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# Modeling and Optimization of Phytoremediation Kinetics of Metals in Soil by A Plant Hyperacumulator

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***Abstract:****Systems of ODEs were used to simulate the xylem and phloem transport kinetics of heavy metals in a phytoremediation process. Experimental data from scholarly works were used to validate the models. Analytical solutions of the models gave accuracies of between 99.79% and 99.91% for the 2nd order pseudo model while the 1st order pseudo model did not apply. The transportation of contaminants through the xylem tissue shows that there is a general decrease in concentration up the plant with time while the transport of heavy metals through the phloem shows an increase or a free-fall profile mechanism. The implication is that if transportation of contaminants in the phloem tissue continues at longer times, the sigmoidal profile may set in since it is a natural process. Results from optimization revealed that in 88.2 days, 25.24mg of lead (Pb) was taken up from the soil by the plant hyper-accumulator while in 1200days (3.3yrs), 65.3735gm of cadmium with an initial concentration of 100μg was taken up from the soil. This shows that the model is a good predictive tool for determining the chunk weights of heavy metals removed in a phytoremediation process.*

***Keywords:****Modeling, Optimization,Phytoremediation,Plant hyperacumulator,Pseudo second order.*

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## I. INTRODUCTION

Remediation of sites contaminated with toxic metals is particularly challenging because of the ills associated with the traditional methods employed as means of control which involve the use of stringent physicochemical agents that inhibit soil fertility and impact negatively on the ecosystem. Phytoremediation involves the use of a different approach which entails the use of eco-friendly plants to remove contaminants from contaminated soils and water. Arshad [1] conducted a field study on lead phytoextraction using scented Pelargonium cultivars. The Richards first and second order models can be used to describe the interactions occurring in plants during phytoextraction of metals from soils [2]. Canales-pastrana and Paredes [3] opined that

Phytoremediation has not been fully commercialized because of the existence of uncertainties (i.e. contaminant, contaminant concentration and the several physiological behaviors of plants) that exist during the process Phytoremediation is a cleanup technology for polluted/contaminated water [4]. The potential for this technology is high in the tropics due to the prevailing climatic conditions which favor plant growth and microbial activities[5]. The efficiency of phytoremediation depends on the nature of the contaminants [6].The cost of remediation by rhizofiltration has been estimated to be \$2-\$6 per 1000 gallons of water [7]. Heavy metals such as Pb are very hazardous to plants and their consumers [8].Previous approaches employed involved the use of mathematical algorithms (differential equation solution jet, statistical correlation and system dynamic approach) to characterize phytoremediation systems. Chrysafopoulou et al. [9] simulated the phytoremediation of a soil using a maize plant based mechanistic model. Their simulation results show that precipitation is the most important mechanism related to the uptake of Pb from the ground.Phytoremediation is brought about by the complex interactions which affects plant activities during the removal of metals from soils [10].Another mechanism is rhizodegradation/phytostimulation which involves the breakdown of contaminants within the plant root zone or rhizosphere [11, 12].Exposuresof non-metal accumulator plants to metals like mercury (Hg) or its compounds can cause irreversible damage to the human nervous system [13]. Although, some plantshave been reported to have genetic potential to remove toxic metals from soils, the method is yet to be established as a commercially available technology [14]. The efficiency and effectiveness of phytoextraction and phytovolatilization depends largely on the hydrophobic nature of the contaminants [15]. Its progressive use is deterred by lack of understanding of the complex interactions in the rhizosphere of plants during metal translocation and accumulation. The existence of plant metal hyper-accumulators capable of accumulating metals, shows that some plants are potential remedies to contaminated soils [16].Despite being energy intensive and expensive, the potential for this technology is high in the tropics due to the prevailing climatic conditions which favor plant growth and microbial activities[17, 18, 19], therefore, there is need to explore alternatives or support methods such as the use of mathematical models that simulate the process mechanisms with the possibility of optimizing plant use for lesser cost implications [20]. In addition, the removal of heavy metals from soils/environs should be a priority to the environmental scientist since they are not easily degraded [21, 22]. The existence of metal hyper-accumulator plants complements the need to maximize the use of these potential plants, for the removal of metals from contaminated soils.In a study, sunflower was found to have reduced the water-lead-concentration significantly after one hour [23].Mechanisms of phyto-extraction include Rhizo-filtration which is employed for the removal of Pb, Cd, Cu, Ni, Zn and Cr; phyto-volatilization is the removal of contaminants from soils using plants which transform the contaminants into volatile matter before transpiring them into the atmosphere; phyto-stabilization involves the use of certain plant species for the remediation of contaminated soil, sediments and sludge; phyto-degradation/phyto-transformation is the disintegration of complex organic molecules to give simple molecules.It has been reported thathigh exposures of heavy metals or their compounds to plants can cause irreparable consequences to humans and their habitations [24]. Although, the implementation of phytoremediation may involve someeconomic implications [25], other less expensive hyper-accumulator plant species capable of accumulating 100 times more metal than a common non-accumulating plant are still being discovered [26-29]. Although the mechanism and efficiency of phytoremediation depends on the type of contaminants [30, 31],the removal of heavy metals from soils should be given special concerns since the metals severely alter soil-chemistry [32-34]. Onemajor factor responsible for the high recommendation of the use of phytoremediation in the tropics, is the average climatic condition of those places [35].

In this work, a mathematical descriptionof the mechanisms of the complex interactions that exist during phytoremediation has been attempted. The model approach also provides a good understanding of the activities of these metals in plants and in turn gives information on how to maximize the clean-up potentials of plant hyperaccummulators that have the ability to take up heavy metals from their host soils. Also, the complex kinetic mechanisms of the phytoremediation stages (phyto-stabilization/phyto-stimulation, phyto-extraction, phyto-volatilization) were modeled for the entire process in order to maximize the effectiveness of the inclusion of plant-accumulators in the contaminated media.

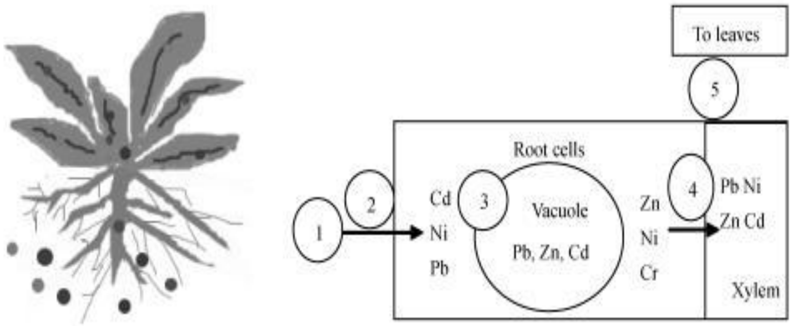

**Fig 1**: Metal transfer in plants (Raskin and Ensley, 2000)

Fig. 1 shows a typical plant-metal uptake process. The plants used for the cleanup process are usually raised in greenhouses with their roots in water rather than soils so as to ensure good adaptation, and as soon as a large root system is developed, contaminated water is then used as their water source. The plants were then planted in the contaminated area where the roots take up the water and the contaminants. Fig. 2 shows the complex interactions that take place in the rhizosphere of plants. These complex interactions are affected by plant activities climatic conditions, soil properties etc. [10].

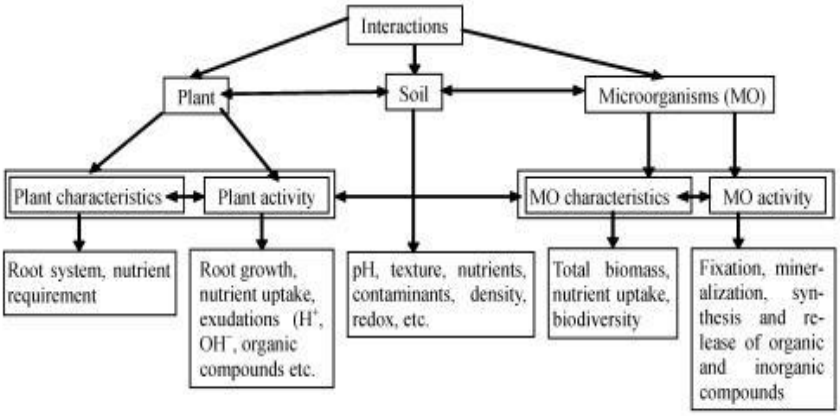

**Fig 2**: Plant soil microbial interactions in rhizosphere (Giller et al., [12])

## II. METHOD

### 2.1 Data Collection

The data in Tables 1 and 2 were used to ascertain the validity of the established models.

**Table 1**: Mass of Pb (mg) phyto-remediated with time

| t (days) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb(mg) | 0 | 20 | 50 | 130 | 255 | 400 | 620 | 850 | 1050 | 1300 | 1550 | 1770 | 2020 |

(Chrysafopoulou et al.[9])

**Table 2:** Cumulative mercury concentration (Hg) volatilized during phytoremediation with time

| t (days) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hg (mg) | 0 | 0 | 0 | 0.46 | 1.65 | 12.5 | 3.131 | 3.35 | 3.4 | 3.4 | 3.4 |

(Canales-Pastrana and Paredes, [3])

**Table 3:** Concentration of Cd (in two phases at 10μm and 100μm) per plant during phytoremediation with treatment time

| t (h) | 0 | 24 | 48 | 72 | 96 | 120 | 144 | 168 | 192 |
|---|---|---|---|---|---|---|---|---|---|
| Cd (10μg/plant) | 0 | 40 | 75 | 104 | 130 | 148 | 162 | 180 | 182 |
| Cd (100 μg/plant) | 0 | 3 | 4 | 5 | 8 | 17 | 28 | 47 | 78 |

(Canales-Pastrana and Paredes, [3])

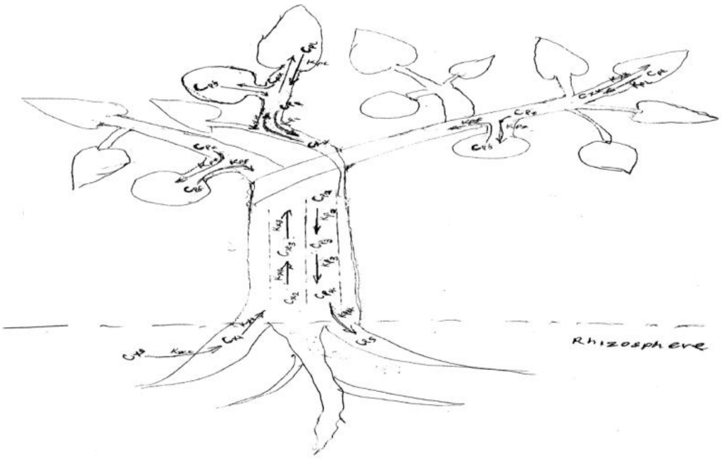

**Fig 3:** Adiagram of a typical hyperaccumulator plant

### 2.2 Model Adoption and Development

The Richard's 1st and 2nd order pseudo models discussed in [2] were adopted. The models were solved analytically and validated with experimental data. A kinetic model of a typical plant hyperaccumulator was developed by first drawing the plant and representing the mechanism from its rhizosphere (phytoextraction into the root) to the atmosphere (phytovolatilization from the leaves into the atmosphere), through the stem (Fig. 3). From the labels following the arrows up through the xylem and down through the phloem, a kinetic model was developed which resulted into the systems of ODE's for the movement of a typical metal up or down the plant. These two groups of systems of ODE's (phloem and xylem ODEs) were solved using MATLAB 7.9 which was also used to present the profile of these metals as phytoremediation was in progress. These profiles will give mankind an in-depth understanding of the mechanisms of phytoremediation process, and of course, provide insight on how to optimize the process.

### 2.3 Analytical Solution of the Richard's Model

### 2.3.1 Kinetics of Phytoremediation as Pseudo First and Second Order Phenomena

**(i) First Order**

$$\frac{dq}{dt} = k_1(q_m - q) \qquad (1)$$

$$\frac{dq}{q_m - q} = k_1 dt \qquad \boxed{\begin{aligned} u &= q_m - q \\ du &= -dq \end{aligned}} \qquad (2)$$

$$\frac{du}{u} = k_1 dt \qquad (3)$$

$$lnu/_{u}^{u_o} = /k_1 t/_{t}^{t_0} \qquad (4)$$

$$ln(q_m - q)/_{q}^{q_0} = k_1 t/_{t}^{t_0} \rightarrow ln(q_m - q_0) - ln(q_m - q) = -k_1(t_0 - t) \qquad (5)$$

$$ln\frac{q_m - q_0}{q_m - q} = -k_1(t_0 - t) \qquad (6)$$

$$ln\frac{q_m - q}{q_m - q_0} = k_1(t_0 - t) \qquad (7)$$

$$\theta = \frac{q_m - q}{q_m - q_0} = e^{k_1(t_0 - t)} \qquad (8)$$

$$\boxed{q = q_m - (q_m - q_0)\, e^{k_1(t_0 - t)} Pseudo -} 1storderequation \qquad (9)$$

**(ii) Second Order**

$$\frac{dq}{dt} = k_2(q_m - q)^2 \qquad \boxed{\begin{aligned} U &= q_m - q \\ du &= -dq \end{aligned}} \qquad (10)$$

$$k_2 dt = \frac{dq}{(q_m - q)^2} = \frac{-du}{u^2} = -u^{-2}du \qquad (11)$$

$$k_2 t/_{t}^{t_0} = u^{-1} = \frac{1}{u} = \frac{1}{q_m - q}/_{q}^{q_0} \qquad (12)$$

$$k_2(t_0 - t) = \frac{1}{q_m - q_0} - \frac{1}{q_m - q} = \frac{q_0 - q}{(q_m - q_0)(q_m - q)} \qquad (13)$$

$$\boxed{q = \frac{q_0 - q_m\ (q_m - q_0)e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} Pseudo -} 2ndorderequation \qquad (14)$$

The derivative of (14), the pseudo 2nd order equation produces a dumb-bell profile which optimizes the model thus:

$$Dq = \frac{k_2^2(q_m - q_0)^2 e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} \qquad (15)$$

And the peak of the model is obtained by taking the 2nd derivative of equation (14), equating to zero and solving for the phytoremediation time parameter gives:

$$\mathrm{t} = t_0 - \frac{1}{k_2}\ln\frac{-1}{q_m - q_0} \qquad (16)$$

### 2.3.2 System of Equations through the Xylem Tissue

At t = 0, $Cx_0$ = 5000ppm

$$\left.\begin{aligned}
\frac{dcx_0}{dt} &= K_{x0}C_{xo} \\
\frac{dcx_1}{dt} &= K_{x0}C_{xo} - K_{x1}C_{x1} \\
\frac{dcx_2}{dt} &= K_{x1}C_{x1} - K_{x2}C_{x2} \\
\frac{dcx_3}{dt} &= K_{x2}C_{x2} - K_{x3}C_{x3} \\
\frac{dcx_4}{dt} &= K_{x3}C_{x3} - K_{x4}C_{x4} \\
\frac{dcx_X}{dt} &= K_{x4}C_{x4} - K_{xX}C_{xX} \\
\frac{dc_{pl}}{dt} &= K_{xx}C_{xx} - K_{pl}C_{pl}
\end{aligned}\right\} \qquad (17)$$

### 2.3.3 System of Equations down the Phloem

$$\left.\begin{aligned}
\frac{dc_{px}}{dt} &= K_{pl}C_{pl} - K_{px}C_{px} \\
\frac{dc_{pf}}{dt} &= K_{px}C_{px} - K_{pf}C_{pf} \\
\frac{dc_{p1}}{dt} &= K_{pf}C_{pf} - K_{p1}C_{p1} \\
\frac{dc_{p2}}{dt} &= K_{p1}C_{p1} - K_{p2}C_{p2} \\
\frac{dc_{p3}}{dt} &= K_{p2}C_{p2} - K_{p3}C_{p3} \\
\frac{dc_{p4}}{dt} &= K_{p3}C_{p3} - K_{p4}C_{p4} \\
\frac{dc_{p5}}{dt} &= K_{p4}C_{p4}
\end{aligned}\right\} \qquad (18)$$

No transpiration from leaf and fruit to the atmosphere

No diffusion from root to the rhizosphere

If $C_x = y$ and $C_1 = x$, $K_x = k$, $k_p = \mu$

Then for the xylem tissue,

$$\left.\begin{aligned}
\frac{dy_0}{dt} &= k_0y_0 \\
\frac{dy_1}{dt} &= k_0y_0 - k_1y_1 \\
\frac{dy_2}{dt} &= k_1y_1 - k_2y_2 \\
\frac{dy_3}{dt} &= k_2y_2 - k_3y_3 \\
\frac{dy_4}{dt} &= k_3y_3 - k_4y_4 \\
\frac{dy_x}{dt} &= k_4y_4 - k_xy_x
\end{aligned}\right\} \qquad (19)$$

For the phloem tissue,

$$\left.\begin{aligned}
\frac{dx_0}{dt} &= \mu_L x_L - \mu_x x_x \\
\frac{dx_f}{dt} &= \mu_x x_x - \mu_f x_f \\
\frac{dx_1}{dt} &= \mu_f x_f - \mu_1 x_1 \\
\frac{dx_2}{dt} &= \mu_1 x_1 - \mu_2 x_2 \\
\frac{dx_3}{dt} &= \mu_2 x_2 - \mu_3 x_3 \\
\frac{dx_4}{dt} &= \mu_3 x_3 - \mu_4 x_4 \\
\frac{dx_5}{dt} &= \mu_4 x_4
\end{aligned}\right\} \qquad (20)$$

# III. RESULTS AND DISCUSSION

## 3.1 Result presentation

The results of the phytoremediation modeling are presented in Figures 4a – 6c, and Tables 4, 5 and 6.

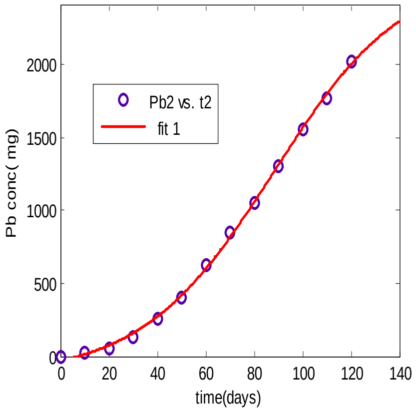

Fig4a: Pb concentration versus time in days (pseudo 2nd order process)

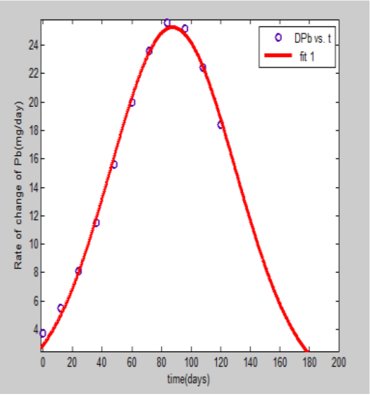

Fig 4b: Rate of change Pb versus time of phytoremediation

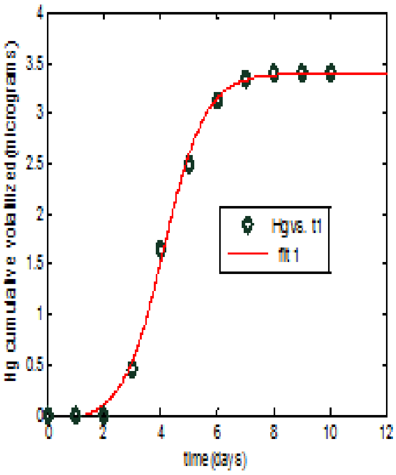

Fig5a:Hg concentration versus time in days (pseudo 2nd order process)

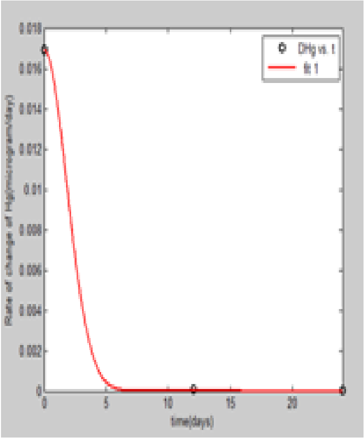

Fig 5b:Rate of change of volatilized Hg versus phytoremediation time

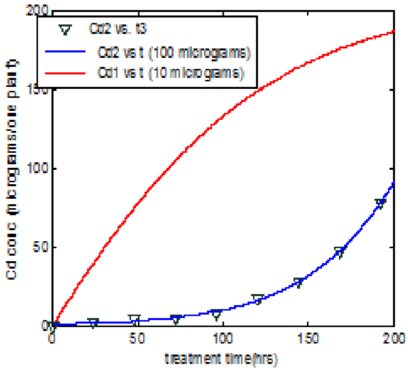

Fig 6.a: Cd concentration versus treatment time (h) (pseudo $2^{nd}$ order process)

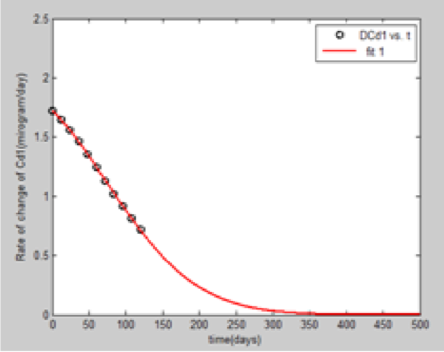

Fig 6b:Rate of change of Cadmium versus treatment of phytoremediation for 10μg

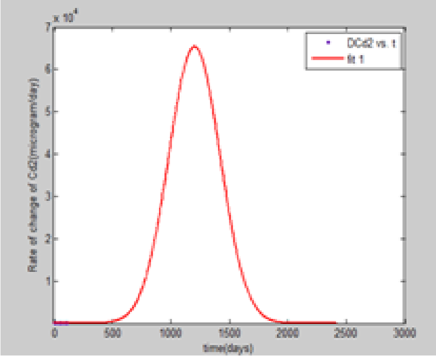

Fig6c: Rate of change of Cadmium versus treatment of phytoremediation for 100μg

**Table 4:** Coefficients and statistical goodness of fit using data in Table 1 ($Pb_2$vs $t_2$)

| | |
|---|---|
| $K_2$ = 0.03697 | SSE = 6243 |
| $q_m$ = -136 | $R^2$ = 0.9990 |
| $q_0$ = 2646 | R Adj = 0.9986 $2^{nd}$ order |
| $t_0$ = -126.7 | RMSE = 26.34 |

**Table 5:** Coefficients and statistical goodness of fit using data in Table 2 (Hg vs $t_1$)

| | |
|---|---|
| $K_2$ = 1.369 | SSE = 0.04999 |
| $q_m$ = -0.08371 | $R^2$ = 0.9979 |
| $q_0$ = 3.397 | R Adj = 0.997 $2^{nd}$ order |
| $t_0$ = 3.207 | RMSE = 0.0845 |

**Table 6a:** Coefficients and statistical goodness of fit (Cd vs t) using data in Table 3 (10μm)

| | |
|---|---|
| $K_2$ = 0.01357 | SSE = 30.62 |
| $q_m$ = -322.8 | $R^2$ = 0.9991 $2^{nd}$ order |
| $q_0$ = 208.4 | R Adj = 0.9985 |
| $t_0$ = -494.7 | RMSE = 2.474 |

**Table 6b:** Coefficients and statistical goodness of fit (Cd vs t) using data in Table 3 (100) μm

| | |
|---|---|
| $K_2$ = 0.02382 | SSE = 6.02 |
| $q_m$ = 0.173 | $R^2$ = 0.9989 $2^{nd}$ order |
| $q_0$ = 510.3 | R Adj = 0.9982 |
| $t_0$ = 2.253 | RMSE = 1.097 |

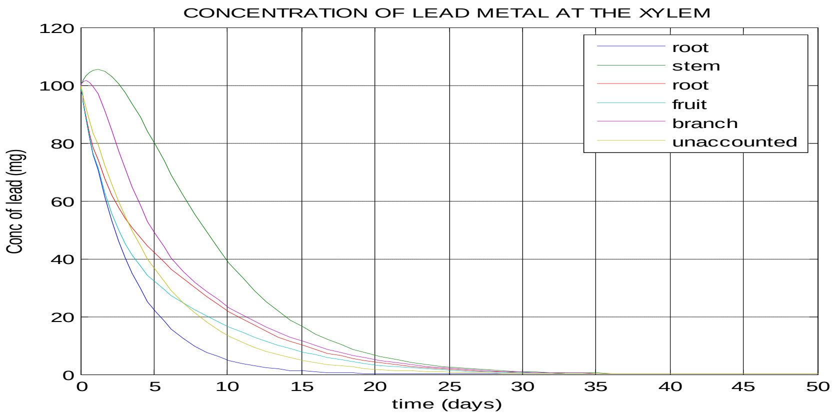

**Fig 7a**: Concentration (mg) of lead metal through the plant Xylem at various plant parts versus phytoremediation time

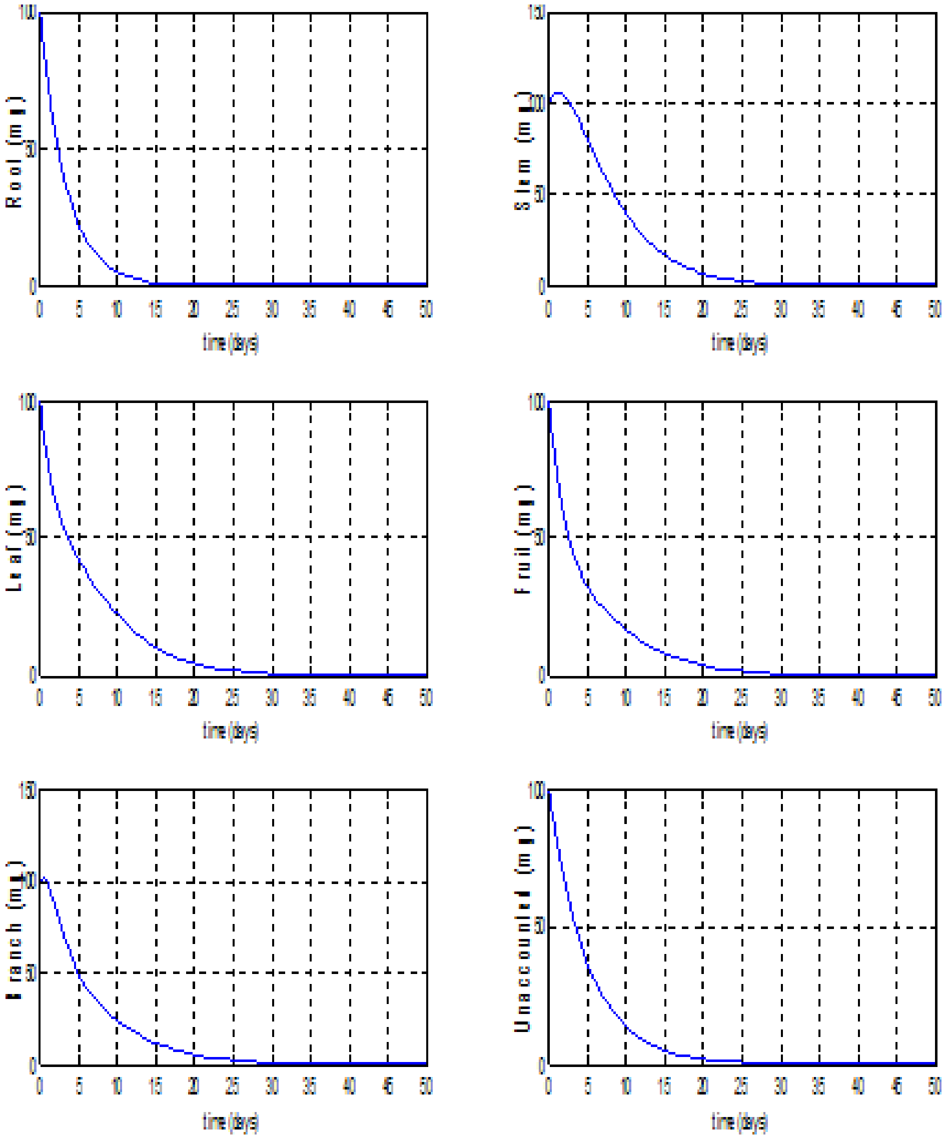

**Fig7b:**Concentration (mg) of lead metal through the plant Xylem at various plant parts versus phytoremediation time

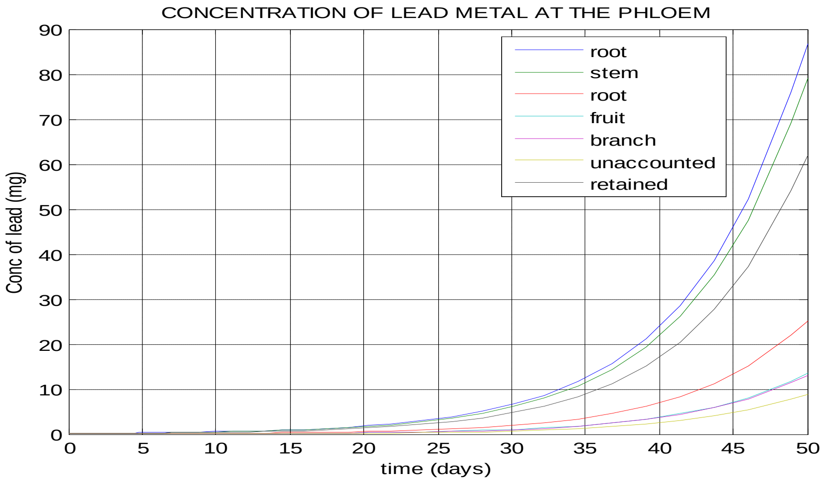

**Fig8a**: Concentration (mg) of lead metal through the plant Phloem at various plant parts versus phytoremediation time

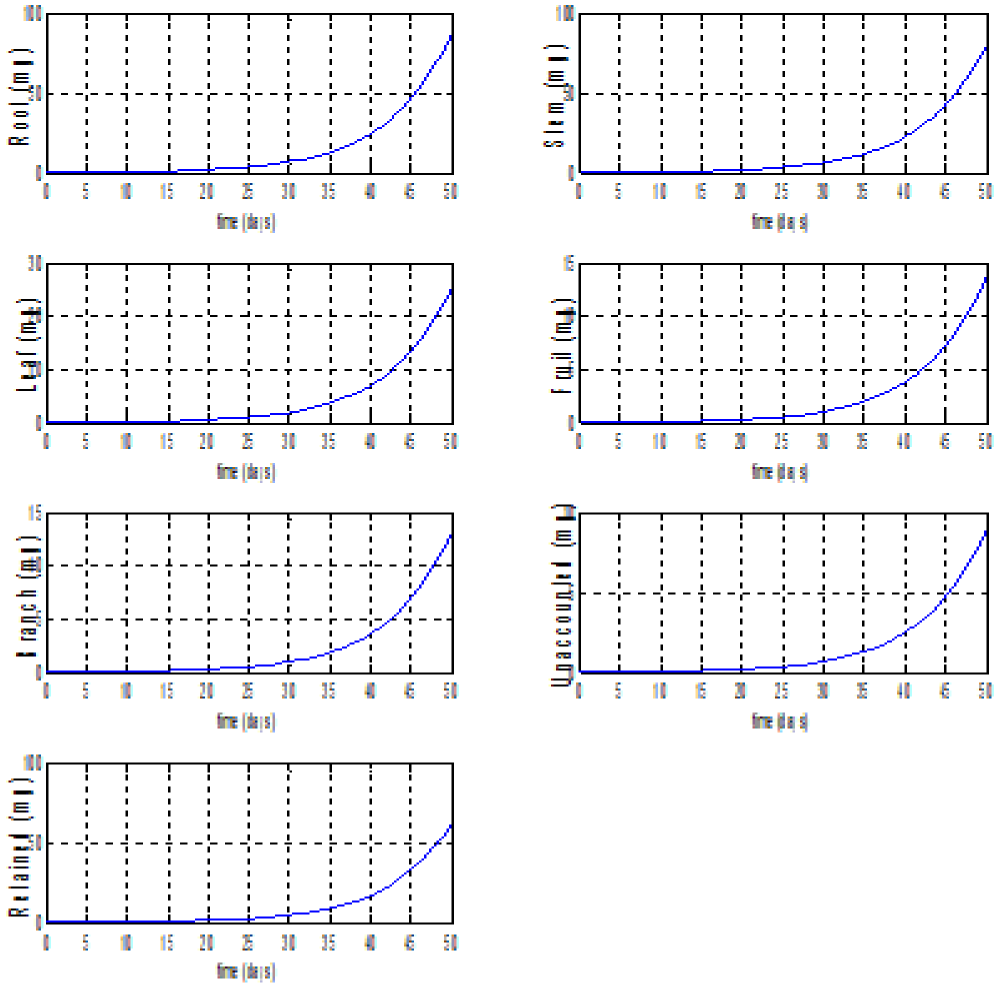

**Fig 8b**: Concentration (mg) of lead metal through the plant Phloem at various plant parts versus phytoremediation time

### 3.2Discussion of Result

The analytical solutions of 1st and 2nd pseudo order of Richard's models were tested with phytoremediation data obtained from literature. The results in Figs. 4a-6c show that the remediation process is a sigmoidal pseudo 2nd order process and does not apply to pseudo 1st order. This shows that the metal concentration in plants phytoremediation obeys a pseudo 2nd order relationship of the Richard's model; this is because almost all natural phenomena have sigmoidal profile or logistic. Tables 4, 5, 6a and 6b are the respective tables of coefficients andstatistical goodness of fit. Fig. 4 shows a 99.9 % fitness/correlation or agreement between experimental data in Table 4 and model prediction. The plot in Fig. 5 gives an accuracy of 99.79% between experimental data and model predictions while Figs. 6a and b show accuracies/agreements of 99.91% and 99.89% between model and experimental measurements for 10μM and 100μM initial concentrations of Cadmium respectively.

The constitutive equations or system of models developed are phenomenal as the ODEs gave rise tothe plots presented asFigs 7a and 7b, 8a and 8b were made. From the plots, it was observed that the concentration of metals flowing through the xylem decreased with time and distance up through the plants from the roots, stem, branch, fruits and leaves). Fig. 7b is a plot of specific parts of plant that underwent phytoremediation. As the roots, fruits and leaves showed a general decline in concentration of heavy metals with time. Therefore, phytoremediation in this plant parts is somewhat similar while its branches and stem show an early peak immediately after metal up-take. This is because there is no perspiration or evaporation from the bark of the plant stem & branches unlike the leaves, and fruits where perspiration and evaporation (phyto-volatilization) takes place. However, for the roots, some heavy metals may have escaped through other available pores. In Fig 8a, the movement reverses; the concentration of metals increase downward with the fluid, time and distance. Also, in Fig. 8b, the characteristic profiles of the root, leaves, stem and branches are almost the same. This is because, the volatilizations in the stem and branches downward do not affect the concentration of metals that flow down through the phloem. Considering Figs. 8a and 8b, if the phytoremediation was continued for more days, thelonger roots may exhibit/show natural phenomena as those of Figs. 7a and 7b which are pure natural decline curves.

Upon optimization of model Equation 14 which incorporates (15), it is evident in Fig. 4b that F (88.2) = 25.24 mg i.e. in 88.2 days (0.24 years = 2.9 months), the optimized concentration of metal uptake for during phytoremediation gave a peak value of 25.24 mg of Pb. In Fig. 4b, upon optimizing the mercury uptake, it is clear that after the initial value of 0.017μg in zero time, this value continues to fall rapidly in about 5-6days.

The optimization of cadmium (Cd) shows some discrepancies for an initial concentration of 10μg. From an initial value of 1.75μg per day in zero time, the fall is very rapid; these values continue to fall gradually between 250 – 350 days. However, for an initial concentration of 100μg, the optimization was different. In a time of 1200days (3.3yrs), the optimized cadmium uptake of the plant is 65,373.5μg or 65.3735 g. Thus, the result shows that the adopted plant can comfortably remove a chunk of metal weights with time during phytoremediation as given by the model. Furthermore, the phytoremediation process can be described as real and effective.

## IV. CONCLUSSION

The modelsused in this work have shown proven to be very useful for describing the xylem and phloem transport kinetics. The model results conformed with the results from experimental data. The analytical solution gave accuracies in the range of 99.79% - 99.91% for thepseudo 2ndorder model while the 1st order pseudo model showed low levels of applicability. The systems of ODEs show that phytoremediation is a natural but phenomenal process; the xylem transportation shows general decrease in concentration up the tree with time while the phloem concentration down the tree shows an increase or a free-fall profile mechanism with time. It is expected that if the transport of metals in the phloem tissues of the plants as shown in Figs. 8a & 8b is continues in the roots at longer times, sigmoidal profile may set in since it is a natural process. Upon optimization, it was evident that at 88.2 days, 25.24 mg of lead (Pb) was taken up from the soil by the hyperaccumulator plant and that after 1200days(3.3yrs),65.3735μg of cadmium (Cd) was removed from the soil. This shows that phytoremediation can comfortably remove heavy metals from the soil. The result of this work is very imperative as it has been discovered that phytoremediation in the plant obeyed pseudo 2nd order reaction and is also a natural process, regardless of whether it occurs inthe xylem or phloem.

## V. RECOMMENDATIONS FOR FUTURE STUDY

The Richard's 1storder pseudo model should undergo further study in order to investigate the possibility of some conformance with some hyperaccumulator during metal uptake. Further studies should be undertaken with this kind of hyperaccumulator plant to see if there may be possible ways of adopting it for the removal of otherunwanted substances (i.e. aside metals e.g. nitrites) from the soils. Hyperaccumulator plants must be uprooted so that fresh ones may be replanted once they are metal-laden so as to avoid plant-metal saturation which may in turn result in supposedly adsorbed metals returning back to the soil; this is because, the xylem transporter must have been loaded up to its maximum capacity in a given plant metal accummulator.

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