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Investigation of Lead Binding by *Tithonia diversifolia*

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Abstract: Mexican sunflower (*Tithonia diversifolia*) had been chosen for metal binding studies as a prelude to finding economic use for it. Adsorption capacity, pH-profile and time-dependency studies were conducted using stem biomass of this plant. Results of the investigation showed that over 96% of the lead content of water were adsorbed even in the first 5 min of interaction. Optimum pH of adsorption was recorded as 5 for the metal while the kinetic study conducted showed that the adsorption process follows a pseudo-second order reaction. In order to understand the effect of NaOH modification on the *Tithonia diversifolia*, batch modification studies were conducted. Results of this modification studies show enhanced metal binding activity. Presence of cations such as calcium and magnesium also interfered with the adsorption process. The adsorption isotherm was apparently Langmuir in nature.

Key words: Binding capacity, pH-profile, interference, isotherm, *Tithonia*

INTRODUCTION

Environmental pollution has become an increasing global problem. Pollution of land, water and air by heavy metals had been reported to cause increased degradation of human health. Heavy metals are often discharged by industries such as metal smelting, plating, tanneries and mining operations into fresh water and marine environment. (Low and Lea, 2000; Bailey *et al.*, 1999; Zafar *et al.*, 2007). According to the world health organization, cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc constitute metals of great concern. Lead is a hazardous metal and highly toxic to plants and animals. It causes brain damage, mental deficiency, anemia in human. The presence of lead in drinking water causes serious health problems and in sever cases death (Nui *et al.*, 1993). Consequent on severity of metal contamination and seriousness of researchers in finding lasting solutions to the menace of environmental degradation, many methods had been developed and adopted though these methods had been of great cost and prohibitive for developing economies. Great deal of attention has been given to the use of both living and nonliving biological materials for the remediation of toxic metal ions from industrial waste water, tanneries and mining effluents (Volesky and May-Philips, 1995; Carvalho *et al.*, 1994; Veglio *et al.*, 1997).

In recent times, new technologies have emerged and plant based biomaterials have been of interest. The ability of plants to uptake metal ions has been studied

(Gardea-Torresdey *et al.*, 1996a, b). In their studies, the mechanism involved in the uptake of metal ions has been reported to be surface adsorption, a passive process in which chemical groups attach to the cell wall of the plants. The ability of dead plant tissues to filter metal ions out of aqueous solution has been taken advantage of by phytofiltration technologies (Gardea-Torresdey *et al.*, 2004).

Metal binding by inactivated biological materials occur through the coordination of different functional groups (Gardea-Torresdey *et al.*, 1998a). Studies performed by Kuyucak and Volesky (1989) established that carboxyl groups are responsible for the binding of cobalt to the non living biomass of the common sea weed (*Ascophyllum nodosum*).

In this study *Tithonia diversifolia* (Sunflower) is tested for lead adsorption at several pH and reaction times. Adsorption capacities of the unmodified biomass were determined. In order to increase the adsorption capacity of the biomass, it was modified at optimal condition with NaOH. In addition, the effect of magnesium and calcium interference on the adsorption process was also monitored.

Tithonia diversifolia is a plant that grows widely in Nigeria. The leaves are mostly used by local farmers to enrich the soil as organic manure for the improvement of phosphorous availability (Ikerra *et al.*, 2006). The stem is of little or no economic importance. Hence, this study was conducted to generate useful information for the utilization of the stem of this weed plant in the removal of lead from aqueous solution.

MATERIALS AND METHODS

Sampling and biomass preparation: *Tithonia diversifolia* (sunflower) population was used for this study. The samples were acquired from road sides along the Federal University of Technology in Akure Ondo State Nigeria in September 2006. The experiments were performed at the Phyto Remediation Research Laboratory of the university. The shoots (stem) were washed thoroughly with water, cut into smaller pieces and oven dried at 90-95°C for 3 days. The samples were then ground with a Victoria grain mill and fine samples were obtained using 100 μ mesh screen sieve.

Ten grams 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 ion. After each washing, samples were centrifuged at 760 rpm for 15 min to obtain pellets (Gardea-Torresdey *et al.*, 1998b). The washed biomass was dried and weighed to account for weight loss.

Time-dependence studies: Solution of 50 mL containing a concentration of 5 mg of biomass per mL of suspension was prepared and adjusted to pH 5.0, with NaOH. The solution was centrifuged at 760 rpm for 15 min and the supernatants discarded, then the biomass pellets were resuspended under continuous stirring by rocking in 50 mL of 0.1 mM metal solution. Three 2 mL aliquots were taken from the stirred suspension and transferred to clean test tube at time intervals of 5, 10, 15, 30, 60 and 90 and 120 min. The samples were centrifuged and the supernatants were collected into clean tubes for metal content analysis.

pH-profile studies: Two fifty milligrams of washed *Tithonia diversifolia* biomass was weighed separately into 9 beakers and suspended in 50 mL deionized water with tissue concentration approximately 5 mg mL⁻¹ solution and was then stirred to give a homogenous mixture. The suspensions in these beakers were adjusted to pH values 1-9 with nitric acid (HNO₃) and sodium hydroxide (NaOH). The solutions were equilibrated for 10 min. Three, 2 mL aliquots of these suspensions at each pH were transferred into clean plastic tubes. The suspensions were centrifuged at 760 rpm for 5 min and the supernatants decanted. Two milliliters of individual metal solution of 0.1 mM which were previously prepared and pH adjusted to 1-9 from Pb(NO₃)₂ salt were then added. All suspensions were kept for one hour after which it was centrifuged for 15 min at 760 rpm. The supernatants were transferred to clean respective plastic tubes for metal analysis.

Adsorption capacity studies: Batch laboratory method was used to determine the adsorption capacity of Pb (II) to *Tithonia diversifolia* biomass. Two fifty milligrams of the treated biomass was suspended in 50 mL deionized water and pH adjusted to 5.0. Three 2 mL aliquots of the suspension were transferred to clean plastic tubes, centrifuged and the supernatant discarded. Two milliliters aliquots of 0.1 mM metal solution were added to the tubes each and all were equilibrated for 15 min. After centrifugation the supernatants were kept for analysis. Again 2 mL of the metal solution were added to the same tubes. The process was repeated for 10 capacity cycles.

NaOH modification studies: Twenty grams of washed biomass was reacted with 80 mL of 0.1 M sodium hydroxide (NaOH) for 24 h. The biomass was pelleted by centrifugation and the supernatant removed. The biomass was then washed with deionized water three times followed by centrifugation each time in order to quench the reaction and then allowed overnight in a freeze dryer and used for series of metal binding experiments.

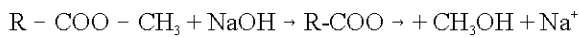
Calcium-magnesium interference studies: 0.8 g of washed biomass was suspended in 160 mL of distilled water with tissue concentration approximately 5mg per ml solution. The pH of the solution was adjusted to 5.0. Two milliliter of the tissue suspension (10 mg in 2 mL) was transferred into each test tube. Solutions were prepared to include 0.1 mM 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. From each solution, 2 mL of various concentrations of calcium and magnesium and 0.1 mM lead (II) ion to respective tubes and reacted to the biomass respectively. The study was also carried out with combined calcium and magnesium concentrations. All tubes were equilibrated on a rocker for 15 min. They were then centrifuged at 760 rpm for 10 min and the supernatants were transferred to clean respective tubes.

Metal analysis: Analyses for the metal ions studied were performed using Perkin Elmer model 3110 atomic absorption spectrometer. The modified methods used for analysis were adopted from the Perkin Elmer model 3110 manual. Analytical wavelength for Lead is 283.3 nm. A calibration curve was obtained with a correlation coefficient greater than 0.98 and the instrument response was checked regularly with known standard. Each sample was read three times, mean value and relative standard deviations were computed.

RESULTS AND DISCUSSION

The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which contaminants are removed from aqueous solutions in order to design an appropriate adsorption treatment plants (Ho and McKay, 2003)

Sorption kinetics: To establish an appropriate contact time between *Tithonia diversifolia* biomass and lead solution, adsorption capacities were measured as a function of time. Kinetic study revealed that metal removal efficiencies for lead were achieved in the first 40 min of contact with *Tithonia diversifolia* biomass. Figure 1 shows the time course of biosorption for the unmodified and NaOH modified biomass with an initial pH of 5 and initial metal concentration of 0.1 mM. Sorption took place very rapidly in the first 5 min then continued at a slower rate until equilibrium was reached in a contact time of 2 h. The unmodified biomass removed between 96.59% at 5 min and 97.73% at 120 min. Modification of the biomass with 0.1 M NaOH appears to have increased metal binding by the *Tithonia diversifolia* biomass. As reported by Low *et al.* (2000), treatment of spent grains with NaOH greatly enhanced Pb and Cd sorption. Soybean and cotton seed hulls improved sorption capacity for Zn (II) when treated with NaOH (Marshall and Jones, 1996). Gardea-Torresdey *et al.* (1998a) had reported a possible Chemical reaction that produces carboxylate groups from methyl esters when treatment is done with NaOH shown:



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

Kinetic model: Various adsorption kinetic models have been adopted to describe the sorption of metal ions. These models include the pseudo first-order Lagergren and pseudo second-order. Pseudo-first order rate equation by Lagergren had been widely used (Low and Lee, 2000). The adsorption rate expression of Lagergren is

$$\text{Log}(q_e - q_t) = \log q_e - K_{pf} / 2.303 t \quad (1)$$

Where, q_e is amount adsorbed (mg g^{-1}) at equilibrium, q_t is the amount adsorbed (mg g^{-1}) 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 $\log(q_e - q_t)$ versus t (Fig. 2).

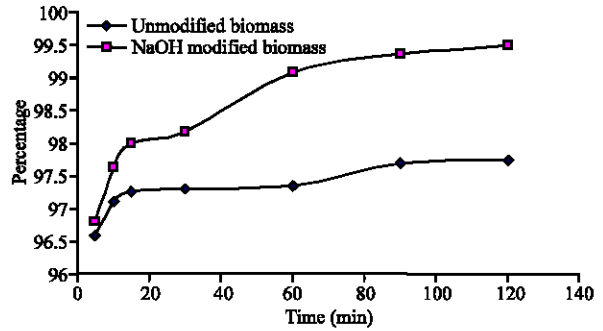


Fig. 1: Percentage metal bound as a function of time

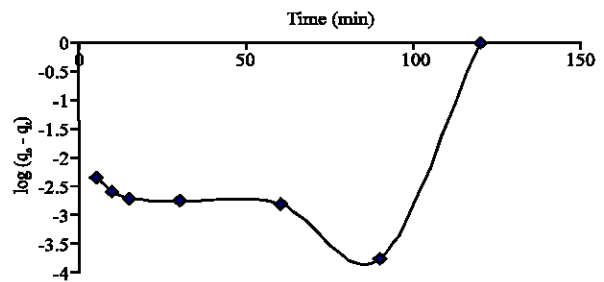


Fig. 2: Lagergren pseudo first order reaction for unmodified biomass

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

Since the system is not first order, a pseudo-second order model was considered. Pseudo-second order model is based on the assumption that the rate limiting step may be a chemical sorption involving forces through sharing or exchange of electrons between lead and *Tithonia diversifolia*.

Bulut *et al.* (2005), Ho and Mc Kay (1999) had reported that most of the sorption system followed a pseudo second-order kinetic model which can be expressed as:

$$t/q_t = 1/K_{ps} + t/q_e \quad (2)$$

where, K_{ps} is the adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) derivable from slope of plot of t/q_t versus t (Fig. 3). The estimated value of q_e fairly aligns with the experimental value suggesting that the sorption of lead followed the second-order kinetic model indicating that the rate-limiting step was a chemical biosorption process between lead and *Tithonia diversifolia* biomass. Similar conclusions were drawn by Ho and McKay. Parameters for Lagergren pseudo-first and Pseudo-second order reactions are presented in Table 1 and 2.

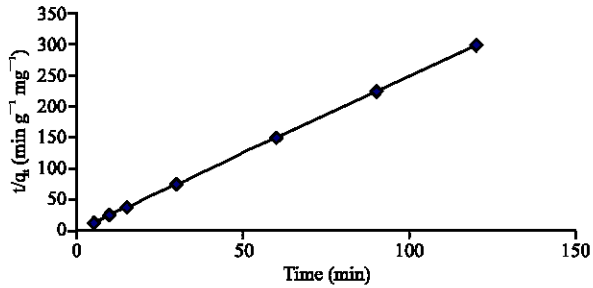


Fig. 3: Lagergren pseudo second order reaction for unmodified biomass

Table 1: Lagergren pseudo-first-order parameter

Experimental q _e (mg g ⁻¹)	4.0498
K ₁ (min ⁻¹)	-2.3558
Estimated q _e (mg g ⁻¹)	-0.0132

Table 2: Lagergren pseudo-second-order parameter

Experimental q _e (mg g ⁻¹)	4.0498
K ₂ (min ⁻¹)	0.2621
Estimated q _e (mg g ⁻¹)	2.4683

This trend is also seen in adsorption process of NaOH modified *Tithonia diversifolia*. (Fig. 4 and 5).

Intra particle diffusion: Kinetic results can be used to determine if particle diffusion is the rate-limiting step for lead adsorption onto the *Tithonia diversifolia* biomass (Hamdaoui, 2006). Weber and Morris (1963) had reported that if particle diffusion is involved in the sorption process then a plot of adsorbate uptake versus the square root of time should give a linear relation. More so if the line passes through the origin then the particle diffusion would be the rate controlling step. The rate constant for intra particle diffusion (K_{id}) is calculated through the relation:

$$q_t = K_{id} t^{1/2} \quad (3)$$

where q_t is the amount adsorbed (mg g⁻¹) at time t (min). Plots of q versus t^{1/2} for the unmodified and the NaOH modified *Tithonia diversifolia* biomass are shown in Fig. 6 and 7. The plots as can be seen have similar features initial curved portion followed by a linear portion. This initial curved portion could be attributed to bulk diffusion. Linear portions in the plot are attributed to the intra particle diffusion and the plateau is the equilibrium. Deviation of the curves from origin indicates that intra particle transport is not the only rate limiting step and other mechanism are involved (Jain, 2001). Such a deviation from the origin may be due to the difference in the rate of transfer at the earlier stage of adsorption.

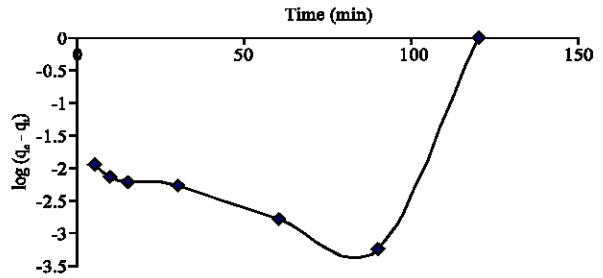


Fig. 4: Lagergren pseudo first order reaction for modified biomass

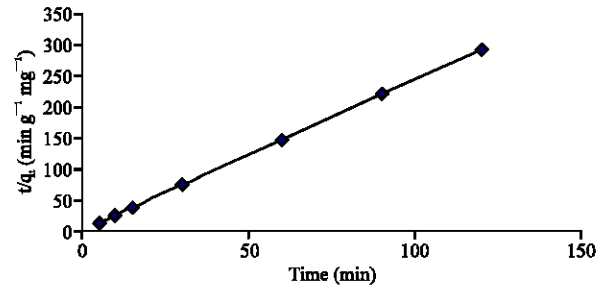


Fig. 5: Lagergren pseudo second order reaction for modified biomass

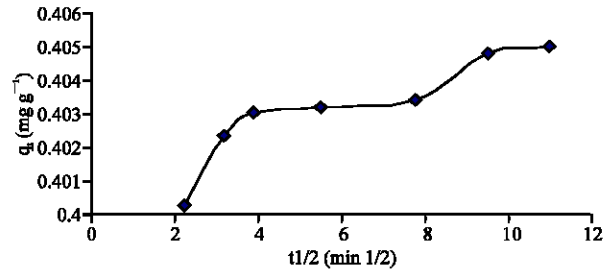


Fig. 6: Intraparticle diffusion for unmodified biomass

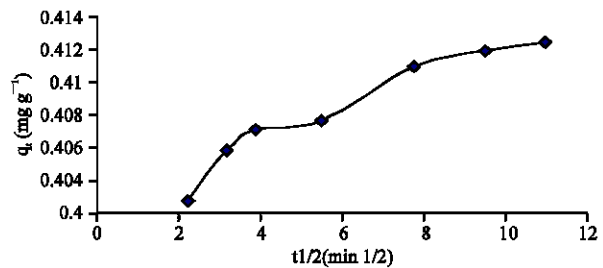


Fig. 7: Intraparticle diffusion for modified biomass

pH-profile studies: The study of pH on the sorption of Pb by *Tithonia diversifolia* is important in establishing the optimum sorption of metal ion at the solid/liquid interphase. It has been reported that adsorption increases

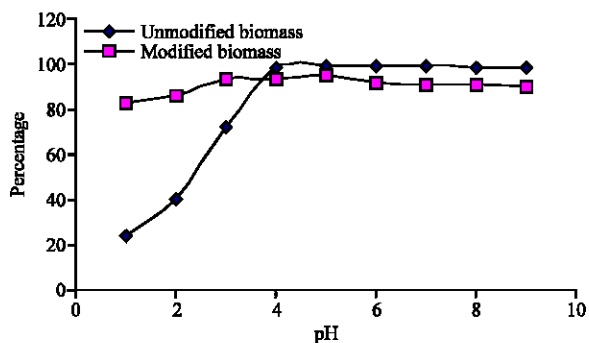


Fig. 8: pH profile study of modified and unmodified biomass

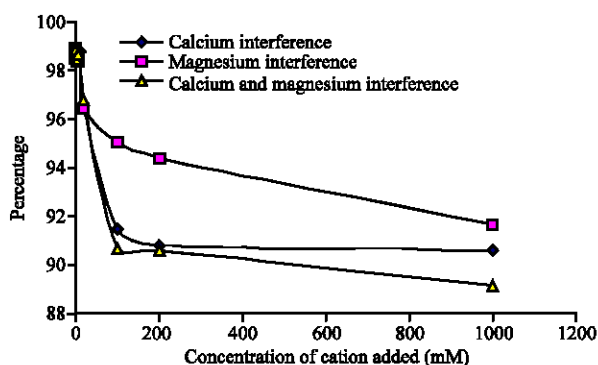


Fig. 9: Effect of cation interference on lead (II) ion binding

as solution pH increases (Yin *et al.*, 1999). Figure 8 shows the effect of pH on the uptake of lead by *tithonia diversifolia* biomass. The unmodified biomass showed a decrease in sorption at pH lower than 4. Invariably this could be due to the excess of H⁺ ions that surround the binding sites hence making adsorption very unfavourable. The NaOH modified biomass presented a different picture at the same pH range. About 80% of lead were removed. As should be expected the presence of OH⁻ group could have created more spaces around the binding sites by reducing the volume of H⁺ ions. Optimum pH for both biomasses was found to be at 5. it should be noted that at this optimum pH and other higher pH range, the adsorption of lead to the modified biomass reduced by about 4.70%. This is to be expected because the presence of more OH⁻ group gradually leads to the formation of insoluble products, perhaps due to chemical precipitation. Investigation at pH higher than 9 became unnecessary.

Calcium and magnesium interference studies: Hard cations such as calcium and magnesium are most times found co-existing with other metals. This is one problem that arises with most metal filtration systems (Gardea-Torresdey, 1997).

Results of the experiment to determine the effect of cation interference on sorption of lead by *Tithonia diversifolia* biomass showed that there is a decline in the ability of the biomass to bind lead in aqueous solution (Fig. 9). The concentration of the introduced cations impacted negatively on the removal process as there is a remarkable reduction in % metal bound with increase in concentration of each cation from 0.1 mmol to 1 mole. The mixture of calcium and magnesium gave the highest interference. Probably this is as a result of combined effects of the cations and the competition for binding sites. This combined effect of cation interference gave rise to about 9.69% reduction in the removal potential of the biomass.

Adsorption isotherm: 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 (Benguella and Benaissa, 2002; Zafar *et al.*, 2007). Two isotherm models Langmuir and Freundlich are widely used to examine the relationship between the sorbed and aqueous concentrations at equilibrium sorption. In this research, the adsorption isotherm for the lead unto *Tithonia diversifolia* biomass at different concentrations of calcium and magnesium interference 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 maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. Linear form of the Langmuir's equation is written as:

$$C_e/q_e = 1/bQ^\circ + C_e/Q^\circ \quad (4)$$

Where, q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium liquid phase concentration of heavy metal ion (mg L^{-1}). Q° and b are Langmuir constants indicating sorption capacity and energy of adsorption respectively (Jain, 2001). Plots of C_e/q_e against C_e for Lead (II) ion under different concentrations of magnesium, calcium and mixed magnesium/calcium interference were found to be linear. This indicates applicability of the Langmuir model. Some plots of the tests are presented as Fig. 10A-C.

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

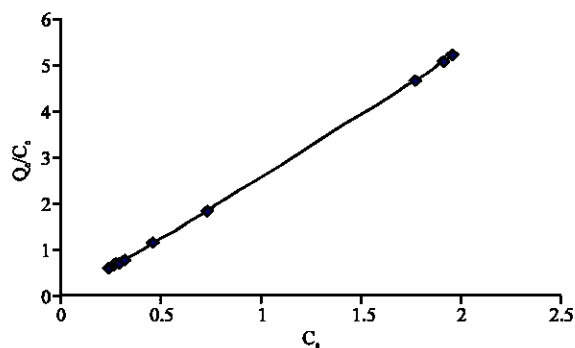


Fig. 10a: Langmuir Isotherm for unmodified biomass based on calcium interference

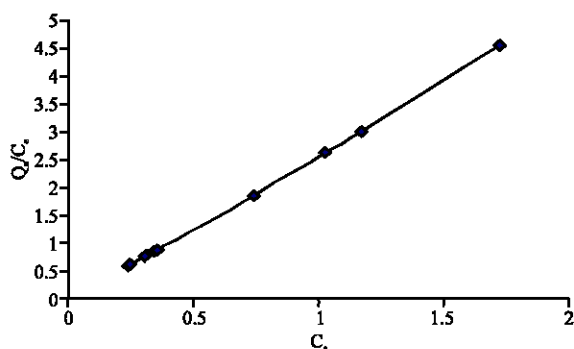


Fig. 10b: Langmuir Isotherm for unmodified biomass based on magnesium interference

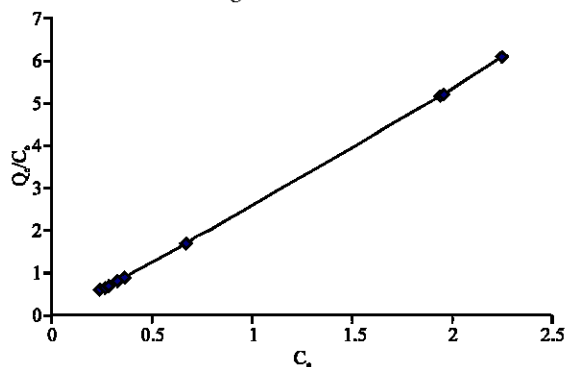


Fig. 10b: Langmuir Isotherm for unmodified biomass based on mixed calcium, magnesium interference

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \quad (5)$$

Plots of $\log q_e$ versus C_e ought to be linear however the adsorption of Pb (II) ion to *Tithonia diversifolia* has not been applicable to the Freundlich model.

CONCLUSIONS

Tithonia diversifolia biomass was selected for this study due to its originality, availability and to access its ability to be utilised as biological filter.

Tithonia diversifolia has demonstrated to be useful sorbent for lead under batch condition.

Results obtained show that pH, contact time, cation interference and NaOH modification affect the uptake capacity of the biomass.

The adsorption process had obeyed Langmuir isotherm model.

The sorption of lead is best described by Pseudo second order chemical reaction.

Further experiments are being conducted to test the impact of immobilization of this biomass on the sorption process.

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