

Biosorption of Cadmium (II) and Chromium (VI) from Aqueous Solution by Chemically Modified *Tithonia Diversyfolia* Biomass

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Abstract: The search for alternative and innovative treatment technologies for the effective removal of heavy metals from aqueous wastes has been a research of concerted effort due to the inherent limitations exhibited by the conventional methods such as less efficiency, sensitive operating conditions, energy requirements and generation of toxic sludge or other waste products. Biosorption, the passive uptake of heavy metals by biomaterials has been studied recently because of its high efficiency and cost effectiveness. Therefore, the biosorption capacity of *Tithonia diversyfolia* biomass chemically modified with sodium hydroxide for the removal of cadmium and chromium ions from aqueous solution was investigated. The effects of temperature, contact time, initial concentration of metal ions, adsorbent dosage and pH on the biosorption of Cd²⁺ and Cr⁶⁺ ions were assessed. Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) during the biosorption were evaluated. The results showed that the biosorption process of Cd²⁺ and Cr⁶⁺ by chemically modified *Tithonia diversyfolia* (CMTD) biomass was feasible and exothermic under the studied conditions. The equilibrium process was well described by the Langmuir isotherm model, with a maximum biosorption capacity of 46.75mg/g and 48.00mg/g for Cadmium and Chromium ions, respectively. Kinetic studies indicated that the biosorption of metal ions followed a pseudo-second order equation.

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1. Introduction

Water pollution by heavy metals is of major environmental concern, as the deleterious effects of these metals to man such as its toxicity, carcinogenicity and mutagenicity cannot be over emphasized. Cadmium, a non-essential and non-beneficial element to plants and animals, is non-biodegradable and travels through the food chain. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anaemia (Cheung et al., 2001; Prez-Marin et al., 2007; Cruz et al., 2004). The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, batteries, mining and refining processes (Malkoc and Nuhoglu, 2005. Guiqiu et al., 2008; Xiaomin et al., 2007). Further, Chromium has also been considered to be a major focus in water and wastewater treatment due to its deleterious effects on the environment. In fact, it has been reported that the hexavalent form is 500 times more toxic than the trivalent form, being carcinogenic, teratogenic and mutagenic in nature (Garima and Dhiraj, 2011). The tanning process is one of the major sources of chromium pollution at global scales, while mining and metallurgy of cadmium, cadmium electroplating, battery and accumulator manufacturing, pigments and ceramic

industries waste waters contain undesired amounts of Cd²⁺ ions (Gabriela et al., 2006).

Numerous techniques have been employed for the treatment of contaminated waste water such as chemical precipitation, electrochemical precipitation, photo-catalytic reduction, evaporation, flotation, ion exchange, membrane filtration, adsorption and biosorption (Garima and Dhiraj, 2011). However, those techniques have their own inherent limitation such as less efficiency, sensitive operating conditions, and production of secondary sludge requiring further costly disposal (Wanna et al., 2009). Hence, the need for economical and effective methods for the recovery of metals from waste water has gained the interest of researchers across the globe. Different types of agricultural biosorbents such as green coconut shell powder (Gabriela et al., 2006), *Cassia siamea* bark (Ajaelu et al., 2011), pomelo peel (Wanna et al., 2009) *Arachis hypogea* shells (Garima and Dhiraj, 2011), spent tea (Fazal and Rafique, 2012) have been investigated for the biosorption of cadmium and chromium ions in aqueous solutions. These agricultural wastes are relatively cheap and show quite high biosorption potential. However, the direct use of the raw plant wastes as adsorbents has been found to be limited due to leaching of organic substances such as lignin, tannin, pectin and cellulose into the solution (Feng et

al., 2009 a). To resolve these problems, chemical modification on solid adsorbents has been adopted as a technique to improve their physical, chemical properties and biosorption capacity (Simkovic and Laszlo, 1997; Unnithan and Anirudhan, 2001; Sreedhar and Anirudhan, 2000; Anirudhan et al., 2006; Feng et al., 2009 b). *Tithonia diversifolia* is an annual and aggressive weed growing widely on abandoned land along major roads, waterways and even, on cultivated farm lands in Nigeria. Previous investigators have shown that the leaves are mostly used to enrich the soil as organic manure while the stem is of little or no economic importance (Okoronkwo and Olasehinde, 2007; Olabode et al., 2007). Therefore, the purpose of this study was to explore the feasibility of using *Tithonia diversifolia* stem that was chemically modified with sodium hydroxide for biosorption of Cd²⁺ and Cr⁶⁺ from aqueous solutions.

2. Material and Methods

2.1 Adsorbent Preparation

Tithonia diversifolia stem was used as the raw material for the preparation of the chemically modified biosorbent. The stem was collected from the uncultivated land at the Federal University of Technology Akure, Ondo State, Nigeria. The plant biomass used was harvested at an average height of 7- 8 feet, cut into smaller pieces, washed with distilled water and oven-dried at 363 – 378 k for 3 days. Dry biomass was crushed into powder and sieved to obtain an average particle size lower than 850 µm and then treated with sodium hydroxide solution to improve the capacity of biosorption to the metal ions.

In this study, 500 g of the dried biomass was soaked with 5000 mL of 0.1M NaOH for 24 hours. After successive decantation and filtration, the modified biomass was washed with distilled water until pH value of the effluent was neutral. The washed biomass was collected and dried in an oven at 363 – 378k and then stored in an air-tight container for subsequent batch sorption studies.

2.2 Adsorbate Preparation:

Stock solutions used in this study were prepared from cadmium chloride and potassium dichromate by weighing and dissolving the required amount in deionized water and using 1.0 M of NaOH and HCl for pH adjustments. The stock solution was diluted with distilled water to obtain metal solutions of the desired concentration.

2.3 Biosorption Procedure

Biosorption procedures adopted in this study have been described elsewhere (Feng et al., 2009;

Adebayo, 2013). Briefly, it was carried out by agitating 0.5 g of the biosorbent with 50 mL of each of the metal solutions in 100 mL Erlenmeyer flasks using an orbital shaker at 118 rpm. The effect of pH on the equilibrium biosorption of Cr⁶⁺ and Cd²⁺ was investigated by adding 0.5 g of the biosorbent to each of the solutions containing 50 mL of 50 ppm of Cr⁶⁺ and Cd²⁺, respectively varying the pH from 1 to 8. To obtain the kinetic data, the biosorption time was varied from 0 to 360 min. In isotherm experiments, 0.5 g of biosorbent was added to 50 mL of each of the metal solutions at various concentrations ranging from 10 ppm to 500 ppm. The solutions were adjusted to the optimum pH of 5 for cadmium and 1 for chromium. At the end of the predetermined contact period, mixtures were filtered and the filtrates were analysed for Cr⁶⁺ and Cd²⁺ by means of atomic absorption spectroscopy. The amount of metal biosorbed (*q*) was calculated using equation (1):

$$m_q = (P_o - P_e) v \quad (1)$$

where *P_o* and *P_e* are the initial and equilibrium metal ions concentrations, respectively (ppm); 'V' is the volume of the solutions (L) and 'm' is the amount of adsorbent used (g). All the biosorption experiments were conducted in replicates, and the mean values were calculated.

3. Results

3.1 Optimization of sorption variables

3.1.1 Effect of pH

Previous investigators have established that pH is an important controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and the ionic form of the metal solution (Garima and Dhiraj, 2011; Feng et al., 2009 a, b; Okoronkwo and Olasehinde, 2007). The results of the effect of pH on the biosorption of Cr⁶⁺ and Cd²⁺ ions by using chemically modified *Tithonia diversifolia* (CMTD) biomass are presented in Figure 1. As shown in the Figure, biosorption of Cd²⁺ increases with increasing pH from 1 to 5 and the highest biosorption efficiency was observed at pH 5. The Cd²⁺ adsorbed increased from 69.20% at pH 1, to 93.95% at pH 5. However, further increase in the pH did not result into an increase in the amount of Cd²⁺ adsorbed but a slight decline was observed. This phenomenon is plausible because at lower pH values, the surface charge of the biomass is positive, which is not favorable to cations biosorption. Hence, a decrease in the amount of Cd²⁺ adsorbed. With increasing pH, electrostatic repulsions between cations and surface sites and the competing effect of hydrogen ions decrease. Consequently, the amount of Cd²⁺ adsorbed increases (Feng et al., 2009 a, b). The slight decline in the amount of Cd²⁺ observed at pH above 6 could be attributed to the precipitation of

Cd^{2+} as $\text{Cd}(\text{OH})_2$ which decreases the concentration of free Cd^{2+} , thereby decreasing the biosorption capacity of cadmium ions. This observation is in agreement with the reports of previous investigators (Gabriela et al., 2006; Wanna et al., 2009; Feng et al., 2009 a, b). However, for Cr^{6+} , there was a sharp decline in the percent adsorption with increase in the pH of aqueous solution. With increasing pH from 1 to 9, Cr^{6+} adsorption decreased from 96% to 75.3%. Maximum adsorption was observed at pH 1 and hence it was taken as the optimal pH value for further adsorption experiment. This is expected because chromium ions co-exist in different forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, and $\text{Cr}_4\text{O}_{10}^{2-}$ in the pH range of 1 to 6. At these pH ranges, HCrO_4^- predominates. However, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ become dominant as the pH of the solution increases. More adsorption at low pH in this study could be attributed to increase in the H^+ ions associated with the adsorbent surface, resulting in sufficiently strong electrostatic attraction between a positively charged adsorbent surface and negatively charged chromate ions (Garima and Dhiraj, 2011). At higher pH, the decrease in the adsorption of Cr^{6+} could be as a result of dual competition of CrO_4^{2-} and OH^- to be adsorbed on the surface of the adsorbent.

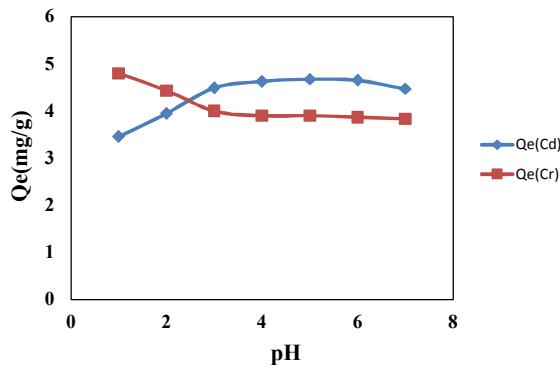


Figure 1: Effect of pH on the biosorption of Cd^{2+} and Cr^{6+} in aqueous solution

3.1.2 EFFECT OF CONTACT TIME

To establish an appropriate contact time between the CMTD and the metal ions under investigation, adsorption capacities were performed as a function of time as presented in Figure 2. The results of this study showed that the removal efficiency and adsorption capacity were initially rapid and slightly decreased with increase in time until equilibrium was reached. The cadmium ion and chromium ion removal were 88% and 93.33%, respectively within 5 min of contact. Thereafter, the rate of adsorption slightly decreased until equilibrium

was reached at 300 min and 60 min for cadmium and chromium ions, respectively. The total cadmium removal was 93.7% while that of Chromium increases was 96.13%. Previous researchers have shown that the initial increase in metal ions removal may be due to a larger surface area of the adsorbent being available for the adsorption of the metals (Gabriela et al., 2006; Wanna et al., 2009; El-Ashtouky et al., 2008). Hence, the rapid removal of Cd and Cr ions may be as a result of a less competition for available active sites by the metal ions in solution. Therefore, 300 min and 60 min were chosen as the optimum contact time for further cadmium and chromium biosorption experiments, respectively.

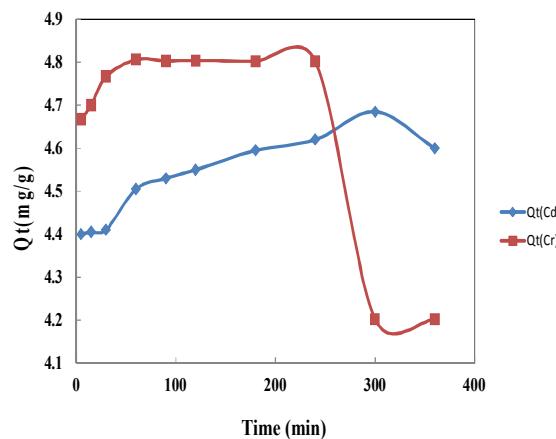


Figure 2: Effect of contact time on the biosorption of Cd^{2+} and Cr^{6+} in aqueous solution

3.1.3. Effect of Initial Metal Concentration

The effect of varying cadmium and chromium concentration on the adsorption under optimized conditions of 300 min contact time for cadmium and 60 min for chromium with 0.5 g adsorbent in aqueous medium is shown in Figure 3. The concentrations of cadmium and chromium were varied from 10 to 500 ppm. Results showed that the adsorption of the cadmium and chromium decrease as the cadmium and chromium concentrations increase. Cadmium has maximum adsorption of 93.8 % between 10 ppm and 25 ppm after which it decreases to 64.7% as the concentration of the metal increases from 50 ppm to 300 ppm while Chromium has 98.33% at 10 ppm and gradually decreases to 92.67% at 500 ppm. This can be explained as follows: at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency. The result of this study is in consonance

with the reports of previous researches (Garima and Dhiraj, 2011; Ajaelu et al., 2011).

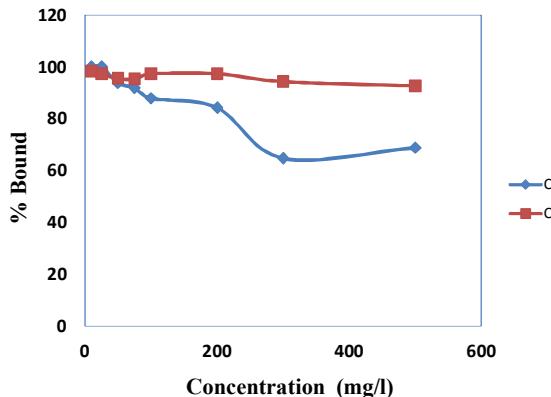


Figure 3: Effect of Cd^{2+} and Cr^{6+} initial concentrations on the biosorption rate

3.1.4 EFFECT OF ABSORBENT DOSE

The surface of contact between any sorbent and the liquid phase plays an important role in adsorption process. The percentage adsorption of Cr^{6+} and Cd^{2+} was studied at different adsorbent doses (0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 3.0 g L^{-1} , respectively) with each dissolved in 50 mL of 50 ppm of the metal solutions at optimum reaction conditions. The result showed that the percentage of metal ions removed increased with increase in adsorbent dosage (Figure 4). This is plausible because increase in the percentage adsorption with adsorbent dose may be due to the increase in the adsorbent surface area and the availability of more adsorption sites (Garima and Dhiraj, 2011). As shown in Figures 4, adsorbent dose of 3.0 g was sufficient to adsorb 99.77% of the initial concentration of each of the metal ions.

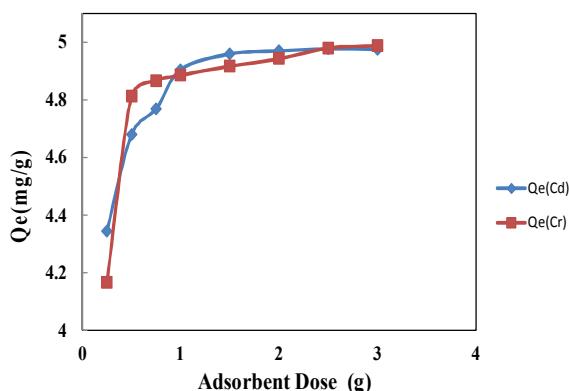


Figure 4: Effect of adsorbent dose on the biosorption of Cd^{2+} and Cr^{6+} in aqueous solution.

3.1.5. Effect of Temperature

The effect of the temperature on the biosorption of cadmium and chromium ions was investigated in the temperature range of 303–333 k. The result shows that increase in temperature has a negative effect on the biosorption capacity of CMTD. As shown in Figure 5, the percentage of cadmium ion adsorbed decreased from 83.34% at 303 k to 54.66% at 333 k while chromium ion decreased from 83.34% at 303 k to 54.66% at 333 k. This is expected because adsorption is a de-concentration phenomenon, responding to decrease in removal with increase in temperature. Previous investigators have shown that temperature adsorption relationship could be explained as being exothermic which implies that an increase in the temperature leads to an increase in the desorption of the sorbed ions, thus deactivation of the binding sites resulting in decline of removal efficacy (Sarkar and Acharya, 2006; Sarý et al., 2007). Therefore, the results presented in this study are in agreement with the previous studies (Fazal and Rafique, 2012; Unnithan and Anirudhan, 2001; Sarkar and Acharya, 2006; Sarý et al., 2007).

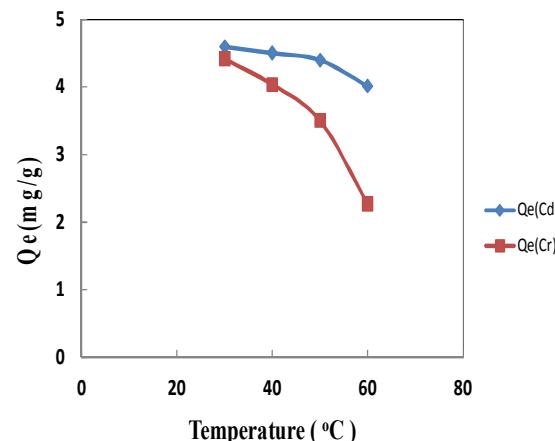


Figure 5: Effect of temperature on the biosorption of Cd^{2+} and Cr^{6+} in aqueous solution.

3.2. Thermodynamic Study

Parameters such as changes in Gibbs free energy change (ΔG), Enthalpy change (ΔH) Entropy change (ΔS) and Activation Energy (E_a) were evaluated in order to describe the thermodynamic behaviour of the biosorption of Cd^{2+} and Cr^{6+} on the modified *Tithonia diversifolia* from aqueous solution. ΔG for the adsorption process was calculated using equation (2).

$$\Delta G = -RT\ln K_D \quad (2)$$

Where R is the molar gas constant (8.314 J/mol/K); T is the absolute temperature and K_D is the

distribution coefficient. The distribution coefficient was calculated using equation (3).

$$K_D = \frac{C_b}{C_e} \quad (3)$$

Where C_b and C_e are equilibrium concentrations of the adsorbed metal ions and that in the solution (mg/L), respectively. The Gibbs free energy change also relates the entropy and the heat of adsorption at constant temperature according to equation (4).

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

Thus, enthalpy change (ΔH) and Entropy change (ΔS) for the adsorption process can be estimated from the combinations of equations 2 and 4 as follows:

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

According to equation 5, a plot of $\ln K_D$ versus $1/T$ is expected to be linear. Thus, ΔH and ΔS can be estimated from the slope and the intercept of the graph as shown in Figures 6a and 6b, respectively. However, it is well known that activation energy is the energy requirement for sorbate species to overcome energy barrier for interaction with functional groups on sorbent surfaces (Fazal and Rafique, 2012). Thus, activation energy values were estimated using equation (6).

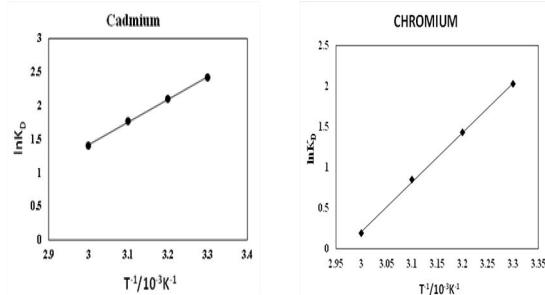


Fig. 6a A plot of $\ln k_D$ versus $1/T$ for Cd^{2+} . $y = 3262.3x - 8.7016$; $r^2 = 0.9992$

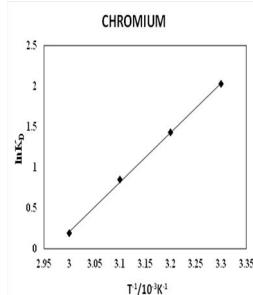


Fig. 6b A plot of $\ln k_D$ versus $1/T$ for Cr^{6+} . $y = 6092.4x - 18.069$; $r^2 = 0.999$

$$\frac{\ln K_D(T_2)}{\ln K_D(T_1)} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (6)$$

The result of the change in the Gibbs free energy in the temperature range 303 -333 K is as presented in Table 1. The negative values of ΔG indicate that the biosorption of Cd^{2+} and Cr^{6+} on CMTD is thermodynamically feasible and spontaneous. From the Table, it is shown that ΔG values vary from - 5.099 kJ/mol at 303 k to - 0.518 kJ/mol at 333k for Cd^{2+} while for Cr^{6+} , it increases from -6.095 kJ/mol at 303 k to -3.890 kJ/mol at 333 k. The increase in ΔG with increase in the temperature shows a decrease in feasibility of the

reaction process. This is expected because increase in temperature results into increase in the desorption of the sorbed ions which will ultimately reduce the removal efficiency of the biosorbent. The Enthalpy changes for the sorption of Cd^{2+} and Cr^{6+} on CMTD are -27.12 and -51.04 kJ/mol, respectively. The exothermic nature of the reaction further confirms the feasibility of the sorption process. The Entropy change for Cd^{2+} and Cr^{6+} are -151.39 and -68.76 J/mol/k, respectively. The negative values suggest a decrease in the randomness at the solid-solution interphase during the biosorption of Cd^{2+} and Cr^{6+} on CMTD. The calculated activation energies for Cd^{2+} and Cr^{6+} are 55.28 and 71.60 kJ/mol. Meanwhile, previous reports have shown that activation energy can be used to classify adsorption process into physisorption and chemisorption (Wanna et al., 2009 Fazal and Rafique, 2012). Physisorption involves weak forces generating values ≤ 4.2 kJ/mol while chemisorption being specific involves much stronger forces with activation energy in the range 8.4-83.7 kJ/mol. From the results of the present study, it is evident that the biosorption of Cd^{2+} and Cr^{6+} on CMTD follows a chemical adsorption process.

Table 1: Gibbs Free Energy Change (ΔG) for the biosorption of Cd^{2+} and Cr^{6+} on CMTD

Temp (K)	ΔG^\ominus (kJ/mol)	
	Cr^{6+}	Cd^{2+}
303	-5.099	-6.095
313	-3.716	-5.717
323	-2.274	-5.323
333	-0.518	-3.890

3.3. Biosorption Kinetics

Kinetic models have been used to test the experimental data in order to investigate the mechanism of biosorption and potential rate controlling step such as the mass transport and the chemical reaction (Gabriela et al., 2006; Wanna et al., 2009; Ajaelu et al., 2011). In the present study, pseudo-first order and pseudo-second order kinetic models have been employed to understand the biosorption kinetics of Cd^{2+} and Cr^{6+} on CMTD. The pseudo-first order Langergren model is expressed as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (7)$$

Where q_e and q_t (mg/g) are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at any time t , respectively; k_1 is the Langergren rate constant of the first order biosorption (min^{-1}). The linearized form of this model is:

$$\log(q_e - qt) = \log q_e - \frac{kt}{2.303} \quad (8)$$

A linear plot of $\log(q_e - qt)$ versus t suggests applicability of this kinetic model (Gabriela et al., 2006). However, it has been reported that in most cases, the first-order equation of Lagergren does not fit well for the whole range of the contact time, it is generally applicable to the initial 20 to 30 min of the sorption process (Gabriela et al., 2006.). The pseudo-second order equation is based on the sorption capacity of the solid phase and it is likely to predict the behavior over the whole range of the adsorption process. The pseudo-second order is expressed as:

$$\frac{dq}{dt} = k_2(q_e - qt)^2 \quad (9)$$

where k_2 is the rate constant of second-order biosorption ($\text{g}/\text{mg min}$). Upon integration within limits, $t = 0$ to $t = t$ and $qt = q_e$;

$$\frac{q}{t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

If second order kinetics is applicable, the plot of t/qt versus t is expected to be linear, from which q_e and k_2 can be estimated from the slope and the intercept of the plot, respectively. The results of the pseudo-first order and pseudo-second order kinetic models for the sorption of Cd^{2+} and Cr^{6+} on CMTD are presented in Table 2. The values of k_1 and q_e for the pseudo-first order kinetic model were determined from Figure 7a while k_2 and q_e values were determined from Figure 7b. However, previous investigators have shown that correlation coefficient (r^2) is used to describe the conformity of the experimental data with the kinetic model and that a relatively high r^2 value indicates that the model successfully describes the sorption kinetics of the metal ions under investigation. From Table 2, it is shown that the r^2 obtained for the pseudo-first order kinetics for Cd^{2+} and Cr^{6+} are 0.092 and 0.071, respectively. However, the r^2 for the second-order kinetic model for Cd^{2+} and Cr^{6+} are 0.999 and 0.979, respectively. Therefore, the r^2 values obtained for pseudo-second order kinetic model are higher than that of the pseudo-first order kinetic model. This shows that the kinetics of Cd^{2+} and Cr^{6+} biosorption on CMTD is better described by pseudo-second order kinetic model. Further, the theoretical q_e values is close to the experimental q_e in the case of pseudo-second order kinetic model suggesting that the sorption process obeys of pseudo-second order kinetic model which is in consonance with the reports of the previous investigators (Gabriela et al., 2006; Fazal and Rafique, 2012; Feng et al., 2009 a,b).

Table 2: Pseudo-first order and pseudo-second order kinetic data for the sorption of Cd^{2+} and Cr^{6+} on CMTD

Metal ions	Pseudo-first order model			Pseudo-second order model			Experimental value	
	$K_1(\text{min}^{-1})$	$Q_e(\text{mg/g})$	R^2	$Q_e(\text{mg/g})$	$K_2(\text{mg min})$	$Q_e(\text{mg/g})$	R^2	$Q_e(\text{mg/g})$
Cd^{2+}	-0.046	-0.337	0.092	4.690	0.152	4.651	0.999	4.690
Cr^{6+}	0.046	-0.831	0.071	4.7765	-0.015	4.202	0.978	4.7765

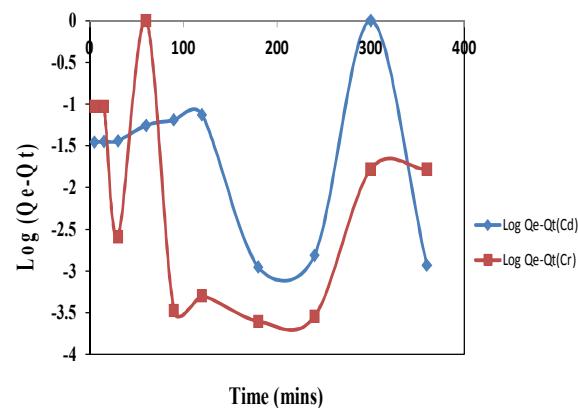


Fig 7a: Pseudo-first order kinetics for the biosorption of Cr^{6+} and Cd^{2+} on CMTD

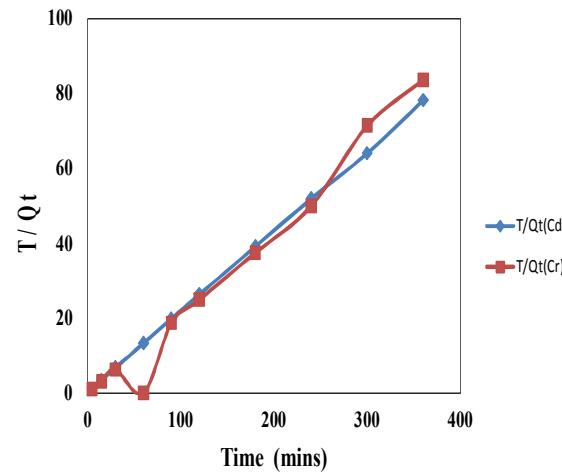


Fig 7b: Pseudo-second order kinetics for the biosorption of Cr^{6+} and Cd^{2+} on CMTD

3.4. Adsorption Isotherm

The equilibrium established between adsorbed metal ions on the biomass (C_b) and the metal ions remaining in the solution (C_e) has been

extensively described by Langmuir and Freundlich models (Garima and Dhiraj, 2011; Ajaelu et al., 2011). The Langmuir model is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface (Ajaelu et al., 2011). The linearized Langmuir adsorption isotherm is given as:

$$\frac{C_s}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e \quad (11)$$

Where q_e is the amount of metal adsorbed (mg/g), Q_m and b are Langmuir constants indicating adsorption capacity and affinity of binding sites with the metal ions, respectively. The logarithmic form of the Freundlich model is described by equation 12.

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (12)$$

where k_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity. The plots of C_e/q_e versus C_e at the experimental temperature are linear, which shows that the adsorption of Cr^{6+} and Cd^{2+} followed Langmuir isotherm model. The equilibrium biosorption parameters of Langmuir and Freundlich isotherms are presented in Table 3. The most appropriate isotherm to describe the results is the Langmuir isotherm. The maximum adsorption capacities for Cd^{2+} and Cr^{6+} adsorption on CMTD are 46.75 mg/g and 48.00 mg/g, respectively. The Q_m in Cd^{2+} adsorption is higher than Cr^{6+} adsorption which shows that higher amounts of Cd^{2+} are needed to form a monolayer. Also, the adsorption capacity (k_L) in Cr^{6+} is higher than in Cd^{2+} suggesting that Cr^{6+} is adsorbed with higher adsorption energy than Cd^{2+} .

Table 3: Langmuir and Freundlich isotherm constants for Cr^{6+} and Cd^{2+} biosorption on CMTD

Metal ions	Langmuir model			Freundlich model		
	$Q_m (\text{mg g}^{-1})$	$B (\text{L mg}^{-1})$	R^2	$k_f (\text{mg g}^{-1})$	$n_f (\text{mg g}^{-1})$	R^2
Cr^{6+}	2.817	0.282	0.746	4.525	6.173	0.145
Cd^{2+}	62.5	0.070	0.864	40.583	83.333	0.000

In addition, the comparison of the maximum biosorption capacities for Cd^{2+} and Cr^{6+} obtained in this study with some other reported low-cost biosorbents is shown in Table 4. Thus, the biosorption capacities for Cd^{2+} and Cr^{6+} using sodium hydroxide modified *Tithonia diversifolia* compare favourably with most of the biosorbents in the Table.

Table 4: Biosorption capacities for Cadmium and Chromium ions using different biosorbents

Ion	Cadmium Ion			Chromium		
	Biosorbent	Biosorption Capacity (mg/g)	References	Biosorbent	Biosorption Capacity (mg/g)	References
Pome洛 peel	Wanna et al, 2009.	DAS	2.23	Mohammad et al., 2013.		
Papaya wood	17.22	Asma et al, 2005.	<i>Aspergillus niger</i>	2.23	Filipovic et al., 2000.	
Coconut copra meal	4.99	HO and Ofomaja, 2006. Vimala and Das, 2009.	Rice husk	48.31	Bansal et al., 2009.	
Mushroom	34.96		Wheat bran	0.94	Nameni et al., 2008	
Cystine- Modified biomass	11.63	Yu et al., 2007.	Pomegranate husk	35.2	Nerm A E, 2009.	
Olive pomace	6.97	Blazquezet al., 2005.	Coconut shell	20	Alaerts et al., 1989	
<i>Cassia siamea</i>	37.7	Ajaelu et al., 2011	Almond shell	190.3	Demirbas et al. 2008	
CMTD	46.75	This study	CMTD	48.00	This study	

4.0 Conclusion

The use of chemically modified *Tithonia diversifolia* could be an eco-friendly method for the removal of Cd^{2+} and Cr^{6+} from aqueous solution. The selected biosorbent exhibits high biosorption capacity which was strongly dependent on the initial pH, initial metal concentration, temperature, and the concentration of the biosorbent. The suitability of the pseudo-first order and pseudo-second order kinetic models was tested. The results showed that the pseudo-second order kinetic model provides the best correlation to the experimental data whereas the pseudo-first order kinetic model does not fit the experimental data well. The Freundlich and Langmuir models were used for the mathematical description of the biosorption equilibrium of Cd^{2+} and Cd^{2+} to *Tithonia diversifolia*. The obtained result showed that the adsorption equilibrium fitted well to Langmuir isotherm model. Thermodynamic study of the biosorption process revealed a spontaneous and exothermic nature of the biosorption process of Cd^{2+} and Cd^{2+} on *Tithonia diversifolia* in the temperature range studied.

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