DEVELOPMENT OF MODEL EQUATION FOR THE ABSORPTION RATE OF MANGANESE FROM POLLUTED SOIL INTO JUTE OR EWEDU ROOTS *(Corchorus Olitorius)* VEGETABLE

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Abstract: This study was conducted to determine the kinetics of absorption and bioaccumulation of Manganese (Mn) in Ewedu roots. A pot culture experiment was conducted to determine Mn uptake by roots of Ewedu vegetable from polluted soil within the seventy-one days of growth period. The amount of manganese ions ($Mn^{2+)}$) in the roots decreased with time in a polynomial fashion. The kinetic model for the rate of absorption is a First order, with mass transport coefficient $K_{Mnrt} = 0.0450\ (\frac{\mu g}{gday})$ and the rate of absorption as $R_{Mnrt} = 0.0450\ (C_{Mnrt} + e^{0.0450t}\ )$. The experimental values of the concentration of Mn in the roots of Ewedu vegetable were in overall agreement with the values predicted by the model, with variations in the range of 1.9% to 17.6%

Key Words: Absorption, Kinetics, Bioaccumulation and Phytoremediation, modelling

Introduction

Soil pollution by heavy metals is of great concern to public health (Goyer, 1996). The source of heavy metals in plants is the environment in which they grow and their growth medium (soil) from which heavy metals are taken up by roots or foliage of plants (Okonkwo et al., 2005). Plants grown in polluted environment can accumulate heavy metals at high concentration causing serious risk to human health when consumed. Moreover, heavy metals are toxic because they tend to bioaccumulate in plants and animals, bioconcentrate in the food chain and attack specific organs in the body ((Akinola et al., 2006; Chatterjee and Chatterjee, 2000).

Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, atmospheric sources (Yang e tal., 2005), also indoctrinate e-waste disposal into the environment (Luo e tal.,2011)

Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins and minerals. Heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of fresh vegetables (Bigdeli and Seilsepour, 2008). A number of elements, such as lead (Pb), cadmium (Cd), nickel (Ni), Manganese (Mn), cobalt (Co), chromium (Cr), Copper (Cu) and Selenium (Se) can be harmful to plants and humans even at quite low concentrations (Bowen, 1979). Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes, etc. (Buchaver, 1973). Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides (Demi˙rezen and Aksoy, 2004). Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality, crop growth (Ma et al., 1994; Msaky and Calvert, 1990; Fergusson, 1990) and environmental health.

Manganese is a naturally occurring element found in rock, soil, water, and food. In humans and animals, manganese is an essential nutrient that plays a role in bone mineralization, protein and energy metabolism, metabolic regulation, cellular protection from damaging free radical species, and formation of glycosaminoglycan (Wedler 1994). Manganese acts as both a constituent of metallic enzymes and an enzyme activator. Enzymes that contain manganese include arginase, pyruvate carboxylase, and manganese-superoxide dismutase (MnSOD) (Keen and Zidenberg-Cher 1990; NRC 1989; Wedler 1994). Manganese, in its activating capacity, can bind either to a substrate (such as adenosine triphosphate, ATP), or to a protein directly, thereby causing conformational changes (Keen and Zidenberg-Cher 1990). manganese has been shown to activate numerous enzymes involved with either a catalytic or regulatory function (e.g., transferases, decarboxylases, hydrolases) (Wedler 1994). Although manganese is an essential nutrient, exposure to high levels via inhalation or ingestion may cause some adverse health effects.

It has been suggested that these adverse health effects, especially neurologic effects, are occurring on a “continuum of nervous system dysfunction” that is dose-related (Mergler et al. 1999). In other words, mild or unnoticeable effects may be caused by low, but physiologically excessive amounts of manganese, and these effects appear to increase in severity as the exposure level or duration of exposure increases. Case reports and occupational studies address this continuum of nervous system dysfunction and help to characterize the apparent dose-response relationship. It is clear that chronic exposure to manganese at very high levels results in permanent neurological damage, as is seen in former manganese miners and smelters. Chronic exposure to much lower levels of manganese (as with occupational exposures) has been linked to deficits in the ability to perform rapid hand movements and some loss of coordination and balance, along with an increase in reporting mild symptoms such as forgetfulness, anxiety, or insomnia.

Manganese can exist in both inorganic and organic forms. Plant species have a variety of capacities in removing and accumulating heavy metals. So there are reports indicating that some plant species may accumulate specific heavy metals (Markert, 1993). The uptake of metals from the soil depends on different factors, such as their soluble content in it, soil pH, plant species, fertilizers, and soil type (Lubben and Sauerberck, 1991). Vegetables, especially leafy vegetables, accumulate higher amounts of heavy metals (Sharma and Kansal, 1986). Roots and leaves of herbaceous plants retain higher concentration of heavy metal than stems and fruits (Yargholi and Azimi, 2008). There are limited or no studies on development of model equation for the absorption rate of Manganese from polluted soil into jute or ewedu *(corchorus olitorius*) vegetable, the most studies focused on the status of metal content in edible parts of vegetables. And an investigation of the literature also shows a scarcity of data on comparison of metal content at different stages of growth in leafy vegetables in areas where these vegetables are mosyly consumed. Therefore, the present study was undertaken to study the absorption mechanism and develop a mathematical model for the process of absorption of manganese (Mn) by the roots of jute plant (*Corchorus Olitorius)* on polluted soils.

- To compare and investigate the concentration levels of manganese (Mn) at different growth stages in the roots of jute vegetable.

Model Development

For the absorption mechanism in the roots of jute vegetable, the following dynamics was preferred to other candidate functions:

Rate of absorption $r_A = \frac{dC_A}{dt} = KC_A^n$ 1

Where C_A is the concentration of the metal in parts of vegetable at any given time t and K is the mass transport coefficient governing the rate of metal uptake, and n is a constant that signifies the rate or order of rate of absorption.

Equation (1) is a special case of Fick's law (Danny, *e tal.,* 2001, Abia and Egwe, 2005) where the mass transfer is governed by the change in concentration in parts of the vegetable with time.

The kinetic model is based on the following assumptions:

- Uptake of the heavy metal is considered to take place in the axial (upward direction.
- The rate is per unit length of transfer from the rhizosphere to the root.
- The concentration of the metal ions is uniform along the length of root, stem and leaf.
- The absence of any reaction between absorbed ions.
- The mechanism of ion transfer is by molecular diffusion.

Pot Culture Experiment

The pot culture experiment was conducted to determine Mn uptake by Ewedu vegetable from the polluted soils. 3 kg of the polluted soil was weighed into five plastic pots. All samples were soaked with distilled water and allowed to stand for three days. 0.3 g of Ewedu seed were weighed and planted into each pot and allowed to germinate for seven (7) days. After germination, the plants were allowed to grow for seventy-one (71) days and each pot was irrigated with 250 mls of clean tap water every evening. The pots were kept in a greenhouse away from aerial pollution of heavy metals. Each vegetable pot was harvested at a specified time interval of 31, 41, 51, 61 and 71 days respectively. The vegetable and soil samples of each pot were taken to the laboratory for analysis.

Sample Preparations

Soil samples

The soil samples were taken to the laboratory, spread on clean glass plate dried in an oven at 105 ^oC to a constant weight. The heavy metals in the soil samples were evaluated using the soil testing method by AOAC (1995). The dried soil samples were ground with a pestle and mortar to pass through 0.5 mm mesh sieve. 2 g each of the sieved soil samples was weighed into a beaker and was digested in a mixture of 50 ml concentrated nitric acid (HNO_3) and 1 ml concentrated perchloric acid ($HClO_3$) on hot plate with gentle boiling. At completion of digestion, the samples were evaporated to dryness. The residue was then mixed with 10 ml of 0.1M nitric acid and filtered into 100 ml standard flask using Whatman No 1 filter and made up to mark with distilled water.

Vegetable Samples

The concentration of heavy metals in vegetable samples were determined using the Atomic Absorption Spectrometer (AAS). The vegetable samples were reduced to fine powder on a grinder prior to drying at 60^oC in an oven to a constant weight. 0.5 g of the fine powdered vegetable samples were weighed into conical flasks and digested in a mixture of 4 ml concentrated per chloric acid ($HclO_4$), 2 ml of concentrated sulphuric acid (H_2SO_4), 25 ml concentrated nitric acid (HNO_3), and 1 ml of hydrogen peroxide (H_2O_2) at 100^oC on a hot plate for two hours in a fume cupboard. The resulting solution was made up to 100 ml with distilled deionized water.

Results and Discussion

The variation in concentration of manganese in different parts of Jute vegetable is presented in figure 1.

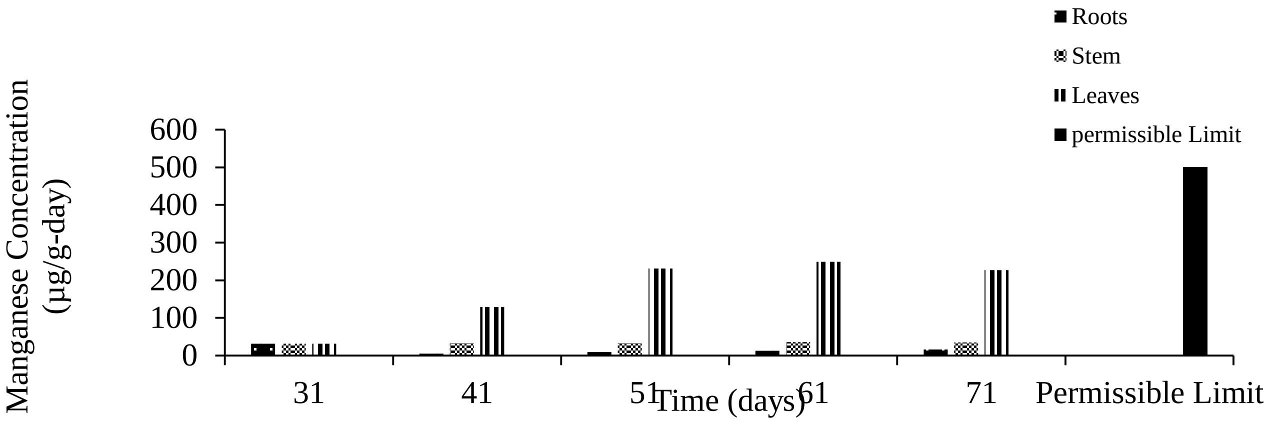

Figure 1: Variation of Manganese concentration in different parts of the vegetable (Jute root, stem, and leaves) with time

From Figure 1, it was observed that the Jute tends to accumulate heavy metals in the leaves, then followed by the stem and then the roots. It can be seen from the distribution of heavy metal (Mn) in parts of Jute (Figure 1) that higher concentrations of the metal ions is found in the leaves. This is in agreement with the findings of Mohamed and Khairia (2012) who concluded after their results that the Mn and other heavy metals uptake can be promoted and accumulated in the leaves as a result of leaves being considered food making factories in plants.

The concentration of Mn in all parts of the vegetable is below the FAO/WHO (2001) maximum permissible level of 500 ug/g. It therefore implies that Jute vegetable is safe for consumption by humans and animals at all stages of its growth. This is in strong agreement with the findings of Jan e tal., (2010). This also reflects the concentration of manganese in the soil on which the vegetable is grown.

Generally, Mn clearly shows higher concentrations in leaves, then stem and then roots. In general, Leaves > Stem > Roots.

This research findings serves as useful knowledge to vegetable farmers in their choice of vegetable to be grown on which type of heavy metal ion polluted soil. It has also been established in this study that, jute or ewedu has very poor absorption capacity for manganese as such, it can be grown on any manganese polluted loamy soil and consumed at any stage of its growth without any health consequence as far as manganese is concern.

Figure 2 shows the variation of manganese (Mn) concentration in Jute roots with time.

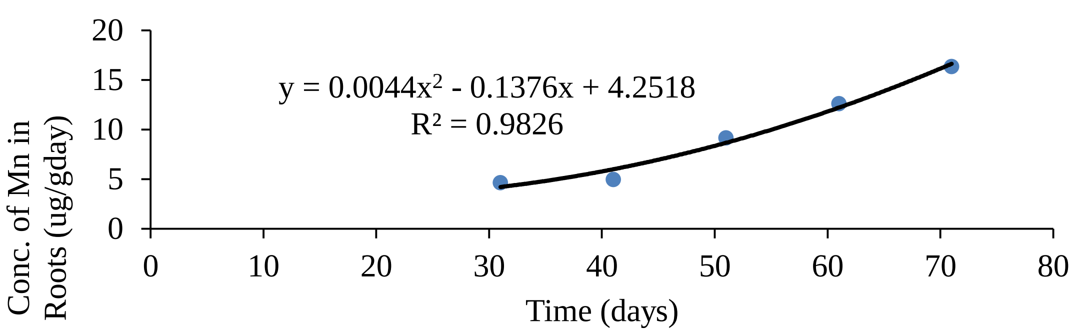

Figure 2: Variation of Manganese (Mn) concentration in Jute/Ewedu roots with time.

Figure 2 suggests a gradual increase and low concentration level of Mn in the vegetable roots with increase in the level of maturity (time). This confirms the findings of Barman and Lal (1994) who reported higher accumulation of heavy metals (Cu, Zn, Cd, Mn) in edible parts than in non-edible plant parts (roots). Analysis of Variance also confirmed the fact that there was significant increase ($p \leq 0.05$) in Mn content in the vegetable roots.

The relationship between Mn root content (ug/gday) and Time(days) is a second order polynomial relationship with correlation ratio of $R^2 = 0.9826$

While the plot of Ln Rate Vs Ln Concentration (Mn) gives a linear relationship with $R^2 = 0.901$

The study also showed that the absorption of manganese by Jute roots followed first order absorption kinetics with the mass transport coefficient $K = 0.0450\,(\frac{\mu g}{gday}$. Some researchers (Selveraj *e tal.*, 2004) who studied the batch absorptive removal of copper ions in aqueous solutions by ion exchange resin (1200H) reported that the absorption followed a pseudo-first order kinetic model.

In this study, it is also discovered that Jute accumulated about half times the maximum permissible level of 500 ug/g for manganese (Mn) (WHO/FAO (2001). This thus imply as earlier stated that Jute at all stages of its growth grown on soils polluted with manganese (Mn) is very, very safe for human and animal consumption.

Overall, the levels of Mn in Jute vegetable increased significantly with increase in maturity(time) ($p \leq 0.05$ in the roots). Fully matured vegetables recorded a significant ($p \leq 0.05$) increase in accumulation of Mn in the vegetable's roots. This confirms the findings of Allinson and Dzialo (1981), Iretskaya and Chien (1998), Kim et al. (2002) and Singh and Aggarwal (2006) who in their studies, discovered low metal accumulation in fruity and leafy parts of vegetable crops and higher concentrations in other vegetative parts (the roots). This may possibly be due to poor metal mobility within the plants. The root concentration of Mn was observed to be well below the FAO/WHO (2001) maximum permissible level of 500 ug/g.

The relationship between Mn root content(ug/gday) and Time(days) is presented graphically in Figure 2.

The empirical equation relating the concentration of Mn in roots with time is a polynomial of second degree and correlation coefficient of $R^2 = 0.9826$.

$$C_{Mnrt} = 0.0044t^2 - 0.1376t + 4.2518 \quad 2$$

Therefore,

$$\frac{dC_{Mnrt}}{dt} = 0.0088t - 0.1376 \quad 3$$

Applying the absorption kinetics:

$$R_{Mnrt} = \frac{dC_{Mnrt}}{dt} = K_{Mnrt}\, C^n_{Mnrt} \quad 4$$

The rate of Manganese uptake, $R_{Mnrt} = \frac{dC_{Mnrt}}{dt}$ at different times is given by Equation (2) in Table 1

Taking the ln of both sides,

$$lnR_{Mnrt} = lnK_{Mnrt} + nlnC_{Mnrt} \quad 5$$

The plot of lnR_{Mnrt} against lnC_{Mnrt} gives a linear relationship with slope n and intercept lnK_{Mnrt} as seen in Figure 3.

Table 1: The rate of Mn uptake of Ewedu root with time.

Time in days	Rate (R_{Mnrt}) in µg/g-day
31	0.1352
41	0.2232
51	0.3112
61	0.3992
71	0.4872

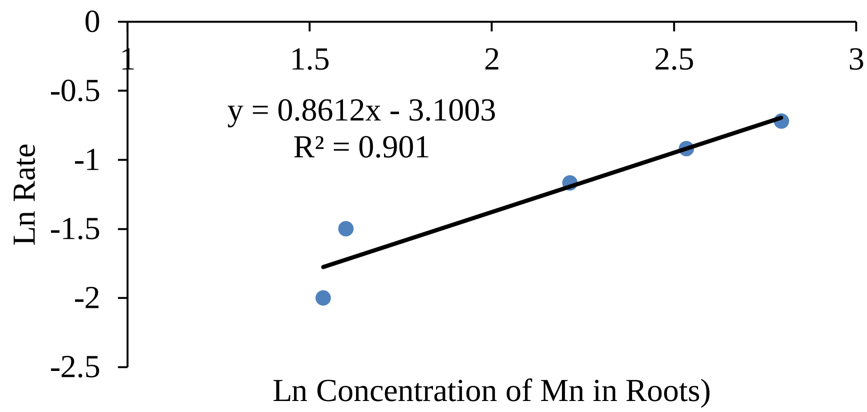

Figure 3: Variation of manganese (Mn) concentration in Ewedu roots with time

From Figure 3, slope n = 0.8612 and intercept lnK_{Cdrt} = -3.1003.

Therefore,

$$K_{Mnrt} = e^{-3.1003} = 0.0450 \left(\frac{\mu g}{gday}\right) \quad 6$$

From the empirical model, the rate of absorption is of first order since n = 0.86 ≈ 1 and therefore the absorption model is given by:

$$R_{Mnrt} = \frac{dC_{Mnrt}}{dt} = K_{Mnrt}\, C^1_{Mnrt} \quad 7$$

Integrating Equation (6) gives the solution:

$$C_{Mnrt} = C_{Mnrto} + e^{K_{Mnrt}t} \quad 8$$

Substituting C_{Mnrt} into Equation (6) gives the Manganese absorption model of Ewedu roots.

$$R_{Mnrt} = K_{Mnrt}\ (C_{Mnrto} + e^{K_{Mnrt}t}) \quad 9$$

Therefore,

$$R_{Mnrt} = 0.0450\ (C_{Mnrto} + e^{0.0450t}) \quad 10$$

The rate of manganese uptake by Jute roots is shown in Table 1. The rate increased with maturity/time, and is in partial agreement with the literature (Alloway 1990) that some heavy metals tend to accumulate in roots of plants. The developed model of the absorption of manganese in Jute roots is first order. It was validated as shown in Table 2. The experimental values of manganese concentrations in Jute's roots agree well with the predicted concentration values by the developed model with variations of 1.9% to 17.6%. The manganese absorption model shows a better prediction than the zinc absorption model reported by Chiroma, T. M (2018). This is further illustrated in Figure 4.

Table 2: Comparison between the experimental and model predicted Mn concentrations.

Time (days)	Conc. of Mn (Experimental) (µg/gday))	Conc. of Mn (Predicted) (ug/gday)	% Difference
31	4.65	4.2146	10.3
41	4.95	6.0066	17.6
51	9.15	8.6786	5.43
61	12.6	12.2306	3.02
71	16.35	16.6626	1.9

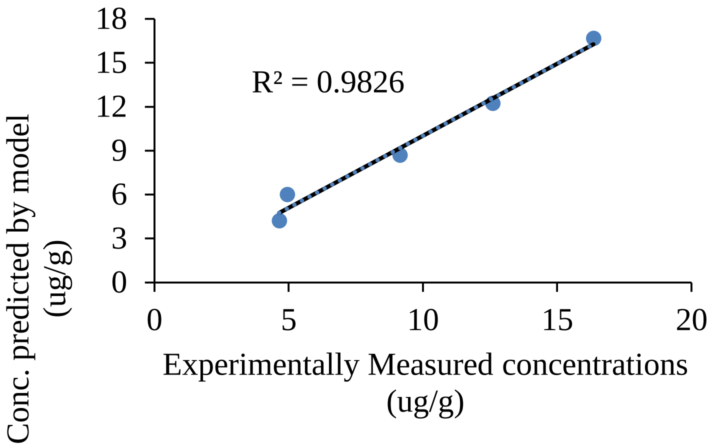

Figure 4: Variation of Mn concentrations predicted by model with experimental measured concentrations.

The experimental values of Manganese concentration in roots of Ewedu vegetable in Table 2 shows a higher degree of agreement with the concentrations of manganese predicted by the developed model. This is because of the lower percentage difference of between 1.9 to 17.6%. This suggest that Manganese has a good absorption rate in Ewedu roots.

The variation of Manganese concentrations predicted by the model with experimental values also gave a linear relationship with high correlation coefficient which also confirms that the experimental values agree with the values predicted by the model. (Figure 4)
It is clear from Figure 4 that deviations are higher at lower concentration values – the trend lines for both experimental and predicted concentrations merge each other, this shows that the model prediction values have a very high degree of agreement with the experimental values. This variation may be due to errors in experimental measurements and sample preparations.

Model Simulation

The concentrations of Manganese (Mn) at the early stage (0-30 days) of the root development (when the concentration was difficult to measure experimentally) and other periods (40, 50, 60, 70, 80 and 90 days) which are outside the experimental values were simulated using the developed model equations. The results of the predicted values are shown in Figure 5. It was observed that the trend of the predicted results is similar to that of the experimental measured values.
This clearly shows that the Mn absorption model equations can be used to simulate and hence predict the concentrations of the metal in Jute roots at any given time of its growth period. Also, Mn follows the same absorption mechanism as reported by Alloway (1990).
It was observed that even before planting, the vegetable seeds had Manganese concentration in it to the tune of about 5ug/g. That is at day zero, the concentration of Manganese in the vegetable was 5ug/g. Therefore, from

day zero and beyond, the Mn concentration in the vegetable could be measured with the aid of the developed model even before the roots starts developing and proper germination takes place.

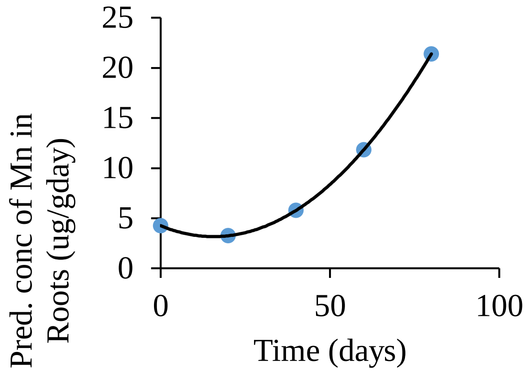

Figure 5: Variation of Mn concentration with time using model for prediction

Conclusion

The following conclusions could be made from the study:

- Jute vegetable is a low accumulator of Mn. Therefore, jute grown on manganese polluted loamy soil is safe for consumption at all stages of its growth.
- The concentrations of manganese ions in the roots of Jute vegetable increased with time of growth.
- The rate of manganese uptake increased with time.
- The kinetic model for rate of absorption of manganese in Jute roots is first order absorption kinetics.
- The mass transport coefficient was found to be $0.0450(\frac{\mu g}{gday})$.
- Jute's seeds have natural manganese content in it even before planting.

The validation of the experimental results of concentration of cadmium in Jute roots with the values predicted by the developed model is in good agreement with variations ranging from1.9% to 17.6%.

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