taq polymerase (Promega) and 10 ng of total DNA. Phylogenetic analysis of sequences was checked for similarity using a basic local alignment search tool (BLAST) (http://www.ncbi.nlm.nih.gov/BLAST/). The algal species of *Desmodesmus multivariabilis* with similarities to the query samples were found to have 98% sequence identities. The pure strain of *D. multivariabilis* was then cultured in AF6 medium under controlled algal lights (Osram L 36W/77 Floura) for 12 h under the light at a temperature range of 20–23 °C. The algal samples were dried in an oven at 50 °C for 24 h and stored for biosorption experiments.

Adsorption equilibrium and kinetics for ternary system

The prepared multimetal component solution used in this study consisted of Cd and La initial concentration in the range 25–150 mg L^{-1} and Tl initial concentration in the range 150–800 mg L^{-1}. The initial concentration for each metal was prepared in 100-mL flasks and the final mixed metal solution was prepared to the desired concentration distribution in 300-mL flasks. Duplicates were prepared by splitting the prepared mixed stock into different reactors. The target total algal mass in each batch was 80 mg. The pH in each batch was adjusted to 6.0 before undertaking biosorption experiments. The target pH of 6.0 was based on the optimum pH range for algal growth determined in earlier studies (Birungi and Chirwa 2014, 2015). The experimental sets were stirred on the magnetic stirrer at a constant speed of 350 rpm under room temperature conditions. Equilibrium and kinetic studies were carried out concurrently for 24 h. 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 0.1 M solutions of NaOH and HCl. The preceding samples were taken at a predetermined time interval between 5 and 1440 min. The dissolved component remaining in solution after centrifugation of the sample at 6000 rpm for 10 min was analysed from the supernatant using the Spectro Arcos FHS12 Inductively Coupled Plasma (ICP) (Oschstroisse, Germany).

Effect of pH on ternary system

A mixture of three metals was used to check the effect of pH on the ternary system at initial concentration of 150, 150 and 250 mg L^{-1} for Cd, La and Tl, respectively. The initial concentration was kept constant for all the pH values in a range of 2–8. The biomass was also kept constant at 0.05 g and the experiment was run for 4 h.

Effect of ionic strength on ternary system

Standard stock solutions of Na$^+$, K$^+$, Mg^{2+} and Ca^{2+} were purchased from Merck, South Africa. All experiments were carried out using a constant biomass and varying initial concentrations. To test for effect of ionic strength, initial experiments were carried out using Na$^+$ at low and high molar concentrations without adjusting the pH as it would bias the final results. NaOH used for adjusting pH contains Na$^+$ which would increase the molar concentration of Na$^+$ in the solution; 250 mg L^{-1} of Tl and 100 mg L^{-1} of Cd and La were measured into 100-mL volumetric flasks and then volumes of 50 mL each were used for ternary experiments. Initial concentrations of 0.65 and 4.35 M for Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} were measured using 50-mL volumetric flasks and poured into the mixture of prepared test metals. A biomass of 0.05 g 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 the ternary system were used in the desorption experiments. The metal loaded samples were rinsed twice in double-distilled water, centrifuged and the biomass weighed. 0.1 M nitric acid was used as the eluent and the experiments were carried out in duplicates. Four eluents were initially tested using Tl and these included H_2SO_4, EDTA, HCl and HNO_3 (Birungi and Chirwa 2015). The results indicated the preference of eluents was in the order of HNO_3 > EDTA > HCl > H_2SO_4 hence selection of nitric acid for this study. The biomass was added to nitric acid and the mixture stirred on the magnetic stirrer for 6 h. A sample was withdrawn, centrifuged and the filtrate was analysed using the ICP.

Data analysis

Empirical modelling of multimetal systems

Biosorption of multiple metals using algae was done using predictive models containing parameters from single metallic systems. The Extended Langmuir Model (Fritz and Schluender 1974) was used in this study and is given by the equation as follows:

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

where $q_{e(i)}$ = equilibrium metal uptake for i metals (mg g^{-1}), $C_{e.i}$ = equilibrium concentration (mg L^{-1}), $q_{m.i}$ = maximum adsorption capacity (mg g^{-1}) and $K_{L.i}$ = Langmuir isotherm parameters (L g^{-1}).

The Combined Langmuir-Freundlich Model (Sips 1948) was also used and is given by the equation as follows:

$$q_{e.i} = \frac{q_{m.i} b_{LF.i} \left(C_{e.i}^{1/n_{LF.i}} \right)}{1 + \sum_{a=1}^{N} b_{LF.a} \left(C_{e.a}^{1/n_{LF.a}} \right)} \tag{2}$$

where $b_{LF.i}$ = affinity constant for adsorption (L mg^{-1}), and n = heterogeneity index of the solution.

Biosorption preference and relative coverage of metals in ternary equilibrium system were assessed using the following equations as given by (Chang and Chen 1998; Sağ and Aktay 2002).

$$Y_i = \frac{C_s}{C_i} \times 100 \tag{3}$$

$$Y_t = \frac{C_{s.t}}{C_{i.t}} \times 100 \tag{4}$$

$$\theta_t = \frac{C_{s.m}}{C_{s.m.t}} \times 100 \tag{5}$$

where Y_i = biosorption preference (%), Y_t = total biosorption efficiency (%), θ_t = relative coverage (%), C_i = initial concentration (mg L^{-1}), C_s = concentration of metal sorbed (mg L^{-1}), $C_{s.m}$ = moles of metal biosorbed and $C_{s.m.t}$ = total moles of metal biosorbed.

Kinetic modelling of multimetal systems

The time series data from the kinetic studies of a ternary system containing La, Tl and Cd were simulated using the Computer Program for the Identification and Simulation of Aquatic Systems AQUASIM 2.01 (AQUASIM, EAWAG, Dübendorf, Switzerland). A non-linear Langmuir-Hinshelwood (L-H) Model which explains kinetics of heterogeneous surfaces was used to describe the sorption behaviour of metallic ions on the adsorbent (Jin et al. 1996; Kumar et al. 2007). The L-H expression is given by the following generic equation:

$$-\frac{dC}{dt}=\frac{q\cdot C}{K+C} \tag{6}$$

where q = rate reaction constant (h^{-1}), C = concentration (mg L^{-1}) at any time t (h) and K = adsorption equilibrium constant (mg L^{-1}).

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:

$$-\frac{dC}{dt}=\frac{q\cdot C}{K+C}\left[A_o-\frac{(C_o-C)}{R_c}\right] \tag{7}$$

where A_o = initial surface area (m^2 g^{-1}), C_o = initial metal concentration (mg L^{-1}) and R_c = reduction capacity (g of metal per gram of algal biomass utilised).

Results

Empirical modelling of ternary system

Two of the derived models, the Extended Langmuir Model (ELM) and Combined Langmuir and Freundlich Model (CLFM) were used in this study to evaluate the experimental data from a ternary metallic system. The adsorption equilibrium analysis was conducted using MATLAB (Version 4). In the ELM, four parameters (q_m, $K_{L.Tl}$, $K_{L.La}$, $K_{L.Cd}$) were determined for each metal using Eq. 1. In the CLFM, seven parameters (q_m, b_{Tl}, b_{La}, b_{Cd}, n_{Tl}, n_{La}, n_{Cd}) were determined for each metal using Eq. 2. From the results, the ELM showed a higher correlation co-efficient (R^2) ≥ 0.90 than the CLFM. The root mean square error (RMSE) was also generally higher in the CLFM than in the ELM (Tables 1 and 2). The ELM for multimetals showed the highest q_{max} for Tl at 77.278 mg g^{-1} compared to La and Cd in the order Tl > La > Cd (Table 1). Generally, the K_L value in the ELM for La was the highest at 0.403 L g^{-1} and the lowest for Cd at −0.0013 L g^{-1} (Table 1). Sorption capacity for multimetal system was compared to that of single metal systems using *D. multivariabilis*. The difference in q_{max} for Tl was significant with 909.09 mg g^{-1} in single metallics as compared to 77.278 mg g^{-1} in the ternary system. The q_{max} for La decreased from 100 in single metallics to 71.307 mg g^{-1} in the ternary, whereas that of Cd from 48.54 to 40.075 mg g^{-1} (Table 1).

The CLFM for multimetals showed significantly lower q_{max} values as compared to ELM with the highest value from Tl at 5.089 mg g^{-1} (Table 2). Cadmium was observed to have the lowest b of −0.356 L g^{-1} but the highest n of 0.546. In addition, the three effects of multimetals on biosorption which include synergism (effect of mixture greater than individual metal), antagonism (effect of mixture less than individual metal) and non-interaction were tested (Agarwal et al. 2013). The interaction of the ternary mixture of Tl, Cd and La was evaluated by the ratio of adsorption capacity of a single metal in the mixture (Q_{mix}) to that of single metal system (Q_o). When the $Q_{mix}/Q_o > 1$, synergism, $Q_{mix}/Q_o < 1$, antagonism and $Q_{mix}/Q_o = 0$, non-interaction. The evaluation for Tl, La and Cd were 0.085, 0.713 and 0.82, respectively, which implied antagonism in the ternary system. The biosorption effect on competing metals in the ternary system was also evaluated using biosorption preference factor (Y_i) and the distribution of metals on the biosorbent (θ_i). The equations used to determine Y_i, Y_i and θ_i were given as Eqs. 3, 4 and 5, respectively. The trend generally showed an increase in Y_i with an increase in initial concentration for Tl than Cd and variations for La (Table 3). Tl had the highest θ_i which generally increased with an increase in initial concentration except at 1000 mg L^{-1} (Table 3).

Kinetic modelling of ternary system

Model simulation and parameter estimation

The kinetics of multimetallic system for the removal of three metals (La, Tl and Cd) simultaneously using *D. multivariabilis* was studied using AQUASIM (version 2.0). Experimental data from the ternary system was used for model optimisation and simulation with non-linear least square algorithm using Eqs. 6 and 7. Parameter estimations were carried out for variables q, K and R_c to determine the most important parameters influencing the prediction. 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 lower concentration in the range of 25–50 mg L^{-1} of Cd, most of the experimental data showed a good fit with the model especially in a period of 4 h which had the highest data points (Fig. 1). The results were further justified by the parameter estimations of which q clearly indicated that the rate of reaction decreased with an increase in initial concentration (Table 4). The adsorption equilibrium constant K increased with an increase initial

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

Metals	q_{max} (mg g^{-1})	K_{Tl} (L g^{-1})	K_{La} (L g^{-1})	K_{Cd} (L g^{-1})	R^2	RMSE	q_{max} (single metals)
Thallium	77.278	0.244	−0.025	−0.095	0.99	26.21	909.09
Lanthanum	71.307	0.047	0.403	0.216	0.95	69.79	100.00
Cadmium	40.075	0.001	−0.001	0.001	0.99	16.35	48.54

concentration while R_c showed an increase with concentration and then decreased at higher concentration.

At higher concentration of La, most of the experimental data fit well with the model (Fig. 2). Parameter K was very low at a lower concentration of 25 mg L^{-1} and then generally showed a decrease with an increase in concentration ≥50 mg L^{-1} (Table 5). Higher concentrations in a range of 150–800 mg L^{-1} for Tl were used to study kinetics due to the complete removal attained at lower concentrations ≤100 mg L^{-1}. The experimental data only relatively fit well with the model for the period studied (Fig. 3). For all the initial concentrations used, a significant reduction was attained from ≤800 to ≤35 mg L^{-1}. The q and R_c values increased with an increase in initial concentration (Table 6).

Sensitivity analysis

In this study, the absolute-relative sensitivity function was used on parameters q, K and R_c after model validation. Sensitivity for q on Cd was the highest in the first 1.47 h showing a fast reduction and then decreased to a stationary phase after a period of 8.44 h. Parameter R_c had a significant impact on Cd adsorption as reduction occurred for up to 10 h before attaining a stationary phase. Uptake of Cd showed no dependency on K as the parameter remained at 0 for a period (Fig. 4a). Parameter q showed a significant reduction of La as it remained at 0 for some period and then increased to a stationary phase after 2.7 h (Fig. 4b). K initially showed an increase in uptake of La for a period of 2.05 h and then decreased to a stationary phase after 11 h. R_c showed a slight increase in uptake of La for 2.2 h and then steadily decreased to a stationary phase (Fig.4b). A sensitivity test on Tl showed that parameter q had a minimal effect on the adsorption of Tl as it remained steadily close to 0 throughout the period of study (Fig. 4c). K showed a significant reduction in Tl concentration for a period of 14.2 h and then desorption occurred until steadiness was attained close to 0. R_c also showed a pronounced reduction for a period greater than 24 h and then stabilised after about 38 h (Fig. 4c).

Effect of environmental factors

Effect of ionic strength on ternary system

The effect of ionic strength on the uptake of Tl, La and Cd was tested using low and high molarities of sodium (Na$^+$) standard solution. At low levels of 0.65 M Na$^+$, uptake of heavy metals significantly decreased with the highest value attained for Tl at 46.34%. La and Cd uptake was attained at the same efficiency of 35%. At higher levels of 4.35 M Na$^+$, the sorption efficiency slightly improved for Tl at 52.61% and La at 38.98% (Fig. 5a). A mixture of different light and heavy metals was also studied at the same molarity. At the molar concentration of 0.65 M, 100% removal was achieved for K$^+$, Na$^+$ and Mg^{2+} except Ca^{2+} (60.67%). The removal of Tl, La and Cd was generally low at 5.39, 47.5 and 47.995%, respectively (Fig. 5b). When the concentration of light ions was increased to 4.35 M, 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%.

Effect of pH on ternary system

The effect of pH on adsorption for mixed system of Tl, La and Cd was studied. Lanthanum showed no removal at very low pH of 2 but an increase in pH improved sorption efficiency with maximum uptake attained between pH of 6 and 8 at 77.53 and 92.2%, respectively. 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% (Fig. 6). Sorption efficiency for Tl increased with increase in pH up to 96.42% at pH of 6. At pH of 8, there was a slight reduction in uptake of Tl to 94.07% (Fig. 6).

Table 2 CLFM parameters for the ternary adsorption of Tl, La and Cd

Metals	q_{max} (mg g^{-1})	b_{Tl} (L g^{-1})	b_{La} (L g^{-1})	b_{Cd} (L g^{-1})	n_{Tl}	n_{La}	n_{Cd}	R^2	RMSE
Thallium	5.089	0.445	−0.076	−0.356	−0.758	0.076	0.546	0.50	564.35
Lanthanum	4.300	0.083	0.005	−0.075	0.207	0.011	0.034	0.95	69.79
Cadmium	4.694	0.077	−0.005	−0.063	−0.209	0.017	0.069	0.95	69.79

Table 3 Comparison of biosorption preference (Yi) and distribution ( ) of metals on the biosorbent

$C_{i.Cd}$ (mg L^{-1})	Y_i (Cd) %	Y_i (Tl) %	Y_i (La) %	θ_i (Cd) %	θ_i (Tl) %	θ_i (La) %	Y_t (%)
5	98.40	72.74	91.6	26.41	53.69	19.90	79.10
10	96.75	81.88	89.75	24.52	57.07	18.41	85.13
15	92.57	85.71	94.47	22.02	59.80	18.18	87.84
20	93.18	80.74	95.73	23.73	56.54	19.73	84.65
35	83.39	91.49	98.84	18.49	63.77	17.74	91.39
80	78.66	94.83	98.76	20.34	59.00	20.66	92.91
120	74.43	96.25	94.06	17.93	63.74	18.33	92.82
250	76.19	96.90	96.73	21.99	55.40	22.60	93.17
500	70.98	92.03	82.45	30.35	41.12	28.53	84.18
1000	73.45	96.45	74.24	39.37	28.43	32.2	81.38

Effect of initial concentration on ternary system

At initial concentration of 250 mg L^{-1} of Tl and 50 mg L^{-1} of La and Cd, reduction was significant at time (t_0) for Tl with 11.88 mg L^{-1} left in solution using *D. multivariabilis*. Lanthanum was reduced from 50 to 9 mg L^{-1} at the start of the experiment (t_0) and further reduction with time until equilibrium was attained at 2.7 mg L^{-1} after a period of 13 h. Initial reduction for Cd at t_0 was the lowest at 45.14 mg L^{-1} and the value was still high after the same period of 13 h at 22.59 mg L^{-1} (Fig. 7a). When the initial concentration for Tl was doubled from 250 to 500 mg L^{-1}, reduction was still very significant with 26.26 mg L^{-1} left in solution at t_0. For the case of La and Cd, when the initial concentration was increased from 50 to 100 mg L^{-1}, La showed no difference with the same value of 2.7 mg L^{-1} left in solution after 13 h. Cd reduction was still the lowest with a significant concentration of 65 mg L^{-1} left in solution (Fig. 7b).

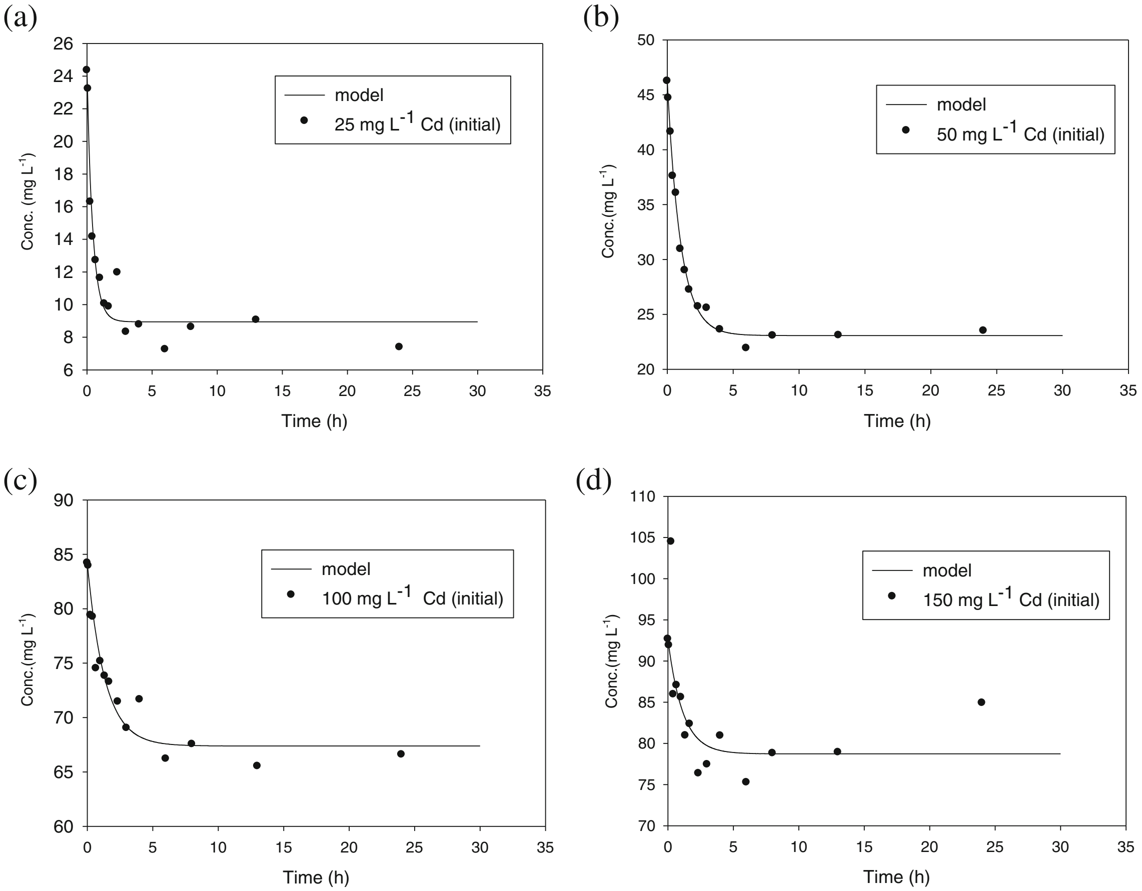

Fig. 1 Experimental and model validation of cadmium adsorption at initial concentrations of **a** 25 mg L^{-1}, **b** 50 mg L^{-1}, **c** 100 mg L^{-1} and **d** 150 mg L^{-1}

Table 4 Parameter estimations for cadmium adsorption

C_o (mg L^{-1})	q (h^{-1})	K (mg L^{-1})	R_c
25	6.621	0.698	2.801
50	4.805	1.226	4.700
100	2.614	3.222	3.494
150	2.006	7.456	2.090

Table 5 Parameter estimations for lanthanum adsorption

C_o (mg L^{-1})	q (h^{-1})	K (mg L^{-1})	R_c
25	9.949	0.008	3.965
50	1.099	9.296	0.677
100	0.015	8.992	0.006
150	4.055	7.565	3.458

Rate of removal/recovery in ternary system

The ability of the algal sorbent, *D. multivariabilis*, was tested for the adsorption/desorption efficiency of a ternary system. Initial concentration of 250 mg L^{-1} Tl and 50 mg L^{-1} of La and Cd was used. 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%. Despite the low uptake of Cd attained at 52.98%, recovery was relatively high at 90.15% (Fig. 8).

Discussion

The composition of industrial wastewater is usually very complex due to the presence of a range of inorganic and organic pollutants at different concentrations and various oxidation states. The efficiency of removal of the pollutants can be modelled using a combination of empirical and mechanistic adsorption models (Chong and Volesky 1996; Pagnanelli 2011; Reynel-Avila et al. 2011). In this study, the ELM and CLFM were used in competitive adsorption of a ternary system. The ELM assumes the surface to be homogeneous with

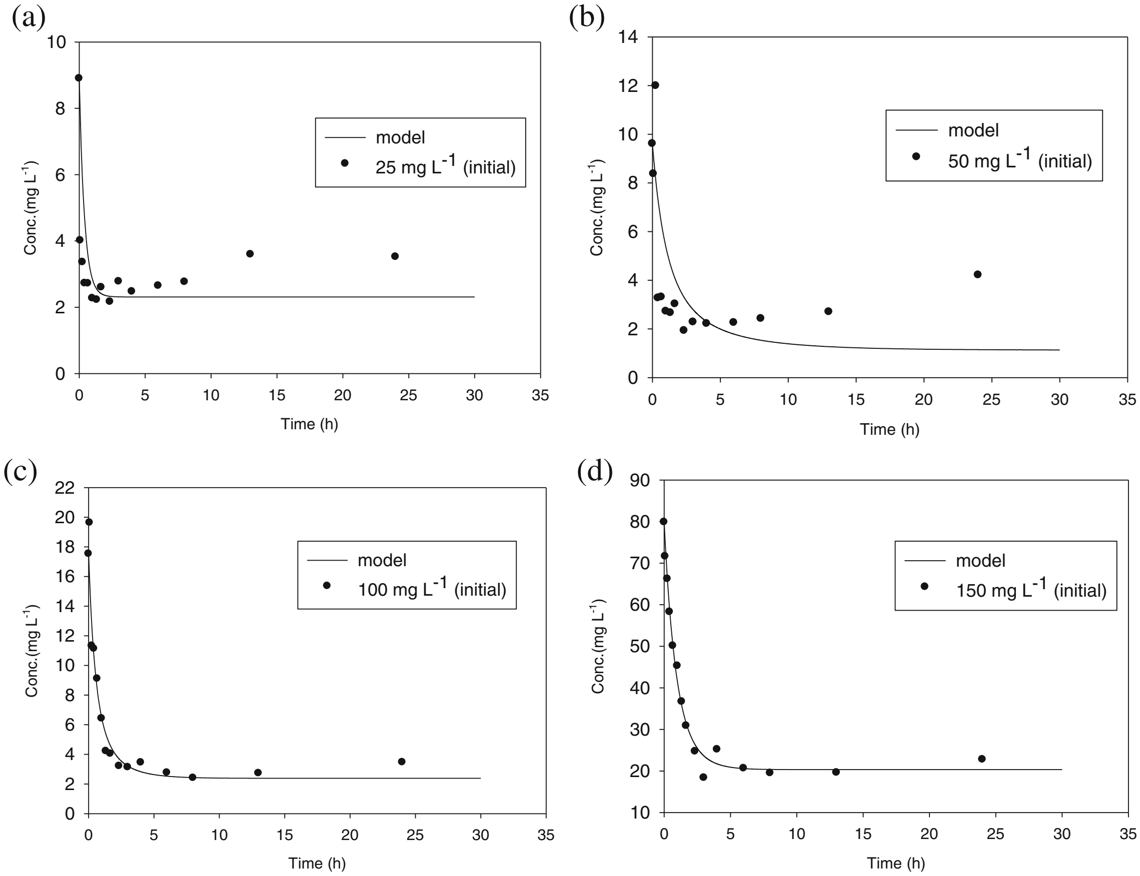

Fig. 2 Experimental and model validation of lanthanum adsorption at initial concentrations of **a** 25 mg L^{-1}, **b** 50 mg L^{-1}, **c** 100 mg L^{-1} and **d** 150 mg L^{-1}

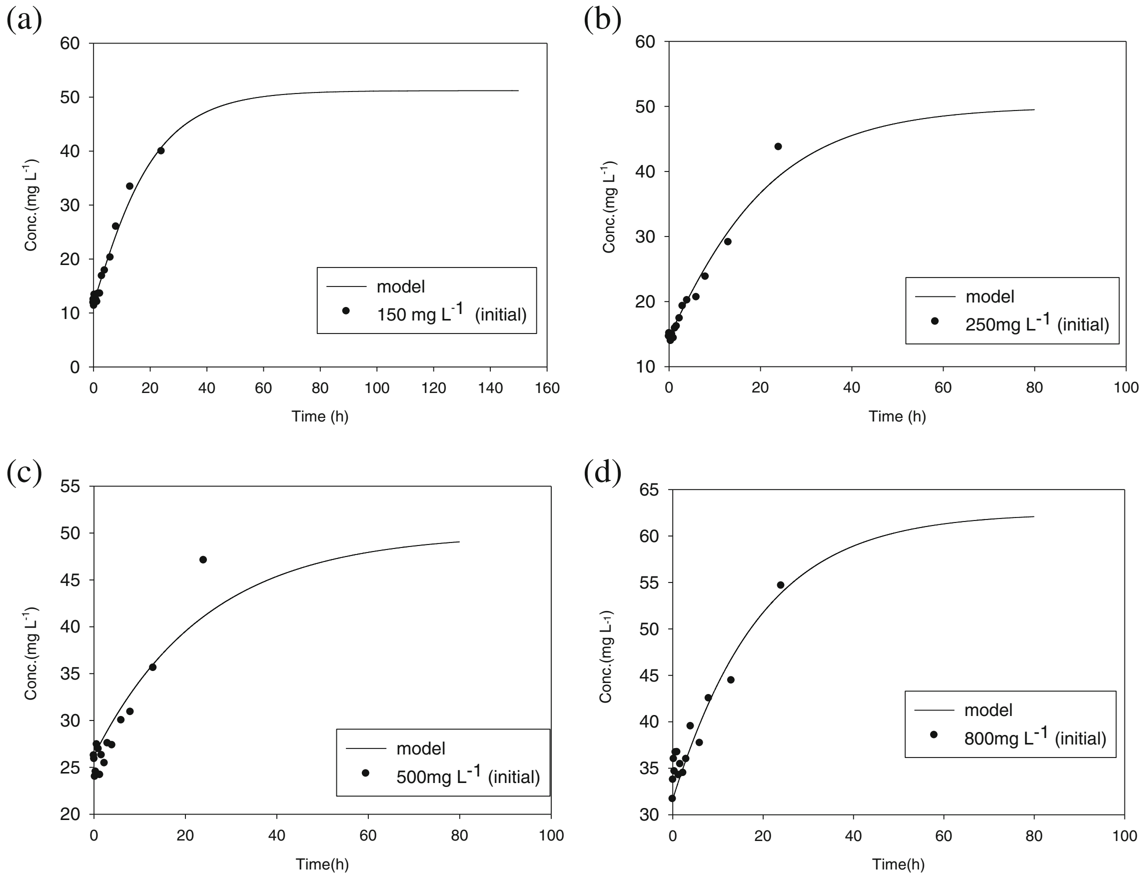

Fig. 3 Experimental and model validation of thallium adsorption at initial concentrations of **a** 150 mg L^{-1}, **b** 250 mg L^{-1}, **c** 500 mg L^{-1} and **d** 800 mg L^{-1}

the sorbate ions competing for the same binding site (Sağ and Aktay 2002; Srivastava et al. 2006). The CLFM assumes both homogeneous and heterogeneity natures of binding sites for the competing ions (Sips 1948; Turiel et al. 2003). From the results, the ELM generally performed better than the CLFM with the former exhibiting a higher correlation co-efficient. The higher RMSE for CLFM also confirmed that the ELM generally performed better than the latter. The higher the RMSE, the less accurate the results (Sag et al. 2001). Lanthanum showed the highest affinity (K_L) in the ELM. The higher the K_L value, the greater the affinity of the metal for the biosorbent and possibility of metal recovery (Sağ and Aktay 2002; Fagundes-Klen et al. 2007; Romera et al. 2007).

Table 6 Parameter estimations for thallium adsorption

C_o (mg L^{-1})	q (h^{-1})	K (mg L^{-1})	R_c
150	0.0006	9.907	0.0074
250	0.0004	9.999	0.0063
500	0.0001	1.000	0.0026
800	0.1929	9.812	2.9686

A comparison of multimetal systems to single metallic systems generally showed a higher sorption capacity for the latter than the former in all the three tested metals. The presence of more than one metal in solution increases competition for the binding sites hence reducing overall biosorption capacities (Kumar et al. 2008; Hossain et al. 2014; Rodrigues et al. 2012). All the n values from this study were less than 1 implying that the tested algal surface was heterogeneous. When the n value is less than 1, then the biosorbent surface is heterogeneous, and $n = 1$ implies homogeneous surface (Turiel et al. 2003; Jeppu and Clement 2012). Generally, from both models (ELM and CLFM), 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 (Mahamadi and Nharingo 2010). Metals with a higher atomic weight and ionic radius generate higher energy which increases the biosorption preference (Sağ et al. 2001; Hossain et al. 2014). The atomic weight of the tested metals was found in the order of Tl > La > Cd which explains the biosorption preference of Tl over the other metals. The relative coverage of metals generally increased with increasing concentration. The

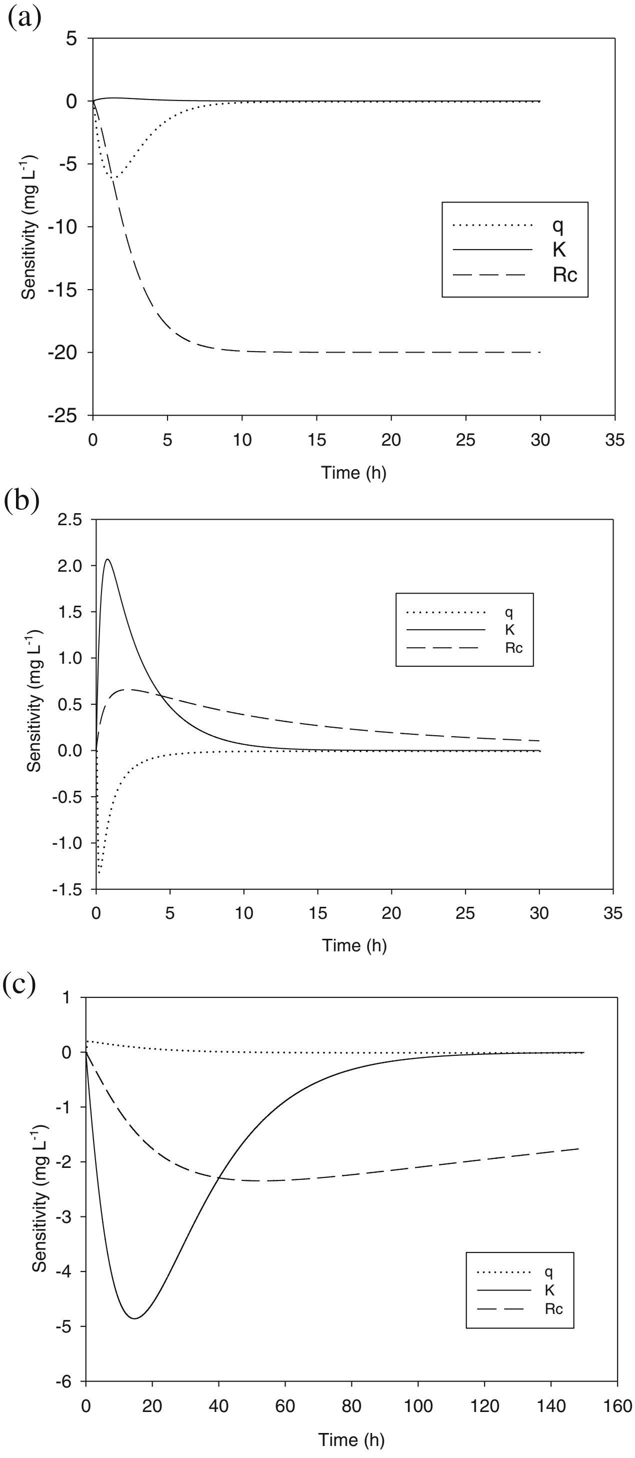

Fig. 4 Sensitivity test on the algal surface at initial concentration of 100 mg L^{-1} for **a** Cd adsorption, **b** La adsorption and **c** Tl adsorption

distribution of metals on the biosorbent strongly depends on the molar concentration ratio of the solution (Sağ and Aktay 2002). The total adsorption preference (Y_i) was generally high and increased with an increase in concentration implying that *D. multivariabilis* is a promising adsorbent for the treatment of actual wastewater.

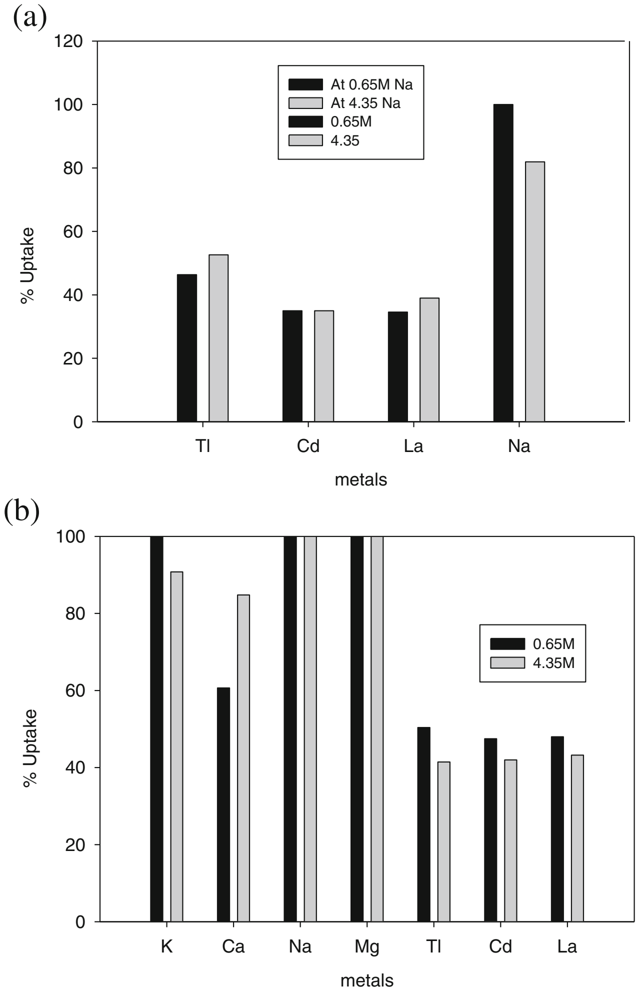

Fig. 5 Effect of ionic strength on uptake of Tl, La and Cd using **a** Na + only and **b** combination of light metals

AQUASIM program was used for simulation of aquatic systems (Reichert 1998). The model has four mutually dependant sub-systems which include variables, processes, compartments and links. Input of data into the sub-systems enables model simulation, parameter estimation and sensitivity

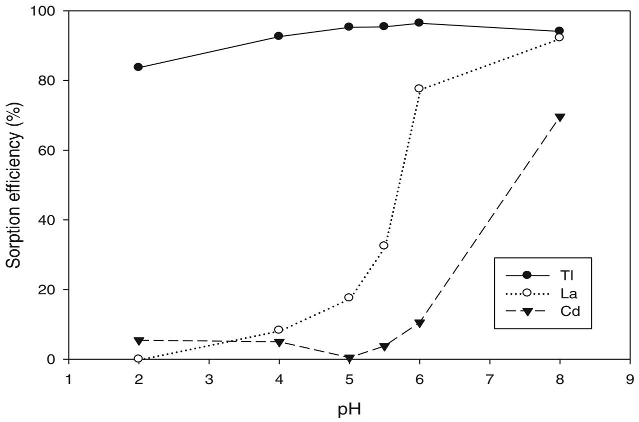

Fig. 6 The effect of pH on the uptake of metals in a ternary system

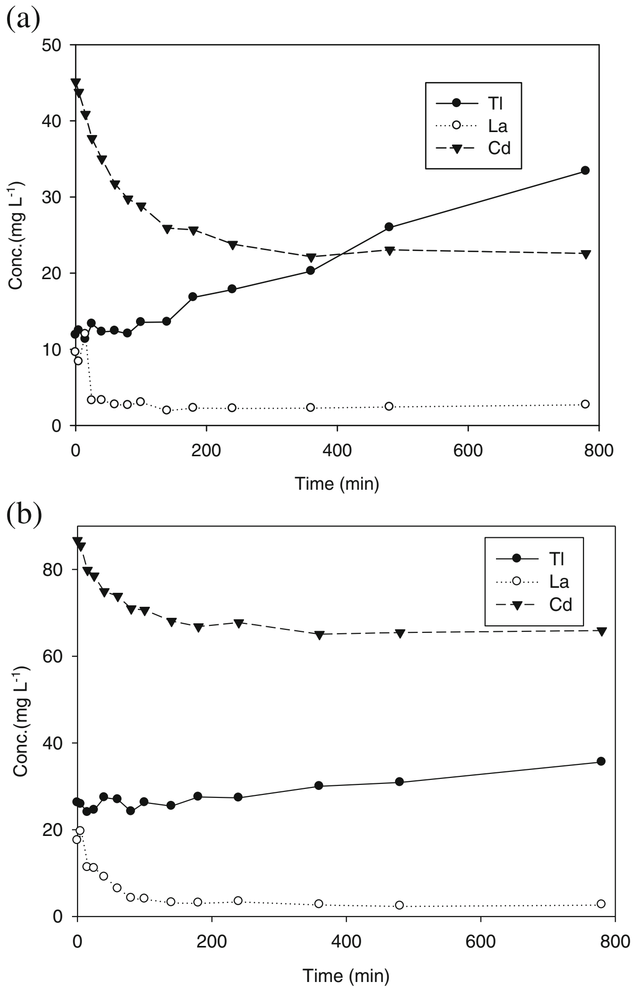

Fig. 7 Effect of initial concentration with time in the ternary system at **a** 50 mg L^{-1} for La, Cd and 250 mg L^{-1} Tl and **b** 100 mg L^{-1} for La, Cd and 500 mg L^{-1} Tl

analysis. The model consists of ordinary and partial differential and algebraic equations which describes the behaviour of important state variables in the system. The advantage of using this model lies in the user friendliness and flexibility to specific transformation processes (Reichert 1998). At a higher Cd concentration, the measured data slightly scattered away from the model with an increase in time. This could be due to the complete saturation of the binding sites and a higher level of ions remaining in the solution. Qin (2006) also indicated that an increase in initial concentration increases equilibrium solution concentration due to saturation of binding sites. In addition, the rate of reaction occurred fastest in minutes and then slowed down to hours until saturation was attained. In most biosorption studies, the rate of reaction is rapid in the first 15–30 min due to the abundance in the available active functional groups (Chojnacka 2010; Oliveira et al. 2012).

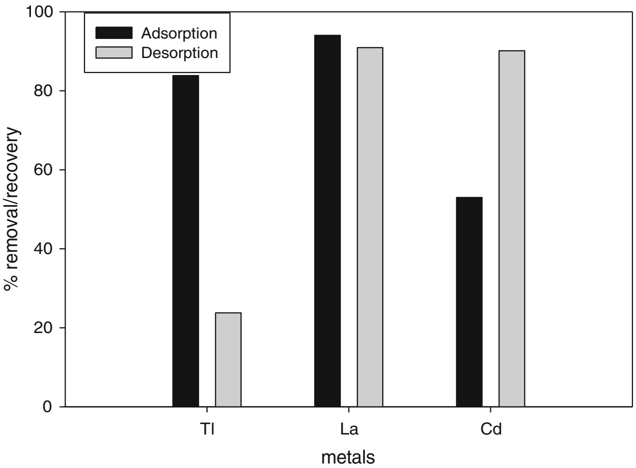

Fig. 8 Adsorption/desorption efficiency for Tl, La and Cd using *D. multivariabilis*

At low concentrations, ≤50 mg L^{-1} of La, the measured data closely fit the model in the first 5 h and then deviated for the rest of the study period. This could be due to competition of distinct ions for the same site especially as all the three metals have different ionic charge and radius. Metals with a higher atomic weight and radius have a higher biosorption preference (Sag 2001). The rate of reaction (q) was the highest at a lower concentration of 25 mg L^{-1} and then significantly decreased with increase in concentration except at 150 mg L^{-1}. A sudden increase in q at higher concentrations could probably imply that some binding sites became available which increased the rate of reaction in the system. An increase in time had an antagonistic effect on Tl as it desorbed back into the system for the period of study. This could probably imply that the effect of contact time for longer periods may be required to better understand the mechanisms involved in Tl adsorption. In single metallic studies, sorption efficiency was high in the first few minutes but an increase in time showed fluctuations until equilibrium was attained (Birungi and Chirwa 2015). The K values for the initial concentration were in the same range of 9.8–1.0 which implied that the initial concentration had no significant influence on the equilibrium.

Sensitivity analysis is used for estimation of uncertainty through calculation of linear sensitivity functions of arbitrary variable with respect to selected parameters. The adsorption of Cd showed that parameters q and K influenced the biosorption process. A sensitivity test on lanthanum showed that all three of the parameters q, K and R_c had a significant influence on biosorption. Parameters K and R_c had a significant influence on the removal of Tl. The behaviour of the parameters is indicative of the actual processes that occur during biosorption as most adsorption occurs in the first few minutes and then decreases until no further adsorption. The fast reaction could be due to ion exchange and or complexation/coordination of the metallic ions with the anions on the surface of the biosorbents (Veglio and Beolchini 1997; Fomina and Gadd 2014).

According to Schiewer and Wong (2000), strong acidic sites are affected by sodium thereby reducing removal of heavy metals. Other studies on ionic strength also showed a similar trend with a general decrease of heavy metal uptake when the ionic strength of light metals was increased (Komy et al. 2006; Ghodbane et al. 2008). Bivalent ions are assumed to have a stronger displacing effect than monovalent cations. This does not necessarily apply to this study which could be due to variations in the nature of biomass and availability of surface ligands.

The experiment was carried out at pH ≤ 8 as precipitation tends to occur at higher pH (Srivasta 2008). At low pH, the presence of excess H^+ on the cell surface inhibits uptake of positively charged metal cations in solution (Ahmaruzzaman 2011; Masood and Malik 2015). Other studies also showed that an increase in pH increases the uptake of multimetals under limited condition like constant temperature and biomass (Guo et al. 2008; Hossain et al. 2014). Sorption efficiency for the tested metal cations generally increased with increase in pH in the order of $Tl^+ > Cd^{2+} > La^{3+}$. This can be attributed to the fact that hydrolysed metal cation appears to be more surface active than divalent and trivalent cations (Mohan 2001).

Lu et al. (2013) noted that the initial metal concentration provided a driving force to overcome mass transfer resistances between the adsorbent and adsorbate. Kwan and Smith (1991) also found an inhibitory effect of Cd uptake with an increase in the concentration of Tl and La. An increase in the concentration of co-ions tends to decrease the adsorption efficiency as the metals have to be diffused into biomass surface by intraparticle diffusion (Sar et al. 1999; Ma and Tobin 2003).

The removal rate of La was higher than that for Tl and this could be due to the effect of contact time. An increase in time tends to release some adsorbed Tl back in the solution therefore some binding sites become available for other metals. In addition, the low recovery of Tl could be due to the short time allocated for desorption studies. Birungi and Chirwa (2015) found that Tl required more than 24 h for recovery of the metal from algal biomass.

In conclusion, the multimetallic systems using *D. multivariabilis* better represented actual wastewater than in single metallic systems with the sorption capacity for the former decreasing due to competition for adsorption sites. The ELM performed better than the CLFM with sorption capacity in the order of Tl > La > Cd. Experimental data from multimetallic kinetic studies showed a relatively good fit with the predicted model in AQUASIM. The sensitivity analysis showed that parameters q (rate of reaction) and K (adsorption equilibrium constant) generally influenced the adsorption process especially for Cd and La. Recovery of the heavy metals by *D. multivariabilis* was achieved highest for La followed by Cd. A mixture of light and heavy metals reduced sorption efficiency due to competing cations for the binding sites. In general, *D. multivariabilis* showed high potential for adsorption and resource recovery of multimetal systems. The authors recommend an investigation into natural and cost-effective immobilising agents to improve the mechanical strength of microalgae for commercial application in industry.

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