Sorption Isotherm Analysis of Trace Metals on a Sandy Textured Coconut Growing Soil

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ABSTRACT

The nature of adsorption of trace metallic plant nutrients, Cu, Mn and Zn, on a coconut growing sandy textured soil (Madampe series) was investigated in 0.050 M KNO₃ medium. Different adsorption parameters, viz contact time, soil mass, initial concentration and pH were optimized for the study. Variation of the mass of each metal ion sorbed on soil and the initial concentration at constant pH was investigated to understand the nature of adsorption. Further, the data at adsorption equilibrium were fitted to two commonly used isotherm models, namely, Langmuir and Freundlich. The optimum parameters were determined as, shaking time: 3 hours; settling time: 30 minutes; soil mass: 1 g; pH: 5-7; and initial concentrations for Mn(II) and Zn(II): 20 mg/L and 15 mg/L, respectively. The experimental data of Mn(II) and Zn(II) lead to regression coefficients (R²) of 0.957 to 0.970, respectively, for the Langmuir model and 0.812 to 0.925, respectively, for the Freundlich model. Although the Langmuir model fitted better with respect to R² values, both Langmuir and Freundlich models could be used to illustrate the trace metal sorption on the soil. Initially, trace metal ions probably interacted with specific sites where soil surface is homogeneous; this was followed by iteration at nonspecific sites leading to multilayers or through the different modes of mass transfer fulfilling the conditions of the Freundlich model. The adsorption capacity of soil for the three trace metal ions varied in the order of Cu (II) > Zn(II) > Mn(II).
INTRODUCTION

Plants require trace metals such as Cu, Fe, Mn, Mo, Zn, Co and Ni, in minute quantities, which are essential for their growth and development (Alloway, 2010). On the other hand, trace metals, such as Pb, Cd, and Cr are toxic and carcinogenic to humans and animals (Zemanova et al., 2014). Moreover, plant nutrients at high concentrations affect the quality of the environment (Chorom et al., 2013). Trace metals accumulate in the environment as they are non-degradable (Wuana et al., 2010), and are discharged from industrial sources, enter through agricultural activities, or various natural processes (Chorom et al., 2013).

Plants generally absorb most of the trace metallic nutrients in divalent cationic form (Markich and Jeffree, 1994). The solubility of a trace metal is controlled by pH and the other factors in the soil. Their fate including mobility, bioavailability, and toxicity, is directly related to the sorption capacity of the soil (Boudesocque et al., 2007). Substantial information is already available on trace metal sorption on activated carbon, soil, clay and other organic material to remove contaminant trace metals from wastewater and soil (Jusoh et al., 2005; Arfaoui et al., 2008; Njoku et al., 2011).

Sorption differs with the type of trace metal and the composition of the adsorbing surface (McLean and Bledsoe, 1992). The soil matrix includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates (McLean and Bledsoe, 1992), all of which acting as metal adsorbing sites. The aforementioned trace metals are present in soluble or non-soluble forms in the soil. Although all soils naturally contain metals in trace levels, the composition changes from place to place based on the parent material from which the soil is formed. Trace metals are found in soil in one or more of the following pools; (1) dissolved in the soil solution, (2) occupying exchange sites on inorganic soil constituents, (3) specifically adsorbed on inorganic soil constituents, (4) associated with insoluble soil organic matter, (5) precipitated as pure or mixed solids, (6) present in the structure of secondary minerals, and/or (7) present in the structure of primary minerals (Wijebandara et al., 2004; Njoku et al., 2011; Preetha and Stalin, 2014). Pools (1) and (2) are mobile and other pools are immobile in the soil system. The sorption affinity depends on the properties of the metals, surface type, and experimental conditions (McLean and Bledsoe, 1992).

Coconut growing soils are categorized under five land suitability classes denoted as S1 to S5 representing most suitable to marginally suitable, respectively, for cultivation. Consequently, the Madampe soil series is classified as most suitable (S1), and it belongs to Red Yellow Podzolic (RYP) Great Soil Group (Somasiri et al., 2006). Further, the Madampe series comprises of loamy sand to sandy loam textured and moderately or well-drained, deep soils. The soil is loose in consistency, and low in clay and organic matter contents. This series is considered as sand dunes and old sand deposits. The most favorable properties of Madampe series soil for the performance of the coconut palm are the soil depth exceeding 2 m, loamy sand to sandy loam texture, friable to loose in consistency (Mapa et al., 2005).

The objective of this study was to compare the sorption affinity of trace metal ions Cu(II), Mn(II) and Zn(II) separately under laboratory conditions using Madampe soil series as the soil matrix. Further, nature of adsorption was also tested using linearized and nonlinear Langmuir and Freundlich isotherm models after optimizing the following parameters: contact time, soil: solution ratio, and pH. To the knowledge of the authors, this is the first laboratory experiment on sorption of trace metallic nutrients in a coconut growing soil series.

METHODOLOGY

Soil characterization analyses were conducted in the laboratory of Soils and Plant Nutrition Division, Coconut Research Institute of Sri Lanka during 2017-2018. Furthermore, batch experiments to optimize the parameters, namely, contact time, soil: solution ratio, pH, and settling time, and identification of the nature of adsorption of trace metal ions on the Madampe soil series were performed under laboratory conditions.

Soil sampling, sample preparation, soil characterization and reagent preparation

Soil belonging to Madampe soil series was collected at the centre of the square of four adult coconut palms (TxCD variety) at 0-10 cm depth at Bandirippuwa Estate, Lunuwila (IL3) of Sri Lanka. Soil samples were air-dried, sieved through a 2 mm sieve to obtain uniform particles, and analysed for pH, electrical conductivity (EC), organic carbon (OC), soil texture and cation exchange capacity (CEC) according to the standard
methods described elsewhere (Dhamakeerthi et al., 2007).

Stock solutions of trace metal ions (Cu, Mn and Zn) of 1000 mg/L concentration were prepared using respective metal nitrates in deionized water, stored in polypropylene bottles, and appropriate dilutions were carried out as per the requirement. For pH adjustments, a series of dilutions of NaOH and HCl were prepared and used as per the requirement.

Research plan

Batch experiments were performed for each element separately to optimize the parameters. Each soil sample was shaken with 20 ml of each metal ion at different concentrations dissolved in 0.050 M KNO₃ using an end-over-end shaker at 22 rpm. The equilibrium concentration of each metal ion was determined with an atomic absorption spectrophotometer (Shimadzu AA-7000). The effect of each parameter was evaluated with calculated adsorbed metal ion percentage on soil using the following equation (Priyantha et al., 2015).

\[
\text{Sorption percentage} = \left(\frac{C_i - C_o}{C_o}\right) \times 100\%
\]

where \(C_i\) and \(C_o\) are the initial and equilibrium metal ion concentrations, respectively.

Optimizing parameters: Contact time, soil: solution ratio, and pH

Shaking time and settling time are the two parameters collectively considered as contact time. Experiments were conducted with varying shaking and settling times with 1 g of soil mass and 20 ml of each trace metal ion at 50 mg/L concentration. Soil: solution ratio (g: mmol/L) was optimized as two parts: first part where initial concentration 40 mg/L was kept constant while changing the mass range from 0.2 g to 1.4 g, and the second part where soil mass was kept constant (1.00 g) while changing initial concentration range from 5 mg/L to 45 mg/L. The pH was optimized using the range of pH 3 to 10 respectively. pH adjustment was not made except at pH optimization, since the starting pH of metal solutions were nearly 6.

Isotherm studies

Adsorption data of all three metal ions were fitted to two isotherm models, i.e. Langmuir and Freundlich models. Their linearized equations are presented in Table 1 (Foo and Hameed, 2010; Desta, 2013), where \(q_v\), \(q_m\), \(C_v\), \(K_L\), \(K_F\), and \(n\) are equilibrium adsorption capacity, maximum adsorption capacity, equilibrium concentration of metal ion, Langmuir constant related to sorption capacity, Freundlich constant related to sorption capacity and sorption intensity respectively.

All analyses were triplicated and standard deviations were calculated. The batch experiment data were plotted where standard deviations were incorporated. Analysis of variance was carried out using Minitab 17 statistical software. Mean separation was done using Tukey’s test.

| Isotherm model | Linearized equation |
|---------------|---------------------|
| Langmuir      | \( \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m} K_L \frac{1}{C_v} \) |
| Freundlich    | \( \ln q_v = \frac{1}{n} \ln C_v + \ln k_F \) |

RESULTS AND DISCUSSION

Properties of the soil belonging to the Madampe soil series used in this research are given in Table 2. Although the soil was sandy loam textured, the sand percentage was 94.05%, which was probably a result of the downward movement of silt and clay particles from top soil to layers below.

| Parameter       | Value   |
|-----------------|---------|
| Sand %          | 94      |
| Silt %          | 2       |
| Clay %          | 4       |
| PH              | 5.03    |
| EC (dS/m)       | 3.97x10⁻⁵ |
| CEC (cmol+/100g) | 6.17    |
| OC content (%)  | 0.31    |

EC: electrical conductivity; CEC: cation exchange capacity; and OC: organic carbon

The pH and EC of soil shown in the table above indicate that the soil was mildly acidic, which is supported by previous reports (Mapa et al., 2005).
Optimizing Parameters: contact time, soil: solution ratio, and pH

Experimental data (Figure 1) revealed that the extents of sorption of the three metal ions were almost similar when the same soil mass (1 g) was shaken with the same initial trace metal ion concentration (50 mg/L) and volume (20 ml) in a polypropylene bottle. Further experiments on optimizing parameters on soil mass and initial concentration (changing soil: solution ratio), settling time, and pH exhibited different extents of adsorption on soil of the three metal ions.

Effect of contact time

The sorbed percentages of the three metal ions over 2 to 36 hour shaking time are shown in Figure 1 and variation of mean data are shown in Table 3, which revealed a maximum sorption value when each adsorption system established equilibrium within a short period of shaking time; even in 2 hours there was no significant increase until 36 hours for Cu and Mn. Exception was Zn which achieved an increased sorption after 24 hours, but this did not significantly differ (p<0.05) from that at 2-4 hours of shaking time. Therefore, three hour shaking time was maintained during the rest of the experiments in optimizing other parameters. The extent of sorption did not change significantly with settling time between 10 to 80 minutes, and hence, 30 min was taken as the optimum settling time to ensure the establishment of adsorption equilibrium.

Effect of soil: solution ratio

For optimizing soil mass, lower concentration (40 mg/L) of each trace metal ion was used to minimize the dilution steps than those conducted in optimizing shaking time where the concentration was higher (50 mg/L). The calculated soil: solution ratio ranged for Cu, Mn and Zn are as follows; from 315 to 2520 gL mmol⁻¹; from 275 to 2200 gL mmol⁻¹ and from 325 to 2600 gL mmol⁻¹ respectively. The results revealed that sorption of Cu(II) on soil surface was higher in comparison with Mn(II) and Zn(II) as shown in Figure 2(a).

Nevertheless, all three metal ions showed a slight increase in the extent of sorption when soil: solution ratio increased which is revealed in Table 4 and 5, as significant (p<0.05) increase of extent of sorption with mass increase. By considering the extent of sorption with the mass of soil, a compromised soil mass of 1 g was used in subsequent experiments as the optimum.
Figure 2: Variation in the sorption of three trace metal ions by soil. (a) with soil mass: 1 g soil, 20 mg/L Mn(II) and 15 mg/L Cu(II) and Zn (II) solutions, 20 ml volume, 3.0 h shaking time and 30 min settling time, and (b) initial concentration: 1 g soil in 20 ml volume, 6 hour shaking time and 30 min settling time. Error bars denote standard deviations of the means.

Table 4: Variation of mean sorption of three trace metal ions with soil mass.

| Mass (g) | Cu   | Zn   | Mn   |
|---------|------|------|------|
| 0.2     | 11.78<sup>a</sup> | 5.41<sup>d</sup> | 3.74<sup>d</sup> |
| 0.4     | 18.61<sup>d</sup> | 8.41<sup>cd</sup> | 7.55<sup>cd</sup> |
| 0.6     | 20.55<sup>cd</sup> | 12.52<sup>bc</sup> | 10.53<sup>bc</sup> |
| 0.8     | 24.08<sup>bc</sup> | 14.01<sup>bc</sup> | 15.07<sup>ab</sup> |
| 1.0     | 26.78<sup>bc</sup> | 16.69<sup>ab</sup> | 15.41<sup>ab</sup> |
| 1.2     | 28.08<sup>ab</sup> | 18.12<sup>ab</sup> | om   |
| 1.4     | 31.21<sup>a</sup> | 22.22<sup>a</sup> | 20.23<sup>a</sup> |
| 1.6     | om   | om   | 14.54<sup>b</sup> |
| p Value | 0    | 0    | 0    |
| CV      | 28.37| 41.21| 44.08|

Note: om: omitted. Values with different letters in each column are significantly different at <i>P</i>&lt;0.05.

Table 5: Variation of mean sorption of three trace metal ions with initial concentration.

| Con. | Cu   | Mn   | Con. | SP   |
|------|------|------|------|------|
| 10   | 75.77<sup>a</sup> | 24.39<sup>b</sup> | 5    | 84.23<sup>a</sup> |
| 20   | 64.58<sup>a</sup> | 67.20<sup>a</sup> | 10   | 57.15<sup>b</sup> |
| 25   | 36.99<sup>b</sup> | 20.41<sup>bc</sup> | 15   | 60.60<sup>b</sup> |
| 30   | 30.47<sup>bc</sup> | 13.48<sup>bcd</sup> | 20   | 18.20<sup>c</sup> |
| 35   | 25.48<sup>bc</sup> | 9.33<sup>cd</sup> | 25   | 5.59<sup>c</sup> |
| 40   | 13.52<sup>d</sup> | 4.77<sup>d</sup> | 30   | 4.107<sup>c</sup> |
| 45   | 20.56<sup>cd</sup> | 7.09<sup>d</sup> | 35   | 8.00<sup>c</sup> |
| p Value | 0    | 0    | p Value | 0    |
| CV   | 58.51| 99.2 | CV     | 92.43|

Note: SP: Sorption percentage Con: Concentration. Values with different letters in each column are significantly different at <i>P</i>&lt;0.05.
Effect of pH

The extent of sorption determined at optimized shaking time, optimized settling time, soil mass and initial metal ion concentration at different solution pH values are shown in Figure 3, which revealed that sorption of Mn(II) on soil with varying pH is different from that of Cu and Zn. The extent of sorption of Mn(II) was very high in strong acidic (pH 3-5) and strong basic (8-10) pH. However, both Cu(II) and Zn(II) showed a gradual increase in extent of sorption in strong acidic pH, followed by a rapid increase through weak acidic to neutral pH and reaching a high constant level at strongly basic pH.

It is documented that solubility of Mn(II) is favoured in acidic pH forming soluble manganese hydroxy cations, such as Mn(OH)₂⁺, which has a higher affinity to be adsorbed on soil (McLean and Bledsoe, 1992; Lyons et al., 2000; Millaleo et al., 2010). Therefore, the adsorbed percentage of Mn is high in strong acidic pH compared to that of Cu(II) and Zn(II). Further, at higher pH, aerobic oxidation of Mn(II) is favoured over MnO₂, Mn₂O₃, MnO₄ and even MnO₂. Furthermore, Mn oxides co-precipitates with iron oxides (Millaleo et al., 2010) contributing to enhanced extent of sorption. However, in the present study, there was a rapid decreasing trend in slightly acidic pH which expressed the presence of Mn(II) in solution. It has been reported that formation of hydrolyzed species of Zn, such as Zn(OH)⁺ and ZnHCO₃⁻, occurs at pH > 7; therefore, adsorption takes place as monovalent cations indicating a higher affinity in adsorption at higher pH thereby greater extension of adsorption (Diatta and Kocialkowski, 1998). Moreover, formation of Cu(OH)₂, a precipitate in solution has a tendency for dissolving through hydrolysis at higher pH values (Vaughan and Malcolm, 1985) resulting in higher adsorption. It is known that pH 5-7 is the suitable pH range for nutrient uptake in coconut. The experimental results on trace metal ion sorption reflects that sorption is comparatively lower in the middle pH range compared with higher range as indicated in Figure 3. Trace metals mostly precipitate irrespective of other sorption mechanisms in basic pH.

Sorption isotherm for Cu, Mn and Zn

Although the adsorption isotherms of the three metal ions show different patterns, it is clear that the amount of adsorbed ions increases (Figure 4), and best fit was with nonlinear Langmuir model than that of nonlinear Freundlich model. It is known that Cu adsorption in acidic soil is higher than that of Zn (Mesquita, 1998).

![Figure 3: Variation in the extent of removal of three trace metal ions by soil with soil mass with: 1 g soil, 20 mg/L Mn(II) and 15 mg/L Cu(II) and 15 mg/L Zn(II) solutions, 3 hour shaking time, and 30 minutes settling time. Error bars denote standard deviations of means.](image)

![Table 6: Variation of mean extent of sorption of three trace metal ions with pH.](table)

| pH  | Cu     | Zn     | Mn     |
|-----|--------|--------|--------|
| 3   | 18.87  | 80.40  | 4.81   |
| 4   | 38.41  | 88.77  | 15.81  |
| 5   | 49.26  | 78.09  | 20.28  |
| 6   | 50.48  | 13.94  | 20.33  |
| 7   | 91.45  | 18.92  | 28.51  |
| 8   | 82.82  | 97.49  | 78.75  |
| 9   | 80.42  | 100.00 | 87.51  |
| 10  | 61.23  | 100.00 | 89.05  |

Note: SP: Sorption percentage. Values with different letters in each column are significantly different at P<0.05.

The isotherm data fitted with linearly transformed Langmuir and Freundlich isotherm equations leading to regression coefficients (R²) and isotherm constants are presented in Table 7. The approximate pH range for the isotherm development was 5-7 as pH changes with the sorption, and pH adjustment is impossible with the continuous shaking in end over end shaker.

Both models gave satisfactory fit with the data as regression coefficients were between 0.812 to 0.925 for the Freundlich model, and 0.957 to 0.970 for the Langmuir model. However, according to the R² values, the better fitted model for each element was the Langmuir model.
Figure 4: Changes in amount of trace metal ions adsorbed (µg) on 1g of soil with the equilibrium concentration (a) Cu(II), (b) Mn(II) and (c) Zn(II). Error bars denote standard deviations of means. Exp: Experimental data, Lan: Fitting of experimental data to Langmuir model, Fru: Fitting of experimental data to Freundlich model.

The Langmuir model generally describes the monolayer nature in adsorption on specific sites which would promote irreversible, electrostatic interactions on a homogeneous surface (Bradl, 2004a; Bradl, 2004b). In addition, reversible monolayer adsorption on soil has also been reported (Jusoh et al., 2005). Moreover, adsorption data reported in Figure 4 provides evidence for multilayer adsorption as well, indicating the validity of the Freundlich isotherm. This is further supported by the n values calculated from nonlinear Freundlich model, which are greater than 1.0 for all three metal ions [Cu(II) - 4.21; Mn(II) - 1.12; Zn(II) - 1.42] suggesting the validity of the Freundlich model towards multilayer adsorption (Table 7). This situation is acceptable when considering the heterogeneous nature of soils. As such, there are two possible pathways of sorption: First possibility is the initial monolayer adsorption, followed by transfer of adsorbate metal ions into micropores and mesopores through inter-particle and intra-particle diffusion processes, thereby providing more vacant sites on the soil surface to transfer metal ions from the solution phase to the soil surface. Solution analysis therefore detects the loss of adsorbate material more than what is required for monolayer coverage although multilayer coverage metal ions (i.e. metal layers on top of metal layer) is unlikely to take place (Wua et al., 2009; Kotabewatta et al., 2020). The other possibility is the Cu(II), Mn(II) and Zn(II) adsorption initially at specific sites with high electronic forces obeying Langmuir model and then sorption to other sites with nonspecific sorption as layers on soil describing the Freundlich model. The affinity of adsorption on heterogeneous surface and multilayer adsorption is expressed by Freundlich model (Foo and Hameed, 2010).

Table 6 further shows that K_L and K_F from both models related to sorption capacity of soil for the Mn(II) is the lowest in comparison with relevant values for the other two trace metals. This phenomenon was also revealed in Figures 1 and 2 as the extent of adsorption of Mn(II) is the lowest among the three trace metals under investigation.

CONCLUSION

Determination of the extent of sorption of Cu(II), Zn(II) and Mn(II) on Madampe soil series, recommended for coconut cultivation in Sri Lanka, under static conditions by varying experimental parameters within a broad range lead to the optimum conditions of 3.0 hours shaking time, 5 - 7 pH, and 20 mg/L initial concentration for Mn(II) and 15 mg/L for Zn(II) and <1 mg/L for Cu (II). According to the R^2 values, experimental sorption data generally fitted with both the Langmuir and Freundlich isotherm models, although the actual mode of transfer of metal ions from the solution phase to the soil phase is complex: This would be initially sorption to specific sites followed by nonspecific sorption...
Table 7. Isotherm constants and regression coefficients ($R^2$) for Langmuir and Freundlich models.

| Metal ion | Langmuir isotherm model | Freundlich isotherm model |
|-----------|--------------------------|---------------------------|
|           | $K_L \times 10^2$ (g/$\mu$g) | $q_m$ ($\mu$g/g) | $R^2$ | $n$ | $K_F \times 10^2$ | $R^2$ |
| Cu(II)    | 18.80                     | 0.13                     | 0.957 | 4.01 | 1.36             | 0.812 |
| Mn(II)    | 5.95                      | 0.16                     | 0.961 | 1.24 | 0.96             | 0.925 |
| Zn(II)    | 23.41                     | 0.22                     | 0.970 | 1.83 | 21.63            | 0.901 |

while promoting multi-layer adsorption processes or initial binding of trace metals to specific sites, followed by transfer of adsorbate species to mesopores and micropores through intra-particle and inter-particle processes. The calculated $n$ values which were greater than 1 indicated multilayer sorption. Further, sorption capacity of trace metal ions in Madampe series soil varied in the order of Cu(II)> Zn(II)>Mn(II). According to the results, the highest sorption percentage was indicated in Cu (II), compared with other trace metals.

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