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RESEARCH ARTICLE

DEVELOPMENT OF MODEL EQUATION FOR ABSORPTION AND BIOACCUMULATION OF COPPER FROM POLLUTED SOIL INTO BUSHGREEN VEGETABLE

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ABSTRACT

The kinetics of absorption and bioaccumulation of copper (Cu) in Bush green roots was studied. A pot culture experiment was conducted to determine Cu uptake by roots of Bush green vegetable from polluted soils within the seventy one day growth period. The amount of copper ions (Cu^{2+}) in the roots increased with time in a polynomial fashion. The kinetic model for the rate of absorption is a second order, with the mass transport coefficient $K_{C_{urt}}$ of 1.05 x 10^{-5} $(\frac{\mu g}{gday})$ and the rate of absorption as $R_{C_{urt}} = \frac{dC_{C_{urt}}}{dt} = K_{C_{urt}}\, C^2_{C_{urt}}$. The experimental values of the concentrations of copper in the roots of Bush green vegetable were, in overall inagreement with the values predicted by the model, with variations in the range of 1.46% to 13.8% differences.

INTRODUCTION

Vegetables constitute an essential diet component by contributing protein, vitamins, iron, calcium and other nutrients, which are usually in short supply. Vegetables also act as buffering agents for acidic substances produced during digestion processes (Ejaz *et al.*, 2006). One major pollution source of heavy metals to the soil in Nigeria is the use of urban grey waste water in the irrigation of vegetables and food crops. The heavy metals from anthropogenic sources usually enter the environment in bioavailable forms, and then they can transform to other speciation. To understand the effects of combined heavy metal and, evaluate, forecast and prevent heavy metal pollution, well – designed studies are needed to determine the extent of heavy metal accumulation in soils and crops and to study the responses and uptake of heavy metals by vegetables (Wang *et al*., 2003, Pulford and Watso 2003). Heavy metals are biodegradable and tend to accumulate as metal organic complexes in living organisms, which increase their concentration in biological cycles (Lidija *et al.*, 2011)

Human intake of excessively large dose of copper leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression, severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur (Selvaraj *et al.,* 2004). Most plants that are able to survive on metal polluted soils have the ability to accumulate metals far in excess of any normal physiological requirements. They can extract metals such as Zn, Mn, Ni, Co and Cu from the soil and accumulate them in their shoots. These plants are known as hyper accumulators (Cristiana *et al.,* 2000). The problem of soil pollution has made hyperaccumulator plants prime candidates for phytoremediation work. Their abilities to extract heavy metals from soil can be exploited to reduce the metal content in polluted areas (Salt *et al.*, 1998). It is necessary to find a fast and reliable way to evaluate how the copper concentration changes with time throughout the bushgreen vegetable growth period. The concentration and time data obtained will be used to develop a kinetic model that will fit the rate of uptake of copper from the polluted soil with time. The developed model could be used to process growth and uptake data for a rapid assessment of time and concentration parameters for the deployment of bushgreen plant as hyperaccumulator of copper for phytoremediation purposes.

For the absorption mechanism in Bushgreen 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 order of rate of absorption.

Model Development

The above kinetic model is a special case of Fick's law (Danny, *et al., 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 metals is considered to take place in the axial (upward) direction.
- The rate is per unit length of transfer from the rhizophere to the root
- The concentration of the metal ions is uniform along the length of root, stem and leaf
- The absence of any reaction(or interaction) between absorbed ions
- The mechanism of ion transfer is by molecular diffusion

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Pot Culture Experiment

A pot culture experiment was conducted to determine Cu uptake by Bushgreen vegetable from the polluted soils. 3 kg of soil from the polluted area were weighed into five plastic pots; all samples were soaked with distilled water and allowed to stand for three days. 0.3g of Bushgreen seeds were weighed and planted into each pot and allowed to germinate. After germination the plants were allowed to grow and each pot were irrigated with 250 mls of clean tap water every evening. The pots were kept in a green house away from aerial pollution of heavy metals. Each vegetable pot was harvested at a specified time interval of 31, 45, 57, 64 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 and were spread on glass plate and dried in an oven at 105°C to a constant weight. The dried soil samples were ground with a pestle and mortar to pass through 0.5mm mesh sieve. Triplicates of 2g each of the sieved soil sample were weighed into a beaker, and was digested in a mixture of 50ml concentrated nitric acid (HNO_3) and 1ml concentrated perchloric acid ($HClO_4$) on hot plate with gentle boiling. At completion of digestion, the samples were evaporated to dryness and the residue mixed with 0.1M nitric acid and filtered into 100ml standard flask using whatman No1 filter paper.

Vegetable samples

The vegetable samples were reduced to fine powder in a grinder prior to drying at 60°C in an oven to a constant weight. 0.5g of the fine powdered vegetable samples was weighed into conical flask and digested in 4ml of concentrated perchloric acid ($HClO_4$), 2ml of concentrated sulphuric acid (H_2SO_4), 25ml concentrated nitric acid (HNO_3) and 1ml of hydrogen peroxide (H_2O_2) at 100°C on a hot plate for two hours in a fume cupboard. The resulting solution was made up to 100ml with distilled – deionized water.

RESULTS AND DISCUSSION

The variations of the concentration copper (Cu) in the roots of Bushgreen with time are shown in Figure 1 below:

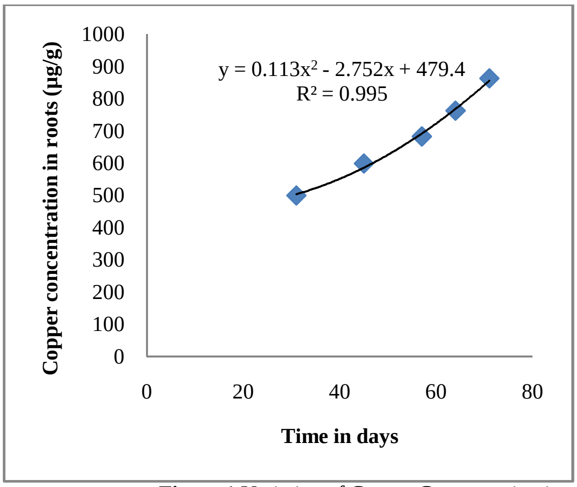

Figure 1 Variation of Copper Concentration in Bushgreen Root with Time

The empirical equation relating the concentration of Cu in bushgreen roots with time is a polynomial of second degree with correlation ratio of $R^2 = 0.995$

$$C_{Cu\,rt} = 0.113t^2 - 2.752t + 479.4 \qquad (2)$$

Differentiating equation (2) leads to

$$\frac{dC_{Cu\,rt}}{dt} = 0.226t - 2.752 \qquad (3)$$

The rate of metal uptake

$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt}$ at different times are given in Table 1

Applying the Kinetic Model to the Obtained Data

$$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt} = K_{Cu\,rt}\ C^n_{Cu\,rt} \qquad (4)$$

Taking the logarithm of both side of equation 4:

$$In\ R_{Cu\,rt} = In\ K_{Cu\,rt} + n\ In\ C_{Cu\,rt} \qquad (5)$$

The plot of $In\ R_{Cu\,rt}$ against $In\ C_{Cu\,rt}$ is expected to give a linear relationship with slope n and intercept $In\ K_{Cu\,rt}$ if the data is consistent with the model.

Table 1 The Rate of Copper Uptake with Time

Time in days	Rate ([illegible]) in µg/g-day
31	4.254
45	7.418
57	10.130
64	11.712
71	13.294

From Figure 2, slope, n = 2.094 and intercept, $In\ K_{Cu\,rt}$. = -11.46

Therefore $K_{Cu\,rt} = e^{-11.46} = 1.0544 \times 10^{-5}\ (\frac{\mu g}{gday})$

The result of the uptake level of copper ions as time increase is shown in Figure 1. It can be seen that the concentration of copper ions in Bushgreen root increase gradually up to maturity. The empirical equation (2) relating the concentration in Bushgreen root with time is a polynomial of second order and correlation ratio of R^2 = 0.995, It was also observed that the uptake rate gradually increases with time as shown in Table 1. This may be ascribed to low translocation of copper from root to the shoot which leads to the accumulation of copper in root of Bushgreen with time (Alloway 1990).

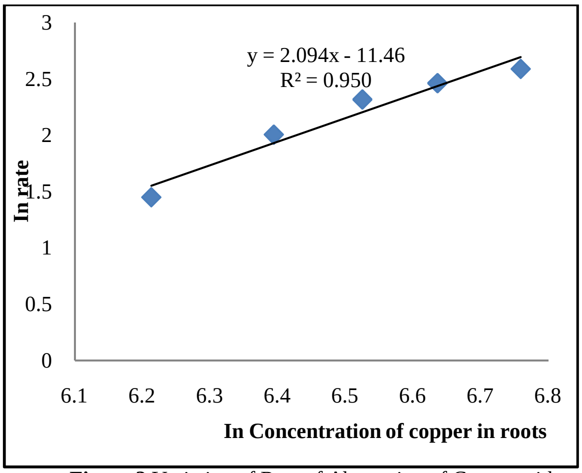

Figure 2 Variation of Rate of Absorption of Copper with Concentration in the Roots

The study also showed that the absorption of copper by Bushgreen roots followed second order absorption kinetics with the mass transport coefficient k as 1.0544×10^{-5} ($\frac{\mu g}{gday}$)). Some researchers (selveraj *et al.*, 2004) who studied the batch adsorptive removal of copper ions in aqueous solutions by ion exchange resin (1200H) reported that the adsorption followed a pseudo-second order kinetic model. From the empirical model, the rate of absorption is of second order since n =2 and therefore the absorption model

$$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt} = K_{Cu\,rt}\; C^2_{Cu\,rt} \quad (6)$$

Rearranging the equation above,

$$\frac{dC_{Cu\,rt}}{C^2_{Cu\,rt}} = K_{Cu\,rt}\,dt \quad (7)$$

Integrating Equation (7)

$$\int_{C_{Cu\,rt\,o}}^{C_{Cu\,rt}} \frac{dC_{Cu\,rt}}{C^2_{Cu\,rt}} = \int_{t_o}^{t} K_{Cu\,rt}\,dt \quad (8)$$

This gives;

$$C_{Cu\,rt} = \frac{C_{Cu\,rt\,o}}{1 - K_{Cu\,rt}\,tC_{Cu\,rt\,o}} \quad (9)$$

But the rate;

$$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt} = K_{Cu\,rt}\; C^2_{Cu\,rt} \quad (10)$$

It implies that

$$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt} = K_{Cu\,rt}\left(\frac{C_{Cu\,rt\,o}}{1 - K_{Cu\,rt}\,tC_{Cu\,rt\,o}}\right)^2 \quad (10)$$

$$but\; K_{Cu\,rt} = 1.05 \times 10^{-5}$$

$$R_{Cu\,rt} = 1.05 \times 10^{-5}\left(\frac{C_{Cu\,rt\,o}}{1 - 1.05\times10^{-5}\,tC_{Cu\,rt\,o}}\right)^2 \quad (11)$$

The rate of copper uptake by the bushgreen roots is shown in Table 1. The rate increased with time, is inagreement with the literature (Alloway 1990) that copper tends to accumulate in roots of plants. The developed model of the absorption of copper in bushgreen roots was validated as shown in Table 2. The experimental values of copper concentrations in bushgreen roots agree well with the concentration values predicted by the developed model with variations of 1.46% to 13.8%. This is further illustrated in Figure 3.

Table 2 The Experimental and Model Predicted Values of Copper Concentration.

Time	Rate	Concentration (experimental µg/g)	Concentration (prediction µg/g)	% Difference
31	4.254	499	568	13.8
45	7.418	598	620	3.67
57	10.13	682	672	1.46
64	11.712	762	707	7.2
71	13.294	862	746	13.45

It is clear from figure 3 that the deviations are higher at lower and higher concentration values – all points would have been on the dotted line if the model prediction had been perfect. This variation may be due to errors in experimental measurements and sample preparations.

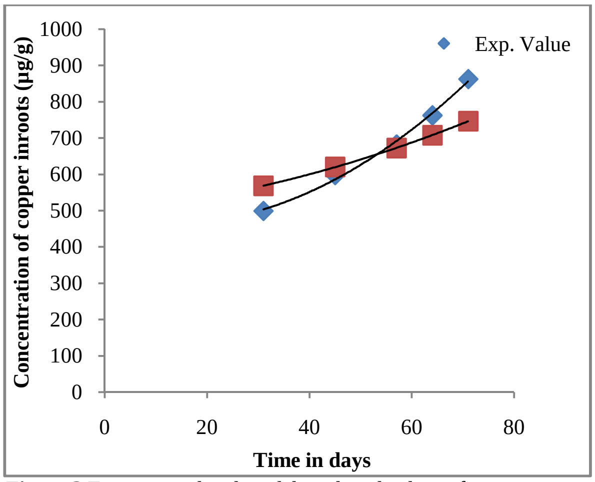

Figure 3 Experimental and model predicted values of concentration of copper with time

CONCLUSION

The following conclusions could be made from the study:
The concentration of copper ions in the roots of bushgreen vegetable increased with time of growth. The kinetic model for the rate of absorption of copper in bushgreen roots is a second order, as is given by

$$R_{Cu\,rt} = \frac{dC_{Cu\,rt}}{dt} = K_{Cu\,rt}\; C^2_{Cu\,rt}$$

The mass transport coefficient was found to be 1.05 x 10^{-5} ($\frac{\mu g}{gday}$).

The validation of the experimental results of concentration of copper in bushgreen root with the value predicted by the developed model is in good agreement with variations ranging from 1.46% to 13.8%.

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