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Predicting Mobility of Cadmium (Cd) and Lead (Pb) in Contaminated Soil through a Mathematical Model

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Abstract. Indiscriminate discharge of industrial effluent particularly pharmaceutical effluent on agricultural soils poses serious health risk to plants, animals and ultimately humans. This study was carried out to predict the mobility of two of the most lethal soil pollutants (Cadmium and Lead). As such, the concentrations of Cadmium and Lead in soil at the initial point of effluent disposal and at subsequent points 4m, 8m, 12m, 16m and 20m away from the point source were determined. A simplified version of transport equation was used to simulate the mobility of Cadmium and Lead in the soil using polymath professional version 6.1. The simulated result showed a good level of agreement with the experimental data with correlation coefficients of 0.92 and 0.96 for Pb and 0.89 and 0.97 for Cd mobility respectively. Thus the model can be considered as a good representation of the phenomenon of mobility of heavy metals in the soil.

Keywords: Industrial effluent, Agricultural soils, Mobility, Simulation, Point source pollution

1. INTRODUCTION

The advent of the 21st century has brought about the proliferation of industrial and manufacturing activities. Though, these industries are contributing immensely to the socio-economic status of the populace, they are also having enormous adverse effects on the environment (Xu *et al.*, 2014). The environment, on which depends the survival and wellbeing of organisms, animals and humans, has been the major recipient of these wastes. The chemical reaction between the wastes constituent and the major components of the ecosystem are usually irreversible leading to undesirable changes in our environment (Odoi *et al.*, 2011). Alteration of the ecosystem by these chemical reactions is not without any implications on health of the rapidly growing world's population (Akanmu and Adenike, 2010).

The introduction of industrial waste like any other pollutants into the environment can either be from a point source where the source of pollutant can be easily traced or a non-point source where the origin of the pollutant is difficult to establish (Animashaun *et al.*, 2016). Depending on their constituent these are either organic or inorganic pollutants. Industrial wastes are mostly inorganic in nature in the sense that

they contain minerals or heavy metals in large quantity (Olaitan *et al.*, 2013).

Contamination of the environment particularly agricultural soil by heavy metals, have received immense attention by researchers all over the world, due to the enormous threat they pose to agricultural produce (Bharti *et al.*, 2013). Heavy metals in agricultural soil are taken up by plant's roots and accumulate in plant's tissues, which alters the plant's potential for maximum yield and quality produce (Animashaun *et al.*, 2015). More so, the tendency of heavy metals for bioaccumulation pose a great risk to human health, as science has not been able to proffer solution on how to effectively eject them from the human system. Some (Such as Cd and Pb) are carcinogenic as they affect a number of human vital organs and cause several forms of diseases (Lokeshappa *et al.*, 2012). The presence of heavy metals in soil indicates the potential for transfer of pollutant from soil to food and eventually to man (Mwegoha and Kihampa, 2010).

Though, a number of researches have been done on the agricultural soils in maitumbi, there is still a knowledge gap needed to be filled. Okoli (2015) revealed that the soil around pharmaceutical industries in Minna contains high content of Cd and Pb but no

work has been done to predict the mobility of these pollutants. Thus, this work aimed at employing a mathematical model in predicting the mobility of Cadmium and Lead in agricultural soil contaminated with pharmaceutical effluent.

2. MATERIALS AND METHOD

2.1. Study Area

The study site was Maitumbi industrial layout located at latitude $9^{\circ} 38' 11''$ N and longitude $6^{\circ} 34' 50''$ E in Minna, Niger State. The study involved sampling of soil around a Pharmaceutical company effluent discharge path. (Figure 1)

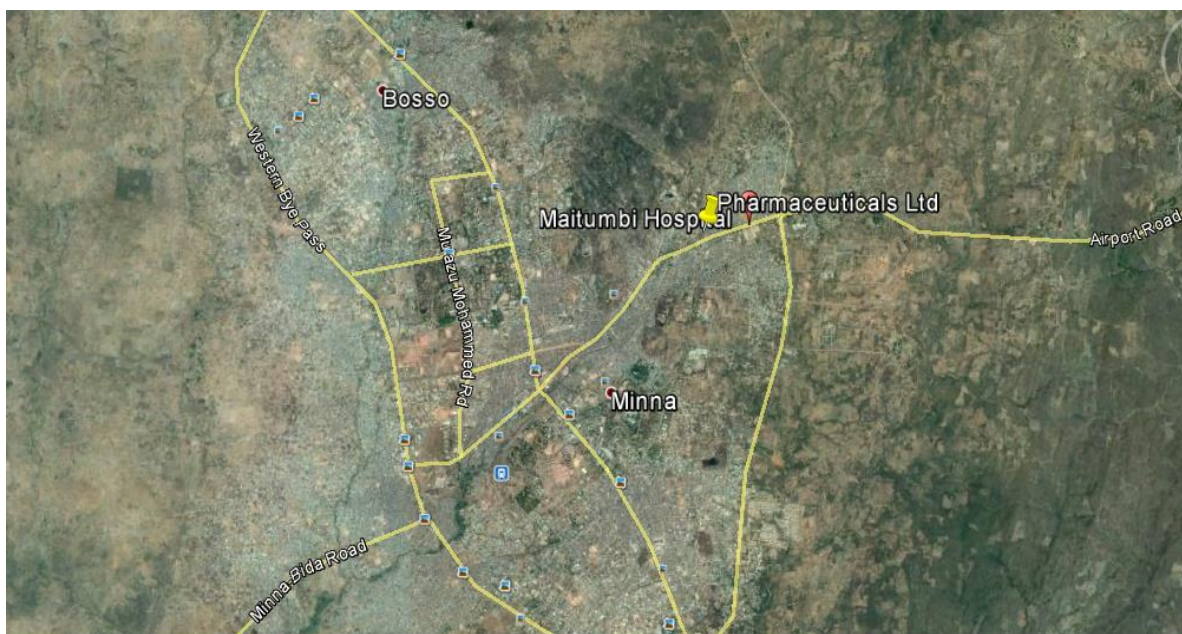


Fig. 1: Map of the study area

2.3. Soil Preparation

The soil samples were dried, crushed and sieved using 0.25 mm sieve mesh to obtain a fine particle. The samples were digested using nitric acid-perchloric acid digestion (Animashaun et al., 2015). Some 0.5 g of the finely ground soil samples were weighed using a digital weighing balance and placed in a 50 ml beaker. Some 20 ml of a mixture of nitric acid and perchloric acid in 1:1 molar ratio was poured into the soil in the beaker and the content was placed on a hot

2.2. Soil Sampling and Analysis

Soil samples were collected at a pharmaceutical company along the flow path of the effluent during the dry and raining season of 2015. The samples were collected using a clean stainless steel auger at 15cm depth from the surface. Six (6) soil samples were collected at a 4m interval from the point of discharge of the effluent. Soil sample was collected at the initial point of disposal and subsequently at 4, 8, 12, 16 and 20 m away from the point source and labeled accordingly.

plate and heated gently at low temperature until dense white fumes of HClO_3 appears. The digested soil sample was allowed to cool before it was filtered into a 50 ml standard volumetric flask which was made up to mark with deionised water and the samples were placed in storage containers and analyzed using Atomic Absorption Spectrophotometer (AAS). The soil textural class and soil pH were determined using Bouyoucos Hydrometer method and pH meter respectively (Animashaun et al., 2015).

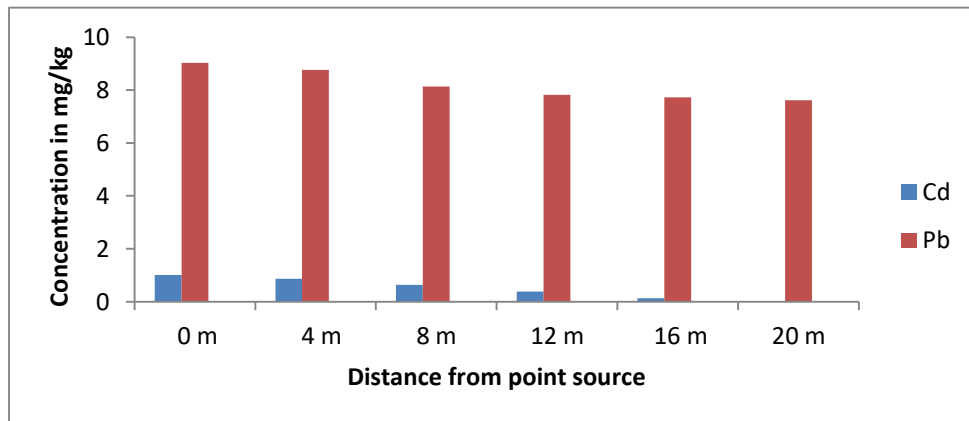


Fig. 2: Concentration of Cd and Pb in the Soil (wet season)

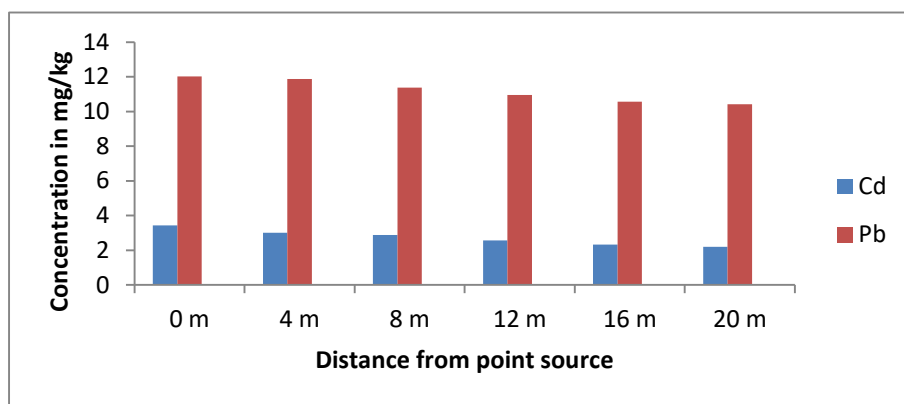


Fig. 3: Concentration of Cd and Pb (dry season)

2.4. Modeling of Cadmium and Lead Mobility in Soil

The interactions and processes taking place in the soil matrix can be understood with the aid of mathematical and computer modelling (Ibrahim et al., 2013). According to Selim et al (1990) and Yahya and Abdulfatai (2007), the mobility of solutes such as heavy metals in the soil, is governed by the convection-dispersion equation (equation 1) under the following assumptions:

- (i) The soil matrix is homogenous; (ii) There is a steady state water flow condition.

The equation is represented as:

$$\rho \frac{\partial s}{\partial t} + \Theta \frac{\partial c}{\partial t} = \Theta D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - Q \quad (1)$$

Where: ρ = Soil bulk density (gcm^{-3}); s = amount of solute retained per unit mass of the soil matrix (mg kg^{-1}); Θ = Volumetric soil moisture content ($\text{cm}^3 \text{cm}^{-3}$); c = solute concentration in the soil solution (mg L^{-1}); D = hydrodynamic dispersion coefficient ($\text{cm}^2 \text{day}^{-1}$); v = Darcy's water flux (cm hr^{-1}); Q = Sink-source term accounting for irreversible reactions in soil such as mineralization and immobilization; x = soil depth (cm); t = time (hr)

However, Ibrahim et al. (2013) reported some associated bugs with the convection-dispersion equation (1), among which are that:

- (i) It requires many parameters at the beginning of the modelling. (ii) The model contains assumptions and approximations which in way transforms the description of transport phenomena.

Recently, a simplified model requiring less parameters at the beginning of the modelling, for predicting solute transport in soil was reported by Tolessa (2004) under the following assumptions:

- (i) There is a steady-state condition, (ii) The principle of first-order kinetics holds, (iii) The decay or decomposition of a pollutant (such as cadmium and lead) is proportional to the initial concentration of the pollutant and the factor of proportionality; the decay rate coefficient (k).

Based on these assumptions, Tolessa (2004) concluded that the mobility of heavy metals can be governed by the transport equation expressed as:

$$\frac{dc}{dt} = -KC \quad (2)$$

Equation (2) was then resolved to give an equation for the concentration of the pollutant (such as cadmium and lead) at any distance x (Tolessa, 2004)

$$C_x = C_0 e^{-\frac{Kx}{v}} \quad (3)$$

Where: C_x = Concentration of heavy metal at distance x (mg kg^{-1}), C_0 = Initial concentration of heavy metal (mg kg^{-1}), K = Decay rate coefficient, V = Flow

velocity ($\text{m}^3 \text{hr}^{-1}$), x = Distance from the point source of pollution (m)

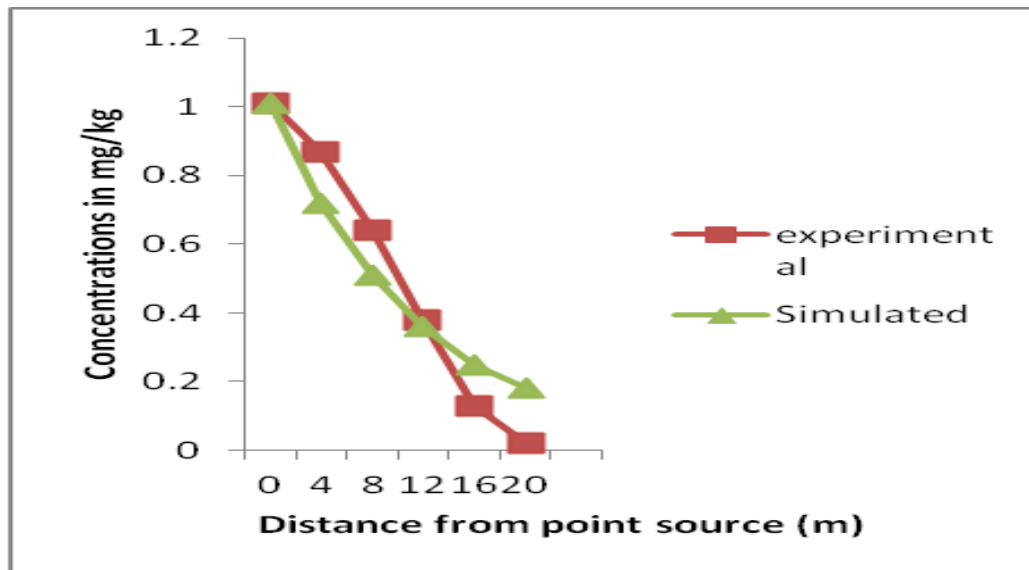


Fig 4: Cd Mobility in the Soil (Wet Season)

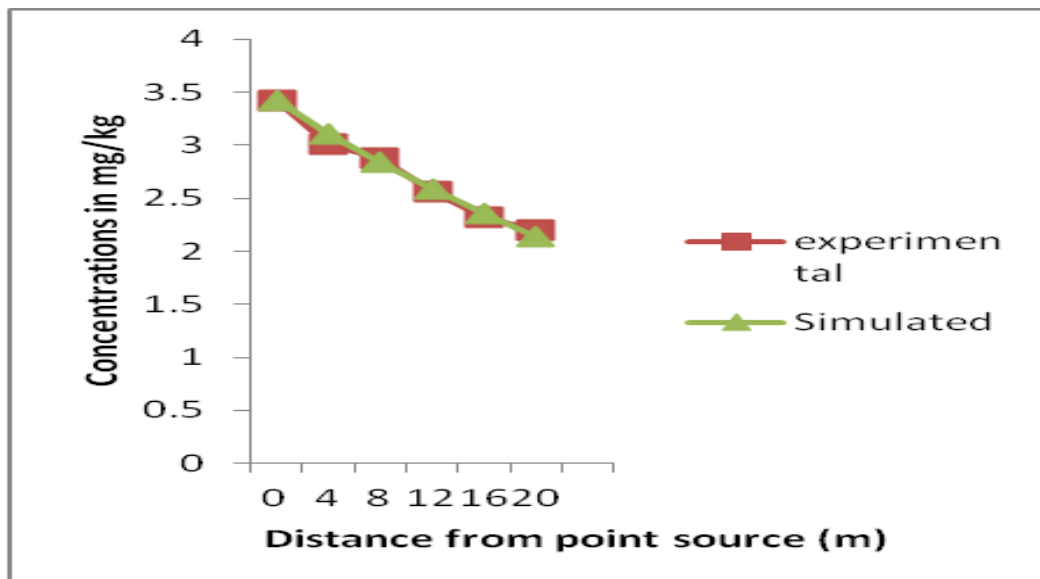


Fig. 5: Cd Mobility in Soil (Dry Season)

This simplified model equation (equation 3) was adopted by Ibrahim *et al.* (2013) to simulate the mobility of lead in mining site. Due to its advantage over the convection-dispersion equation, it was adopted in this study to predict the mobility of Cadmium and Lead in the agricultural soil contaminated with industrial effluent. The mathematical model was simulated using Polymath professional version 6.1. The experimental results obtained for each of the metals in the two seasons (wet and dry) were used for validation and prediction of Cadmium and Lead mobility at different distances along the flow path of the effluent. In order to check whether it can predict the metals concentrations at

distances outside the experimental studies, the degree of correlation between the experimental and simulated values was determined.

3. RESULTS AND DISCUSSIONS

The soil textural classification, pH and heavy metals concentrations of the soil samples under consideration were assessed at six sampling points. The soil can be classified as loamy sand and the soil pH ranges from 4.9 to 6.3 over the two seasons indicating the slightly acidic nature of the soil along the effluent flow path. During the rainy season, the mean concentrations of Cd of the 1st (point 0 m) to 6th (point 20 m) samples

decrease from 1.01 mgkg^{-1} to 0.02 mgkg^{-1} and the mean concentrations of Pb from 1st to 6th samples also decrease from 9.03 mgkg^{-1} to 7.62 mgkg^{-1} respectively (Figure 2).

During the dry season, a similar trend was also observed as the mean concentrations of Cd from 1st to 6th points decrease from 3.42 mgkg^{-1} to 2.20 mgkg^{-1} , and the mean concentrations of Pb decrease from 12.01 mgkg^{-1} to 10.41 mgkg^{-1} (Figure 3).

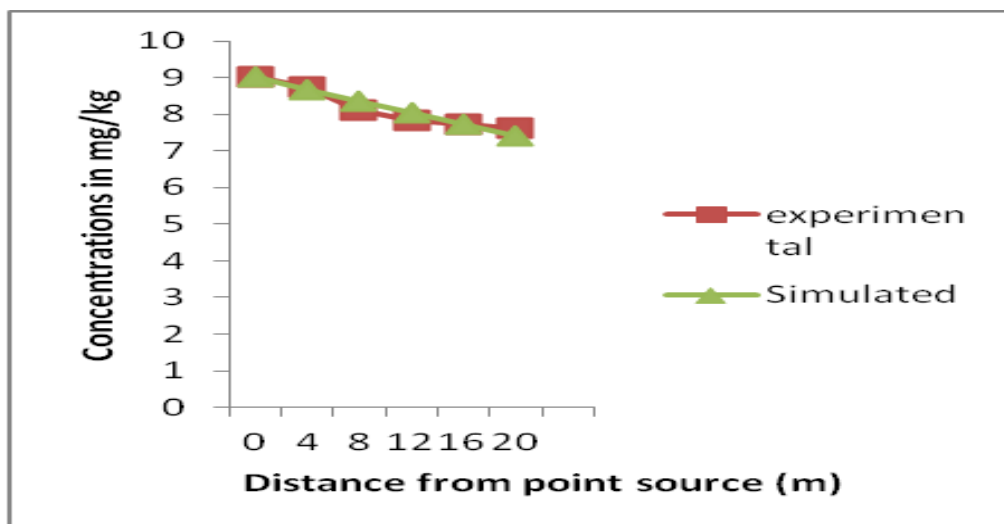


Fig. 6: Pb Mobility in Soil (Wet Season)

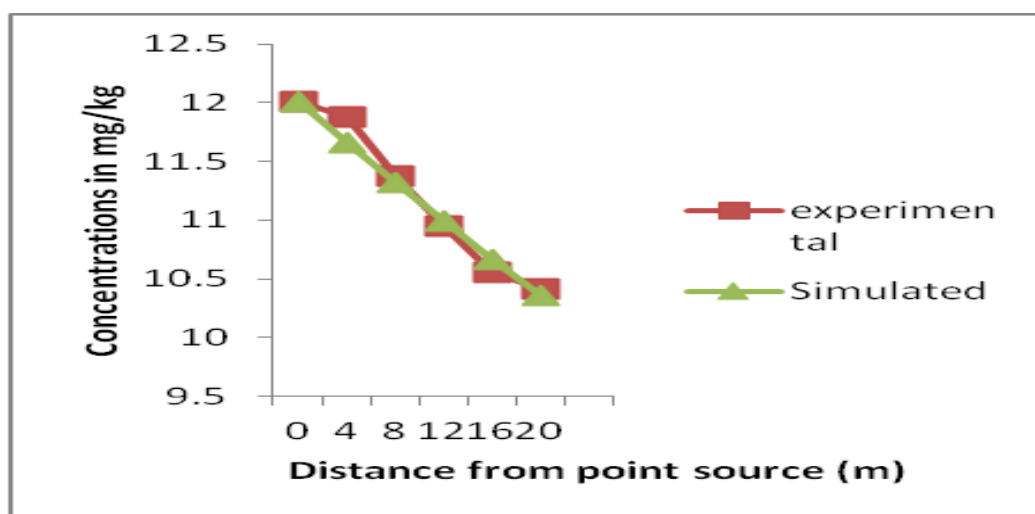


Fig. 7: Pd Mobility in Soil (Dry season)

The results showed that Cd and Pb are present in all the sampling points at different concentrations. The highest concentrations of Cd and Pb were observed at the initial point of effluent disposal suggesting the point source as a probable source (or one of the sources) of the metals. There was a decrease in concentrations of both metals for every corresponding increase in distance (0, 4, 8, 12, 16, 20 m) from the point source. This could be as a result of the solute absorption tendency of soils as opined by Dube et al. (2001). While the wide variation in concentration of successive points could be as a result of surrounding geological environment and anthropogenic and natural activities occurring or once occurred at the point (Dube et al., 2001), decrease in the value of the metals at some other successive distance was not drastic. This

could be as a result of the co-existence of the two metals in the soil. This according to Serrano et al. (2005) reduces their tendency to be sorbed on the soil solid phases. The results showed that Pb poses no threat to the soil as the obtained values were below the established limits of 300 mg/kg for soil by World Health Organisation and Food and Agriculture Organisation (WHO/FAO) as reported as by Adah et al. (2013). On the other hand, Cd poses serious threat at certain points (points close to the point source) as the values were above the established limits (3 mg/kg) by WHO/FAO.

Though, the European Union Standard for Cd and Pb agree with WHO and FAO, FEPA fixed no threshold for Cd and affirmed a threshold of 1.6 mg/kg for Pb (Mohammed and Folorunsho, 2015).

Thus, there is need for remediation of the soil to prevent probable transfer of the two heavy metals into the man system through the food chain. The observed values for Pb and Cd along the path of point source of effluent discharge were lower than the respective values (15 mg/kg - 38 mg/kg; 7.20 mg/kg – 7.28 mg/kg) reported by Iyaka and Kakulu (2012) and Okoli (2015) in the pharmaceutical industrial site. This suggests that the high values recorded for the two metals in their studies could be from other sources such as direct air pollution and runoff (Adekola et al., 2001)

3.1. Cadmium and Lead Mobility in Soil

A simplified mathematical models reported by Tolessa was adopted to predict the mobility (in terms of concentration) of Cadmium and Lead in agricultural soils in the neighbourhood of the pharmaceutical company. The model was simulated and the results obtained were compared with the experimental data. Figures 4 - 7 showed both the experimental and simulated results for both the Cd and Pb concentrations in soil samples collected at a successive interval of 4 m from the point source of the effluent discharge, for both seasons.

The results of the simulated data for Cd in wet season decrease from 1.01 mg/kg to 0.02 mg/kg (Fig. 4) and in dry season it decreases from 3.42 mg/kg to 2.14 mg/kg (Fig. 5). The simulated data assumed the same value as with the experimental at the first point but differ slightly at the remaining points. The coefficients of correlation for wet and dry season were 0.89 and 0.97 respectively. This showed that the simulated data showed a better agreement with the experimental data in dry season.

The results of the simulated data for Pb in wet season also decrease from 9.03 mg/kg to 7.42 mg/kg and in dry season it decrease from 12.01 mg/kg to 10.36 mg/kg. It assumed the same value at the first and last points with the experimented in the two seasons. Like Cd, the simulated data for Pb showed a good agreement with the experimental data from the mathematical model as the coefficients of correlation for wet and dry season were 0.92 and 0.96 respectively.

These results further consolidate the fact that the mathematical model equation is a good transport model for predicting Cd and Pb mobility in soils. Though, the model relatively performed better in predicting Pb mobility as similar graphical pattern was followed by the experimental and simulated values. The little deviation of the experimental data from the simulated data (particularly in figure 4) could be as a result of a number of factors (which include pH) that affects solute's transport in soil (Sherene, 2010).

4. CONCLUSION

The level of contamination of agricultural soil around the pharmaceutical company was assessed and the mobility of two specific contaminants (Cd and Pb) was predicted. The result showed that soils around the study area contained appreciable amounts of Cd and Pb. Though, the mean values of both metals are below WHO/FAO, caution should be taken as Cd is above the standard at some points and Pb could be poisonous even at a lower concentration. The models show agree with experimental values as the concentration of both Cadmium and Lead were decreasing with increase in distance from the point of discharge of the pharmaceutical effluent. The mathematical model proposed by Tolessa was found to be a good model for predicting the mobility of heavy metals in soil contaminated with pharmaceutical effluent. Polymath professional used for the simulation of the mathematical model, proved to be effective and convenient software for modeling of heavy metal transport in soil.

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