Desalination and Water Treatment
www.deswater.com

12 (2009) 352–359

1944-3994 / 1944-3986 © 2009 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2009.833

Biosorption of nickel from aqueous solution by *Tithonia diversifolia*

Afamefuna Elvis Okoronkwo*, Ademola Festus Aiyesanmi,
Emmanuel Folorunso Olasehinde

Chemistry Department, School of Sciences, Federal University of Technology, PMB 704 Akure, Nigeria
Tel. +234 803 404 7318; emails: afamex@yahoo.com, demolaktp@yahoo.co.uk, folasemb2004@yahoo.com

Received 28 February 2009; Accepted in revised form 26 August 2009

ABSTRACT

This study investigated the feasibility of Mexican sunflower (*Tithonia diversifolia*), a common plant that inhabits the highway of the south western Nigeria, as a novel biosorbent for nickel from solutions. pH profile, time dependency and cation interference studies were conducted using stem biomass of this plant. Nickel uptake exhibited substantial enhancement both in terms of the kinetics of uptake as well as the loading capacity. Results of the investigation showed that the unmodified biomass was able to remove over 70% of the nickel content of a solution, whereas NaOH modification improved the adsorption efficiency to over 77% in the same contact time of 60 min. The optimum pH of adsorption was recorded as 5 for the metal using both types of biomass. However, modification improved the adsorption efficiency to a pH lower than 4. The kinetic study conducted showed that the adsorption process follows Lagergren's pseudo-second order reaction with R^2 values equal to 0.9988 and 0.9989 for both types of biomass. The presence of cations such as calcium and magnesium also interfered negatively with the adsorption process. Between 20–35% reductions in the metal adsorbed were recorded in the presence of a 1 M concentration of Mg, Ca or mixed Mg and Ca ions. Langmuir model of adsorption isotherm gave the best fit for this sorption process with R^2 values of 0.994, 0.995 and 0.997 for Mg, Ca and mixed Mg and Ca studies, respectively.

Keywords: Binding; Nickel; *Tithonia diversifolia*; Isotherm; Adsorption

1. Introduction

Environmental pollution has remained an increasing global problem. Pollution of land, water and air by heavy metals has been reported to cause increased degradation of human health. These metals find their way into the human system through military, industrial and agricultural processes that often discharge wastes into water bodies [1–3].

Technologies for treatment of wastewater bearing heavy metals, such as reduction, solvent extraction, precipitation, ion exchange and membrane processes have been used [4–7]. These methods have several disadvantages which include either being of great cost and prohibitive for developing economies or incomplete removal process. As a result, new methods for removing heavy metals are constantly being sought. In recent time considerable attention has been devoted to the study of removal of heavy metal ions from solutions by adsorption using plants and agricultural waste materials such as saw dust, grape stalks wastes, rice bran, tree barks, cotton and nut wastes [8–14]. The use of both living and nonliving biological materials for the remediation of toxic metal ions from industrial wastewater, tanneries and mining effluents has also been explored [15–18].

---

* Corresponding author.

The ability of dead plant tissues to uptake metal ions has been studied and the mechanism involved in the uptake of metal ions is reported to be surface adsorption, a passive process in which chemical groups attach to the cell wall of the plants [19–21]. The nonviable forms have been proposed as potential sorbents, since these are essentially dead materials requiring no nutrition to maintain the biomass and the problems associated with metal toxicity in living biomass do not arise [17]. *Tithonia diversifolia* is a perennial plant cultivated for its beautiful flowers and enormous size. The plant flowers are the favorites of bees, and African farmers have many uses for it, the most popular being as an organic fertilizer for vegetable crops. The leaves are also used in the treatment of hematomas, inflammations [22] and malaria [23]. Though this plant contains phytochelatins, potentially capable of binding heavy metals, limited information is available on the removal of some metals such as nickel, copper and zinc from aqueous solution by it. In this study *Tithonia diversifolia* (sunflower) was tested for nickel adsorption at several pH values and reaction times. Adsorption capacities of both the unmodified and NaOH modified biomass were determined. In addition, the effect of magnesium and calcium interference on the adsorption process was also monitored. The objective is to evaluate potential use for the stem of this plant as a readily available and cheaper alternative to expensive adsorbents for water treatment processes.

2. Materials and methods

2.1. Reagents

All reagents used in this study were of analytical grade. Concentrated HNO_3, HCl, NaOH pellets, $NiSO_4.6H_2O$, $CaSO_4.2H_2O$ and $MgSO_4$ were purchased from Aldrich Chemical and were used without further purification.

2.2. Metal analysis

Nickel contents in the samples were analyzed using Perkin Elmer Model 3110 atomic absorption spectrometer. The modified methods used for analysis were adopted from the Perkin Elmer model 3110 manual. The analytical wavelength for nickel used was 232 nm. A calibration curve was obtained with a correlation coefficient greater than 0.98 and the instrument response was checked regularly with a known standard. Each sample was read three times, and the mean value and relative standard deviations were computed.

2.3. Biomass preparation

The *Tithonia diversifolia* (sunflower) population used for this study was collected within the environment of the Federal University of Technology Akure in Ondo State, Nigeria. The plants were harvested at an average height of 2.0–2.5 m and estimated growth stage of 3 months. The experiments were performed at the Phyto-Remediation Research Laboratory of the university, shoots (stem) washed thoroughly with water, cut into smaller pieces and oven dried at 90–105°C for 3 days, then ground with a Victoria grain mill and fine samples were obtained using 100 μm mesh screen sieve.

10 g of *Tithonia diversifolia* biomass was washed twice with 0.1 M HCl by vortexing and with deionized water to remove any debris or soluble biomolecules that might possibly interact with the metal ions. After each washing, samples were centrifuged at 760 rpm for 15 min to obtain pellets [24]. The washed biomass was dried and weighed to account for weight loss.

2.4. pH profile studies

Washed *Tithonia diversifolia* biomass (250 mg) were weighed separately in 9 beakers, suspended in 50 ml deionized water with tissue concentration approximately 5 mg per ml solution, and stirred to give a homogenous mixture. The suspensions in these beakers were adjusted to pH values of 1–9 (determined using a pH meter) from dilute solutions made out of 65% nitric acid (HNO_3) and 1 M sodium hydroxide (NaOH), and each equilibrated for 15 min. Four 2 ml aliquots of these suspensions were withdrawn from each of the beakers designated for a particular pH and were transferred into clean plastic tubes, centrifuged at 760 rpm for 5 min and the supernatants decanted. 2 ml of 0.1 mM metal solutions which were previously prepared and pH adjusted to 1–9 from $NiSO_4.6H_2O$ salt were added to the respective tubes as designated. All suspensions were kept for 1 h after which they were centrifuged for 15 min at 760 rpm. The supernatants were transferred to clean respective plastic tubes for metal analysis.

2.5. Time dependence studies

Batch experiments to determine the affinity of *Tithonia diversifolia* to adsorb nickel were carried out at room temperature. In 4 separate beakers for each of the different time intervals to be studied, 50 ml solution containing a concentration of 5 mg of prepared biomass per ml of suspension was adjusted to pH 5.0. The solutions were centrifuged at 760 rpm for 15 min and the supernatants discarded, then the biomass pellets were re-suspended under continuous stirring by rocking in 50 ml of a 0.1 mM metal solution previously prepared from $NiSO_4.6H_2O$ at pH 5.0. Aliquots (2 ml) were taken from the stirred suspensions at time intervals of 5, 10, 15, 30, 60, 90 and 120 min, transferred to clean test tubes, centrifuged, and the supernatants were collected for metal content analysis.

2.6. NaOH modification studies

The washed biomass (20 g) was reacted with 80 ml of 0.1 M sodium hydroxide (NaOH) for 24 h at room temperature, pelleted by centrifugation and the supernatant removed, then washed with de-ionized water three times followed by centrifugation each time in order to quench the reaction and then kept overnight in a freeze dryer by placing the material in a freeze-drying flask and rotating the flask in a bath cooled by mechanical refrigeration, dry ice and methanol. The biomass was subsequently used for series of metal binding experiments at the same conditions as the untreated biomass.

2.7. Calcium–magnesium interference studies

Washed biomass (0.8 g) was suspended in 160 ml of distilled water with tissue concentration approximately 5 mg per ml solution. The pH of the solution was adjusted to 5.0, 2 ml each of the tissue suspension (10 mg in 2 ml) was transferred into two separate test tubes. Solutions were prepared to include 0.1 mM of heavy metal ions at pH 5.0 for the following calcium, magnesium concentrations: 0.0 M, 0.1 mM, 0.2 mM, 1 mM, 2 mM, 10 mM, 20 mM, 0.1 M, 0.2 M and 1 M. For the study, each test tube contained 2 ml of the biomass suspension, 2 ml of 0.1 mmol nickel solution and 2 ml of the designated concentration of calcium or magnesium interference. The study was also carried out with combined calcium and magnesium concentrations. All tubes were equilibrated on a rocker for 30 min allowed to stay for 90 min, centrifuged at 760 rpm for 10 min and the supernatants were transferred to clean respective tubes.

2.8. Biosorption data analysis

Data analysis was conducted using one way Anova, Duncan and LSD post Hoc test for significance. The results of the replicates of each group were pooled and expressed as the mean ± standard deviation (SD). T-test for paired pH and time factor sample means was carried out using Statistica and SPSS software programmes. Significance was accepted at $P \leq 0.05$.

The quantity of nickel adsorbed by the biomass was extrapolated from Eq. (1), where C_b is the metal sequestered on the biomass; C_0 is the initial metal concentration; C_e the final metal concentration in the solution; V is the volume of the metal solution used.

$$C_b = \left[\left(C_0 - C_e\right)V\right] \tag{1}$$

Biosorption capacity (q_e) of the biomass was calculated by dividing C_b by the mass of the biomass used, i.e. 10 mg.

3. Results and discussion

Information on the kinetics of metal uptake by biosorbents plays a major role in selecting optimum operating conditions for industrial scale batch metal removal processes and in designing appropriate treatment plants [25–27].

3.1. Sorption kinetics

The result presented in Fig. 1 shows the percentage of nickel removed by *Tithonia diversifolia* vs. contact time for both unmodified and NaOH modified biomass. The plots reveal that in both biomasses, sorption took place very rapidly in the first 15 min and then continued at a slower rate until equilibrium was reached after a contact time of 2 h. Similar sorption kinetics was found by other authors using agricultural wastes and other biomass [9,28]. The rate of removal is higher at the start due to the larger surface area of the biomass available for the adsorption of the metal. It is observed that the NaOH modified biomass showed better efficiency in the removal process. After 30 min of interaction the NaOH modified biomass had an increased percent removal of 6–8%. This increase is considered statistically significant as a result of the high T value and very low P value ($P \leq 0.005$) for all the time intervals investigated (Table 1).

Table 1
T-test of the mean metal bound (ppm) for unmodified and modified biomasses

Time (min)	Mean metal bound (ppm)		T value	P value
	Unmodified (±SD)	Modified (±SD)		
5	3.243^{a}±0.008	3.315^{g}±0.01	9.730	0.0006
10	3.325^{b}±0.005	3.395^{h}±0.015	7.668	0.0016
15	3.367^{b}±0.008	3.520^{i}±0.005	33.653	0.0001
30	3.795^{c}±0.039	4.158^{j}±0.003	16.074	0.0001
60	4.187^{d}±0.008	4.545^{k}±0.013	40.622	0.00002
90	4.380^{e}±0.005	4.821^{l}±0.006	97.799	0.0001
120	4.605^{f}±0.009	5.028^{m}±0.06	12.076	0.0004

SD = standard deviation; Confidence interval = 95% ; $^{a–m}$ indicate differences

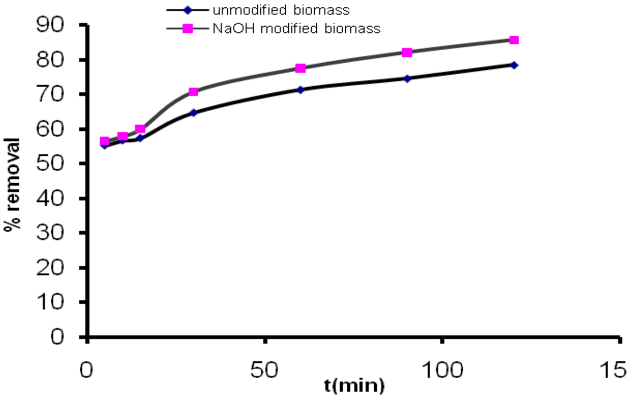

Fig. 1. Effect of contact time on nickel binding.

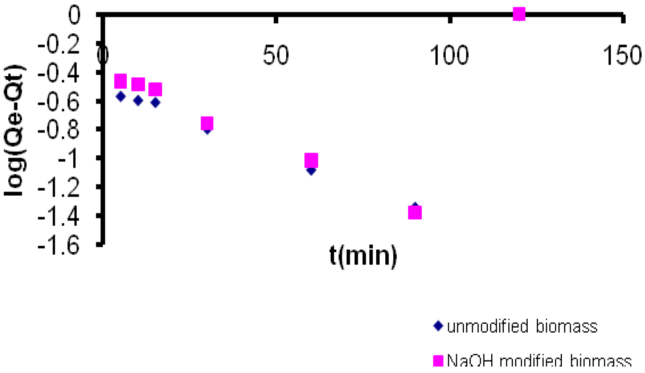

Fig. 2. Lagergren pseudo-first order reaction.

Improved performance as a result of NaOH treatment had been reported by some authors [1,29]. A possible chemical reaction that produces carboxylate groups from methyl esters when treated with NaOH is shown as [24].

$R - COO - CH_3 + NaOH \rightarrow R - COO^- + CH_3OH + Na^+$

This formed carboxylate group tended to have a much higher metal binding ability than the methyl ester groups.

Various adsorption kinetic models have been adopted to describe the behaviour of batch biosorption process under different experimental conditions. Lagergren pseudo-first order and pseudo-second order kinetic models were used to evaluate the experimental data of nickel biosorption by *Tithonia diversifolia.* The adsorption rate of Lagergren is expressed as Eq. (2) [2].

$$\log\left(q_e - q_t\right) = \log q_e - K_{pf} / 2.303\, t \qquad (2)$$

where q_e is the amount adsorbed (mg/g) at equilibrium, q_t is the amount adsorbed (mg/g) at any time t and K_{pf} is the Lagergren adsorption rate constant (min^{-1}). q_e and K_{pf} can be calculated from the slopes and the intercept of the plot of log ($q_e - q_t$) vs. t (Fig. 2).

Linear plots of log ($q_e - q_t$) vs. t having high value of coefficient of correlation (R^2) indicates the applicability of this kinetic model. As can be seen from Fig. 2, adsorption process using *Tithonia diversifolia* biomass does not follow pseudo-first order kinetic model.

Lagergren first order equation did not apply well as the K_{pf} and q_e determined from the plot could not estimate q_e.

The main assumption of pseudo-second order kinetic model is that rate limiting steps may be chemical sorption involving forces through sharing or exchange of electrons between nickel ions and the biomass. It has been reported that most sorption systems followed a pseudo-second order kinetic model which can be expressed as Eq. (3) [26,30]:

$$t / q_t = 1 / K_{ps} + t / q_e \qquad (3)$$

where K_{ps} is the adsorption rate constant (g/mg.min) derivable from the slope of plot of t/q_t vs. t.

Adsorption data of nickel uptake by *Tithonia diversifolia* fitted with the pseudo-second order kinetic model as shown in Fig. 3 and Table 2.

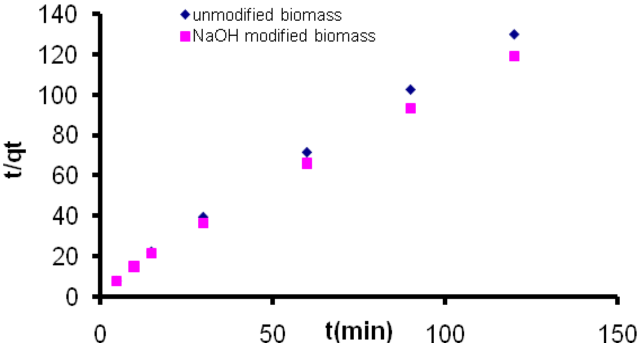

Fig. 3. Pseudo-second order reaction.

Table 2
Comparison of adsorption parameters of Lagergren pseudo-first order and pseudo – second – order kinetic models

Biomass	Pseudo-first-order model			Experimental	Pseudo-second- order kinetic model		
	q_e (mg/g)	K_{pf} (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	K_{ps} (g/mg.min)	R^2
Unmodified	–0.00911	–0.4980	–0.9982	0.922	1.0650	5.4674	09988
Modified	–0.1072	–0.3905	–0.9969	1.006	0.9718	5.7130	0.9989

It is evident from Table 2 that the experimental value of q_e(mg/g) derivable from the slope of the plots for pseudo order kinetics (Figs. 2 and 3) tallied with the estimated q_e(mg/g) using the second order kinetic model. Equally the coefficient of correlation for the pseudo-second order is much higher than the pseudo-first order model. These facts suggest that the sorption of Ni(II) ions followed the second order kinetic model.

Sorption kinetics are controlled by different steps including solute transfer to the sorbent particle surface, transfer from the sorbent particle surface to the intra particle active sites and retention on these active sites via sorption, complexation and intraparticle precipitation phenomena [10]. Intra particle diffusion is characterized by the relationship between specific sorption (q_t) and the square root of time according to the relation in Eq. (4).

$$q_t = K_{id}\, t^{1/2} \tag{4}$$

where q_t is the amount of solute adsorbed (mg/g) at time t (min) and K_{id} is the rate constant of intra particle diffusion determined by plotting q_t vs. $t^{1/2}$ (Fig. 4). This plot shows a partial linear distribution of points with an initial curved section. The linear portions indicate the existence of intraparticle diffusion in the process and the initial curved portion attributed to bulk diffusion. However deviation of the curve from the origin indicates that intra particle transport is not the only rate limiting step and other mechanisms are involved [31]

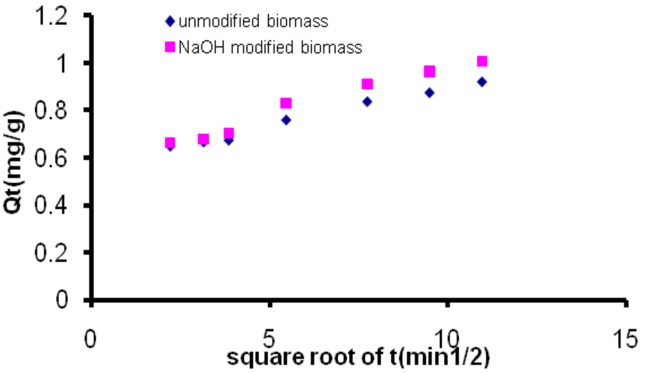

Fig. 4. Intra-particle diffusion.

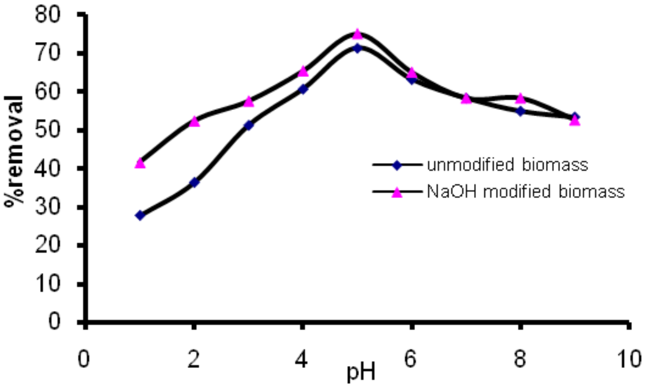

Fig. 5. Effect of pH on nickel binding.

3.2. *pH profile studies*

The study of pH on the sorption of nickel by *Tithonia diversifolia* is important in establishing the optimum sorption of metal ions at the solid/liquid inter-phase. Since pH is one of the main variables affecting the biosorption process [18,30], the optimum pH value for the uptake of the metal was determined for both biomass types. It has been reported that adsorption increases as solution pH increases [3,16]. Fig. 5 shows the effect of pH on the percentage uptake of nickel by *Tithonia diversifolia* biomass. The unmodified biomass showed a decrease in sorption at pH lower than 5.0. It was reported by Gupta

Table 3
T-test of the mean metal bound (ppm) for unmodified and modified biomasses at different pH values

pH	Mean metal bound (ppm)		*T* value	*P* value
	Unmodified (±SD)	Modified (±SD)		
1	1.615^{a}±0.005	2.448^{j}±0.008	152.936	<0.0001
2	2.120^{b}±0.003	3.076^{k}±0.008	193.802	<0.0001
3	3.033^{c}±0.008	3.378^{m}±0.006	59.756	<0.0001
4	3.563^{g}±0.006	3.842^{p}±0.006	56.951	<0.0001
5	4.188^{i}±0.003	4.404^{q}±0.010	35.835	<0.0001
6	3.705^{h}±0.005	3.815^{o}±0.005	26.944	<0.0001
7	3.422^{f}±0.002	3.420^{n}±0.004	0.776	0.4818
8	3.216^{e}±0.006	3.165^{l}±0.005	11.310	0.0003
9	3.130^{d}±0.005	3.070^{k}±0.002	19.298	<0.0001

SD = standard deviation; Confidence interval = 95%; $^{a–o}$ indicate differences et al. [33] that at a low pH of 2.0 all the binding sites may be protonated, thereby desorbing originally bound metals from the biomass. As pH increases, percent nickel adsorbed also increases until a peak is obtained at pH 5 for both biomass types. NaOH modified biomass showed an improved performance between the pH of 1 and 5, a phenomenon that can be corroborated by the findings of other researchers [24]. Statistical data presented in Table 3 shows that there is a significant difference between the mean metal bound to the biomass at pH values 1–4 for both types of biomass. In all the cases the confidence factor is ≥95% and the *P* value obtained is far lower than 0.05. More OH^- groups create more spaces around the binding sites favoring electrostatic interactions between cationic species. The efficiency for metal ions sorption can also be attributed to carbonyl groups (C=O) or to hydroxyl group (OH) of polyphenols [10]. Complexation phenomena can also occur, especially for the carboxylic groups. As pH increases from 6 to 9 for both biomasses the percentage nickel adsorbed expectedly decreases. This is assumed to be so because the presence of more OH^- groups gradually leads to the formation of insoluble products, perhaps due to chemical precipitation. There appears to be little or no advantage of modification on the sorption in this range. The decrease in the removal efficiency not with standing, the biomass could remove as much as 53% of the metal ions even at a pH of 9.0. Removal efficiency of nickel (75–80%) by sawdust at a pH of 9 had been reported in [8].

3.3. Calcium and magnesium interference studies

Hard cations such as calcium and magnesium are often found co-existing with other metals and could cause problems for metal removal processes [34]. The results of the experiment to determine the effect of cation interference on sorption of nickel by *Tithonia diversifolia* biomass showed that there is a decline in the ability of the biomass to bind nickel in aqueous solution (Fig. 6).The concentration of the introduced cations impacted negatively on the removal process. Each study involved the use of varied concentrations of the respective cations while solutions for the mixed cation investigation contained 1:1 ratio of the Ca and Mg ions. There is a remarkable reduction in the percent metal bound with increase in concentration of each cation added from 0.1 mmol to 1 mole. Calcium ions appear to give the highest interference. These cations have accounted for about a 35% decrease in nickel sorption. The decrease in sorption can be explained on the basis of competing Ca^{2+}, Mg^{2+} ions for metal binding sites. It can also be explained as a function of SO_4^{2-} ions present which could cause increased formation of sulfate complexes consequently decrease in free nickel ions in solution. A similar scenario has been reported in a work using NaCl [9].

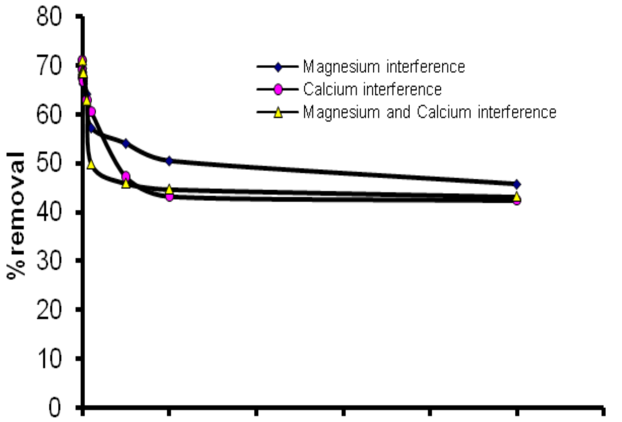

Fig. 6. Effect of cation interference on nickel binding.

3.4. Adsorption isotherms

Adsorption isotherms are very fundamental to industrial application and give information for the comparison of different biomaterials under different operational conditions, designing and optimizing operating procedure [3,35]. Two isotherm models Langmuir and Freundlich are widely used to examine the relationship between the adsorbed and aqueous concentrations at equilibrium adsorption. In this research, the adsorption isotherm for the nickel unto *Tithonia diversifolia* biomass at different concentrations of calcium and magnesium are described to relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate consideration in the bulk fluid phase C_e Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a definite number of identical sites and the treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir's equation is written as

$$C_e / q_e = 1/bQ^o + C_e / Q^o \tag{5}$$

where q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium liquid phase concentration of heavy metal ion (mg/l). Q^o and b are Langmuir constants indicating sorption capacity and energy of adsorption respectively [31]. Plots of C_e/q_e against C_e for nickel ion under different concentrations of magnesium, calcium and mixed magnesium/calcium solutions could be said to be linear. This indicates applicability of the Langmuir model (Fig. 7).

Freundlich isotherm is applied to non-ideal sorption on heterogeneous surfaces and also to a multi-layer sorption, suggesting that binding sites are not equivalent and/or independent [10]. The Freundlich equation which has

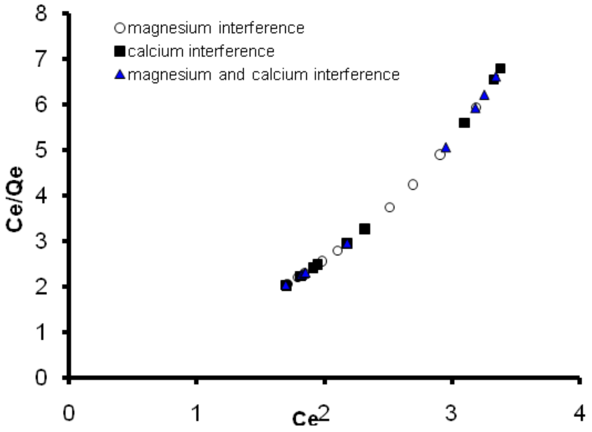

Fig. 7. Langmuir sorption isotherm based on cation interference.

been widely used for isotherm adsorption was applied to the investigation under review. The logarithmic form of the equation is:

$$\log q_e = \log K_f + 1/n \log C_e \tag{6}$$

where K_f indicates the adsorption capacity and $1/n$ is an arbitrary constant related to the adsorption intensity. K_f and n can be derived from plots of log q_e vs. log C_e which ought to be linear. Table 4 presents the adsorption parameters calculated for biosorption of nickel on untreated *Tithonia diversifolia* biomass.

Adsorption of nickel ions unto *Tithonia diversifolia* could also be said to fit to the Freundlich model by virture of the linear curve (Fig. 8). However with a higher correlation coefficient, the Langmuir model provides a better fit. Our presumed adaptability of *Tithonia diversifolia* biomass to both adsorption isotherm models further buttress the earlier assumption that intra particle transport is not the only rate limiting step and other mechanisms are involved.

Table 4
Sorption isotherm parameters for biosorption of nickel by *Tithonia diversifolia*

Model	Parameter	Interfering ions		
		Mg	Ca	Mg and Ca
Langmuir	Q^o, mg/g	2.508	2.820	2.741
	b, L/mg	–2.352	–2.962	–2.778
	R^2	0.994	0.995	0.997
Freundlich	K_f	–0.669	–0.732	–0.738
	n	0.083	0.101	0.102
	R^2	–0.991	–0.993	–0.996

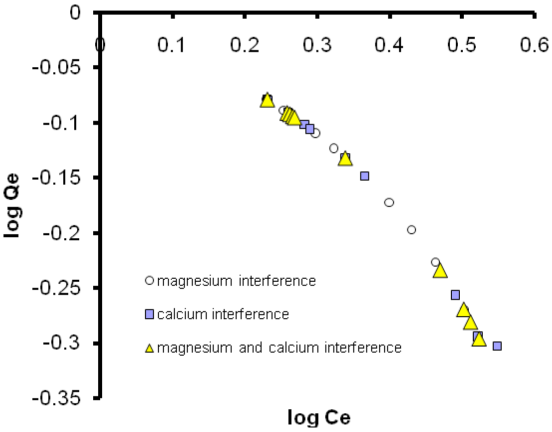

Fig. 8. Freundlich sorption isotherm based on cation interference.

4. Conclusions

Tithonia diversifolia biomass was selected for this study due to its originality, availability as well as to access its ability to be utilized as biological adsorbent. The biomass has been demonstrated to be a useful sorbent for nickel under batch condition. Obtained results showed that this biomass was able to remove nickel from its solution and the sorption capacity was strongly dependent on the pH of the solution, duration of contact between the biomass and the pollutant, the presence of cations co-existing with the metal and the modification of the biomass with NaOH.

The kinetics of sorption of nickel on the *Tithonia diversifolia* biomass was studied. Intra particle diffusion and chemical reaction seem to be significant in the rate controlling step but the pseudo-second order chemical reaction kinetics provide the best fit.

The results presented also demonstrate that adsorption equilibrium data in the concentration range of the interfering cations best fitted Langmuir adsorption isotherm models.

In order to realize the full potential of *Tithonia diversifolia* as a commercial sorbent, nickel uptake from industrial wastewater must be evaluated. This investigation is currently on going in addition to investigating the impact of immobilization of this biomass on the sorption process.

References

[1] K.S. Low and C.S. Lee, Sorption of cadmium and lead from aqueous solutions by spent grain, Process Biochem., 36 (2000) 59–64.

[2] S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, A review of potentially low cost sorbents for heavy metals, Wat. Res., 33(11) (1999) 2469–2479.

[3] M.N. Zafar, R. Nadeem and M.A. Hanif, Biosorption of nickel from protonated rice bran, J. Hazard. Mater., 143 (2007) 478–485.

[4] A.B. Blanco, B. Sanz, M.J. Llama and J.L. Serra, Biosorption of heavy metals to immobilized *Phormidium laminesum* biomass, J. Biotechnol., 69 (1999) 227–240.

[5] O. Keskinkan, M.Z.L. Goksu, A. Yuceer, M. Basibuyuk and C.F. Forster, Heavy metal adsorption characteristics of a submerged aquatic olant (*Myriophylum spicantum*), Process Biochem., 39 (2003) 179–183.

[6] C.W. Cheung, C.F. Porter and G. MacKay, Sorption kinetics for the removal of copper and zinc form effluents using bone char, Separ. Purif. Technol., 19 (1997) 55–64.

[7] S.P.K. Sternberg and R.W. Dom, Cadmium removal using *Cladophora* in batch, semi-batch and flow reactors, Bioresour. Technol., 81 (2002) 249–255.

[8] S.S. Shukla, L.J. Yu, K.L. Dorris and A. Shukla, Removal of nickel from aqueous solutions by sawdust, J. Hazard. Mater., B121 (2005) 234–246.

[9] I. Villaescusa, N. Fiol, M. Martinez, N. Miralles, J. Poch and J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Wat. Res., 38 (2004) 992–1002.

[10] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nobrega and M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, Process Biochem., 40 (2005) 3485–3490.

[11] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla and K.L. Dorris, Use of maple sawdust for removal of copper from wastewater, J. Hazard. Mater., B80 (2000) 33–42.

[12] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla and K.L. Dorris, The removal of lead from aqueous solutions by maple sawdust, J. Hazrad. Mater., B84 (2001) 83–94.

[13] S.S. Shukla, A. Shukla, K.L. Dorris, L.J. Yu and J.L. Margave, Adsorption of chromium from aqueous solutions by maple sawdust, J. Hazard. Mater., B100 (2003) 53–63.

[14] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater., B135 (2006) 264–273.

[15] B. Volesky and H.A. May-Philips, Biosorption of heavy metals by *Saccharomyces cervisae*, Appl. Microbiol. Biotechnol., 42 (1995) 797–806.

[16] P.H. Yin, Q.M. Yu and Z. Ling, Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater. Wat. Res., 33 (1999) 1960–1963.

[17] P.X. Sheng, Y. Ting, J.P. Chen and L. Hong, Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interf. Sci., 275 (2004) 131–141.

[18] H.A. Hawari and C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. Bioresour. Technol., 97 (2006) 692–700.

[19] J.L. Gardea-Torresdey, K.J. Tiemann, J.H. Gonzales, J.A. Henning and M.S. Towsend, Ability of silica-immobilized *Medicago sativa* (alfalfa) to remove copper ions from solution, J. Hazard. Mater., 48 (1996) 181–190.

[20] J.L. Gardea-Torresdey, K.J. Tiemann, J.H. Gonzales, J.A. Henning and M.S. Towsend, Biosorption of cadmium, chromium, lead and zinc by biomass of *Medicago sativa* (alfalfa), Proc. 11th Annual Conference on Hazardous wWste Research, L.E. Erickson, D.L. Tillison, S.C. Grant and J.P. McDonald, eds.,Kansas State University, Manhattan, KS, 1996, pp. 209–214.

[21] J.L. Gardea-Torresdy, G.D. Rosa and J.R. Peralta-Videa, Use of phytofiltration technologies in the removal of heavy metals: A review, Pure Appl. Chem., 76(4) (2004) 801–813.

[22] J. Morton, In Atlas of Medicinal Plants of Middle America, Bahamas to Yucatan, C. Thomas, ed., Springfield, 1981, p. 973.

[23] E. Goffin, Ziemons, P. De Mol, M.D. De Madureira, A.P. Martins, A.P. Da Cunha, G. Philippe, M. Tits, L. Angenot and M. Fredrich, In vitro antiplasmodial activity of *Tithonia diversifolia* and identification of its main active constituent: Tagitinin C. Planta Medica, 68 (2002) 543–545.

[24] J.L. Gardea-Torresdey, K.J. Tiemann, A. Hernandez, O. Rodriguez and S. Sias, Enhanced metal-binding capacity of NaOH treated *Larrea tridentata* leaf tissue, Proc. Conference on Hazardous Waste Research, 1998, pp. 101–110.

[25] M.A. Hanif, R. Nadeem, M.N. Zafar, K. Akhar and H.N. Bhatti, Kinetic studies for Ni(II) biosorption from industrial wastewater by *Cassia fistula* (golden shower) biomass, J. Hazard. Mater., 145 (2007) 501–505.

[26] Y.S. Ho and G. McKay, Sorption of dyes and copper ions onto biosorbents, Process Biochem., 33 (2003) 1047–1061.

[27] M.A. Hashim and K.H. Chu, Biosorption of cadmium by brown, green and red seaweeds, Chem. Eng. J., 97 (2004) 249–255.

[28] D. Feng and C. Aldrich, Biosorption of heavy metals by biomaterials derived from marine alga *Ecklonia maxima*, Hydrometal., 3 (2004) 1–10.

[29] W.E. Marshall and M.M. Jones, Agricultural by-products as metal adsorbent: sorption properties and resistance to mechanical abrasion, J. Chem Technol. Biotechnol., 66 (1996) 192–198.

[30] Y. Bulut, H. Aydin and Z. Tez, The removal of heavy metals from aqueous solution by sawdust adsorption, Bul. Pure Appl. Sci., 24C (2005) 4–14.

[31] C.K. Jain, Adsorption of Zinc onto bed sediments of the river Ganga: Adsorption models and kinetics, Hydrol. Sci., 46(3) (2001) 419.

[32] J.M. Lecano, F. Gonzalez, I. Perez, M.L. Blazquez, J.A. Munoz, A. Ballester and A. Hammaini, Use of waste biomass for decontamination of liquid effluents by biosorption. In Biohydrometallurgy: Fundamentals, Technology and Sustainable Development, Part B, 2000, pp. 217–226.

[33] R. Gupta, P. Ahuja, S. Khan, R.K. Saxena and H. Mohaptara, Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions, Current Sci., 78 (2000) 967–973.

[34] J.L. Gardea-Torresdey, K.J. Tiemann, J.H. Gonzales and O. Rodriguez, Phytofiltration of hazardous metal ions by alfalfa: a study of calcium and magnesium interferences, J. Hazard. Mater., 56 (1997) 169–179.

[35] B. Benguella and H. Benaissa, Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies, Wat. Res., 36(10) (2002) 2463–2474.