

Evaluation of Adsorption Dynamic Retention of Copper Ion in Porous Agricultural Soil

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ABSTRACT The persistence of heavy metals on the environment is very harmful because they cannot be degraded and likely to accumulate in the soil. Agricultural activities, industrial waste or even industrial accident often contain appreciable amounts of heavy metals that leads to heavy metals pollution on soil, which may reduce soil fertility as well as health effect of the plant consumer. Therefore, it is important to know the ability and capacity of soil in retaining heavy metals. This study aims to measure and evaluate the adsorption equilibrium data of Cu(II) onto kaolinite clay soil in batch experimental. The equilibrium data was fitted using Langmuir and Freundlich isotherm model to represent the liquid-solid equilibrium condition. The maximum adsorption capacity of Cu(II)-clay of 2.015 mg/g was observed. In addition, this work contributes to model the transport of Cu(II) in the porous media of clay soil, using numerical computation. The simulation utilized mathematical model framework of well-known Advection-Dispersion-Diffusion (ADDE) equation model to predict the retention time of Cu(II) in kaolinite clay soil, by taking a small section of 30 cm × 1.6 cm clay soil as a representative elementary volume. The result from numerical computation revealed that kaolinite clay soil have a relatively low capability for Cu(II) uptake, most probably due to its lower cation exchange capacity (CEC), which responsible for holding positively-charged ions.

KEYWORDS: Adsorption; Clay; Soil; Numerical computation; Solute transport model

Received 21 August 2020 Revised 25 September 2020 Accepted 28 September 2020 Online 6 October 2020

© Transactions on Science and Technology

Original Article

INTRODUCTION

Soil is an essential element of ecosystem, which subjected to abundant exposure of pollutants including heavy metals. These heavy metals presence in the ecosystem may occurred through natural and anthropogenic activities (Tan et al., 2018). Anthropogenic activities viz. industrial activities, agricultural activities and domestic disposal have been proven to be the primary source of heavy metal pollution. Upsurge in heavy metals content affects all organisms by biomagnification due to their toxicity and non-biodegradable, as well as non-thermodegradable characteristics (Kumar et al., 2019). Although heavy metals are key components in maintaining soil health, but even a small increase in their concentration above threshold limit can adversely affect the soil hydrology, biota and soil chemistry, and decreases the productivity of soil (Kumar et al., 2019). This leads to serious heavy metal pollution which results in diminishing availability of arable lands.

Soil can be regarded as adsorbent, in which it has its own capacity in holding certain pollutants such as heavy metals. The accumulation of heavy metals in soil is depending on the strength of chemical form or affinity of the soil and the particular heavy metal. The affinity of soil surfaces towards heavy metal ions may involve several mechanisms, including surface complex formation and precipitation (Bhakta & Munekage, 2013). However, the ability of soil to bind with heavy metals always related to adsorption, surface precipitation and fixation processes (Bradl, 2004). Kaolinite clay, as one of the different clay minerals types, is one of the major and most found clay in the agricultural soil composition. Different clay minerals (bentonite, montmorillonite, smectite etc.) have different adsorption capacity for metal ions. Owing to their cation exchange capacity (CEC), heavy

metal ions can be retained by the soil. It is a measure of soil ability in holding metal ions. Typically, kaolinite clay has a CEC of 3 to 15 meq/100 g, which is relatively low compared to other types of clay minerals (Jiang et al., 2010; Suraj et al., 1998).

In order to understand the dynamic solute distribution in the soil, it is often predicted using mathematical models that describe the phenomenological behavior of the solute. The development of geochemical transport model is an important predictive tool, perhaps responsible in determining the movement of the chemical species. Dynamic behavior of flowing heavy metal ions through a porous soil often important in determining the transport time (or retention time) of the metals in the soil, before the soil loses its capacity. It measures the time taken for a certain heavy metal to remain in the soil before run off into nearby groundwater receiver. Solute transport in porous media such as clay is usually described by Advection-Dispersion equation (ADE) (Zaheer et al., 2017). However, since soil has the capacity to hold and release the solutes, the latter model used is Advection-Dispersion-Diffusion equation (ADDE). Several authors have successfully described the solute transport in soil using ADDE in their respective works (Cameron & Klute, 1977; Murali & Aylmore, 1983; Travis & Etnier, 1981).

The aim of this present study is twofold: First, to measure and interpret the adsorption isotherm of Cu(II) onto clay soil to obtain the capacity of clay in holding Cu(II), and fitted using Langmuir and Freundlich isotherm model. Second, this study contributes to establish a one-dimensional solute transport model in clay soil based on well-known Langmuir model adsorption isotherm. Numerical calculation was done using implicit Euler integration method built in Aspen Adsorption V11. A continuity equation of a dispersed flow packed bed column model was utilized as a representative elementary volume for the clay soil. Parametric studies were conducted to investigate the dynamic retention of Cu(II) in clay soil by varying three parameters, which are soil depth, inlet Cu(II) flow rate and inlet Cu(II) concentration. The rationality of the model in predicting retention time of Cu(II) in clay soil are discussed in detail.

EXPERIMENTAL SETUP

Reagents and Adsorbent

The reagents used in this work are all analytic grade. Adsorbate Cu(II) as copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and copper standard solution (1000 mg/L) were purchased from Sigma-Aldrich, whereas adsorbent clay (kaolin, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) represented as agricultural soil was purchased from R & M Chemicals. The composition of clay is shown in Figure 2. All materials were directly used in experimental analysis work without any further purification.

Analysis of Adsorption Isotherm

Batch mode experiments were conducted on the adsorption of Cu(II) onto clay. A range of concentrations 10 - 6000 mg/kg, Cu(II) solutions were prepared. The quantities of adsorbent and Cu(II) solution were set to a weight ratio of 1:50. Samples were prepared in 3 replicates. The samples were kept in a 250 mL sealed conical flask and then placed in incubator shaker at room temperature 30 °C and shaken at a constant rate of 100 rpm for 24 h, for achieving the equilibrium. Subsequently, samples were centrifuged and the concentrations of the solutions were determined using Perkin Elmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

MATHEMATICAL MODELLING

Underlying Assumptions

The one-dimensional solute transport model was developed in Aspen Adsorption V11 process simulator. A continuity equation of a packed bed column was taken as a representative elementary volume for a small section of the clay soil (Figure 1). Several assumptions need to be established in order to model the packed bed adsorption column. The assumptions follow:

1. The behavior of the fluid across the soil depth is assumed to be axially dispersed flow with isothermal flow condition along the bed
2. The velocity variation along the bed is negligible due to constant fluid moment assumptions
3. Bed (soil) porosity is radially uniform throughout
4. A linear driving force model (LDF) approximation is considered to represent the movement between liquid-solid phase.

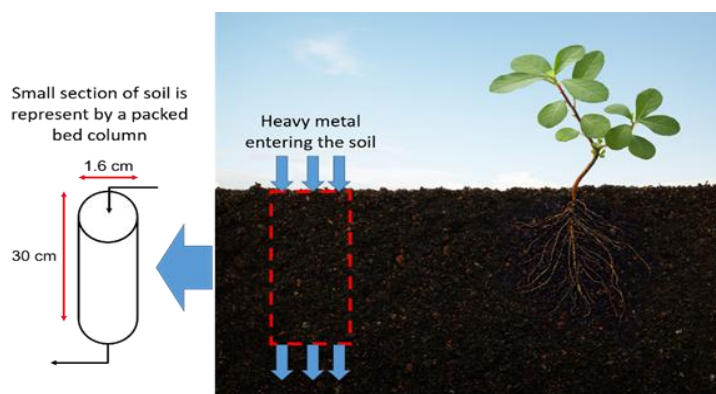


Figure 1. Representative elementary volume of a small section agricultural soil using packed bed column. (Modified from Photo: ifong/Shutterstock)

The LDF mass transfer coefficient (k_{LDF}) takes into account the lumping addition of both external mass transfer and surface diffusion (Bono, 1989; Shafeeyan et al., 2014).

$$\frac{1}{k_{LDF}} = \frac{r_p}{3k_f} + \frac{r_p^2}{15k_s} \quad (1)$$

where r_p is the average particles radius. The first term on the right hand side represents external film mass transfer coefficient, and the second term on the right hand side represents the surface mass transfer coefficient.

The external film mass transfer resistance (k_f) is obtained through empirical correlations of dimensionless Sherwood number. The correlations formulated by Ohashi et al. (1981) was used to estimate the k_f .

$$\begin{aligned} 0.001 < Re < 5.8 & \quad Sh = 2.0 + 1.58 Re^{0.4} Sc^{\frac{1}{3}} \\ 5.8 < Re < 500 & \quad Sh = 2.0 + 1.21 Re^{0.5} Sc^{\frac{1}{3}} \\ Re > 50 & \quad Sh = 2.0 + 0.59 Re^{0.6} Sc^{\frac{1}{3}} \end{aligned} \quad (2)$$

The surface mass transfer diffusion (k_s) is calculated using empirical correlations developed by Worch (2008).

$$k_s = 8.6 \times 10^{-5} r_p \sqrt{\frac{D_L C_0}{w_0}} \quad (3)$$

where D_L is liquid diffusivity coefficient (m^2/s) and are open for prediction from various correlations in literatures, C_0 is the aqueous phase solute concentration (mg/L), and w_0 is the corresponding solid phase solute loading (mg/g).

The axial dispersion coefficient can be estimated knowing the Reynolds and Schmidt numbers. In general, the axial dispersion is a function of Reynolds number, and therefore it changes as the fluid flow properties changes. At very low Reynolds number, the axial dispersion become appreciable as the fluid flow is lower. Wakao & Funazkri (1978) suggested a correlation for predicting axial dispersion coefficient as expressed in Equation (4).

$$D_z = \frac{D_L(20 + 0.5(R_e)(Sh))}{\varepsilon} \quad (4)$$

Governing Equations

The differential mass balance of an axially dispersed flow model in a packed bed adsorption column is expressed as in Equation (5). This equation is used to obtain concentration profile along the soil depth, coupled with other PDEs (AspenONE, 2009; Bono, 1989).

$$(v_i c_i) \frac{\partial}{\partial t} + \varepsilon_i \frac{\partial c_i}{\partial t} + \rho_s \frac{\partial w_i}{\partial t} = \varepsilon_i D_{z,i} \frac{\partial^2 c_i}{\partial z^2} \quad (5)$$

The above expression indicates three forces involves in the model, which are convective force responsible for adsorption, accumulation and mass transfer from aqueous-phase to solid phase.

For the mass balance in the solid phase, two possible mass transfer resistances have been considered: (i) external mass transfer resistance and (ii) internal mass transfer resistance. The assumption of linear driving force (LDF) approximation is used to represent the transport from liquid-phase to solid phase adsorbent. The LDF mass transfer model is described as in Equation (6). These two resistances are lumped, forming a single LDF mass transfer coefficient, k_{LDF} .

$$\frac{\partial w_i}{\partial t} = k_{LDF} (w_i^* - w_i) \quad (6)$$

The mass transfer from liquid-phase to solid phase term in (5) was represented using Langmuir isotherm model, with two parameters, IP_1 and IP_2 , to describe the equilibrium condition between liquid and solid phases. The non-linear Langmuir isotherm model is given in Equation (7)

$$w_i = \frac{IP_1 IP_2 c_i}{1 + IP_2 c_i} \quad (7)$$

Model Parameters

Table 1. Model parameters of base case simulation for Cu(II) transport in clay soil

Parameters	Value
F (mL/min)	10
EBCT (min)	5
Q_p (kg/m^3)	2,611
d_p (μm)	25 - 35
MTC (1/s)	3.41346×10^{-2}
E_z (m^2/s)	3.89611×10^{-8}

The model parameters for base case Cu(II) transport in clay soil are listed in Table 1. The mass transfer coefficient and dispersion coefficient were estimated using well-established correlation from literatures (See Supplementary Material 1). The source concentration of Cu(II) was kept constant and taken as 3.0 mmol/L, with soil depth of 30 cm and constant porosity of 0.545. The numerical

simulation was conducted using the implicit Euler as integration method to solve sets of PDAEs, with 0.01 step size.

The properties of kaolinite clay which referred to the experimental data obtained from Tan et al., (2018). This was the source for the input for some of the parameters that were fed into the simulation tool as to characterize the packed bed column that is used in the current simulation. The properties are clay particle density (ρ_p) and clay particle diameter (d_p).

Parametric Studies

The dynamic behavior of the clay soil was investigated by performing simulation at different conditions. The varying parameters including clay soil depth, inlet Cu(II) concentration and flow rate are presented in Table 2.

Table 2. Parametric studies with their respective varying parameters

Simulation no.	Soil depth (cm)	Inlet concentration (mM)	Inlet flow rate (mL/min)
1	24	3.0	10
2	30	2.4	10
3	30	3.0	10
4	30	3.6	10
5	30	3.0	8
6	30	3.0	12
7	36	3.0	10

RESULT AND DISCUSSION

Clay Soil Composition Analysis

Figure 2 shows the XRF spectrum of clay. The presence of Silicon (Si) is shown at peak $2\theta = 101^\circ$, 108° and 109° . Meanwhile the presence of Aluminum (Al) is shown at peak $2\theta = 131.5^\circ$, 142° and 145° . The obtained percentage of SiO_2 (45.91%) and Al_2O_3 (38.05%) indicate the clay is kaolinite type.

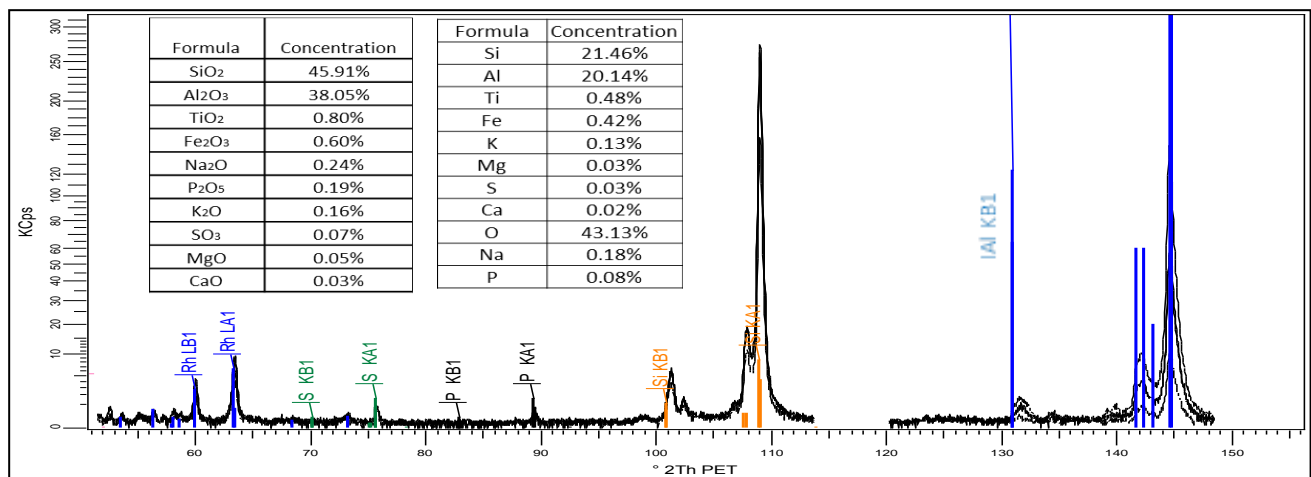


Figure 2. XRF spectrum of clay and its percentage of compounds and elemental composition.

Copper Ion Adsorption Isotherms

The adsorption equilibrium is usually described through isotherm that relate with the surface properties and affinity of the adsorbent. Distribution of heavy metal ions between the solid phase and liquid phase can be described by the basis of models such as Langmuir model and Freundlich model. The Langmuir adsorption isotherm model describes the surface as homogeneous with the

assumption monolayer adsorption onto the adsorbents surface sites with no transmigration of adsorbate in the plane surface (Dada et al., 2012). Langmuir adsorption model can be expressed as in Equation (8) and (9).

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (8)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (9)$$

where q_{\max} (mg/g) is the adsorption capacity and K_L (L/mg) is the Langmuir constant related to the energy of adsorption. The obtained values are presented in Table 3.

The Freundlich adsorption isotherm is used to describe the multilayer adsorption due to solute-solute interaction in the system. The Freundlich model is expressed by Equation (10).

$$q_e = K_F C_e^{\frac{1}{n}} \quad (10)$$

where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e represents the equilibrium concentration (mg/L), K_F adsorption capacity and n adsorption intensity. The linearization form of (6) is given as in Equation (11).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

In the present study, collected experimental data were fitted to Langmuir and Freundlich isotherm models to identify the most relevant model for the adsorption of Cu(II) onto clay. Result revealed that Langmuir adsorption isotherm was the best model for adsorption of Cu(II) onto clay with the correlation coefficients R^2 of 0.98 (Table 3). Therefore, the adsorption of Cu(II) onto clay is monolayer adsorption type.

Table 3. Estimated isotherm parameters for adsorption of heavy metal ions onto clay by linear regression using Equation 5 (Langmuir) and Equation 8 (Freundlich)

Adsorbate	Langmuir			Freundlich		
	q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F ([mg/g]/[L/mg] ^{1/n})	n	R^2
Cu(II)	2.015	1.016	0.98	5.424	6.124	0.70

Influence of Soil Depth on Soil Retention Time

The effect of varying clay soil depth (24, 30 and 36 cm) on copper metal ion adsorption at constant inlet concentration of 3.0 mmol/L and constant inlet flow rate of 10 mL/min is shown in Figure 4(a). Q_{total} , M_{total} , percentage removal and breakthrough time are tabulated in Table 4. Generally, the retention time is directly proportional to the soil depth.

Table 4. Parametric values - dependence on clay soil depth

Soil depth (cm)	Q_{total} (mmol)	M_{total} (mmol)	% Removal	t_b (min)
24	0.2933	0.4875	60.15	9.29
30	0.3666	0.5525	66.35	11.73
36	0.4399	0.6250	70.38	14.18

Overall, the results show that at increasing soil depth, the breakthrough time of clay towards copper metal ion is prolonged. The zone where most of the copper ion are bonded is called the adsorption zone and it is arbitrary depending on the amount of adsorbates in the bulk fluid (Gabelman, 2017). Increasing soil depth means the adsorption zone is larger. As the fluid moving through the soil depth, the copper ion is being adsorbed and the soil is slowly saturated with copper ion (Figure 3). This is primarily due to abundant surface area are available at higher clay soil depth,

providing plentiful of adsorption sites (Meshram & Bhagwat, 2019). In addition, higher soil depth corresponds to higher contact time of copper metal ion with the soil, enhancing the liquid-solid transfer from the flowing fluid to the adsorbent surfaces (Hymavathi & Prabhakar, 2019). In addition, enhanced percentage removal was observed at higher soil depth from 60.15, 66.35 and 70.38% for the clay soil depth of 24, 30 and 36 cm.

Influence of Inlet Concentration on Soil Retention Time

The effect of varying inlet copper ion concentration on the soil retention time at constant inlet Cu(II) concentration and soil depth was presented in Figure 4(b). The inlet Cu(II) concentration tested was 2.4, 3.0 and 3.6 mmol/L, while maintaining the inlet flow rate at 10 mL/min and soil depth at 30 cm. The breakthrough curve profiles revealed that the breakthrough occurred faster at higher inlet Cu(II) concentration, with 13.92, 11.73 and 10.28 min for 2.4, 3.0 and 3.6 mmol/L concentration, respectively. The result related to that diffusion has a direct relation to the inlet Cu(II) concentration. Increasing inlet Cu(II) concentration means greater concentration gradient between liquid-solid phase, developing greater driving force for the transport of Cu(II) from liquid phase to solid clay soil, consequently faster metal uptake (Banerjee et al., 2019). At the highest inlet Cu(II) concentration of 3.6 mmol/L, the lowest percentage removal of 65.01% were observed, indicates unfavorable process at relatively higher inlet Cu(II) concentration. The Q_{total} , M_{total} , percentage removal and breakthrough time are tabulated in Table 5.

Table 5. Parametric values - dependence on inlet concentration

Concentration (mM)	Q_{total} (mmol)	M_{total} (mmol)	% Removal	t_b (min)
2.4	0.3470	0.5160	67.24	13.92
3.0	0.3666	0.5525	66.35	11.73
3.6	0.3862	0.5940	65.01	10.28

Influence of Inlet Flow Rate on Soil Retention Time

Influence of inlet liquid flow rate also plays important role in determining the dynamic retention of solute in the soil. The results of varying copper metal ion flow rate; 8, 10 and 12 mL/min at constant inlet concentration and clay soil depth of 3.0 mmol/L and 30 cm is presented in Figure 4(c) as breakthrough curve profiles. The breakthrough data showed that increasing inlet flow rate caused the breakthrough time to decrease. The breakthrough time decreases from 14.78 to 9.70 min when inlet flow rate increased from 8 to 12 mL/min. The results related to a shorter residence contact time of solute Cu(II) in the column, made the clay soil to have insufficient time to interact and attract the Cu(II) for effective binding (Zhang et al., 2019). This study also revealed that increasing inlet flow rate results in reduced utilization efficiency of adsorbent, from 70.22 to 60.79% as the flow rate increases from 8 to 12 mL/min. Table 6 details the values of Q_{total} , M_{total} , percentage removal and breakthrough time. Overall, all the breakthrough curves from Figure 4(a) to 4(c) showed a nearly stepwise function, owing to the low transfer resistance from liquid to solid phase. This most probably by cause of the smaller particles size (25 – 35 μm), which would lower the particle's Reynolds number, and consequently improving the contact between liquid-solid phase, and thus lowering the resistance of the clay soil to attract the Cu(II) ions.

Table 6. Parametric values - dependence on inlet flow rate

Flow rate (mL/min)	Q_{total} (mmol)	M_{total} (mmol)	% Removal	t_b (min)
8	0.4582	0.6525	70.22	14.78
10	0.3666	0.5525	66.35	11.73
12	0.3055	0.5025	60.79	9.70

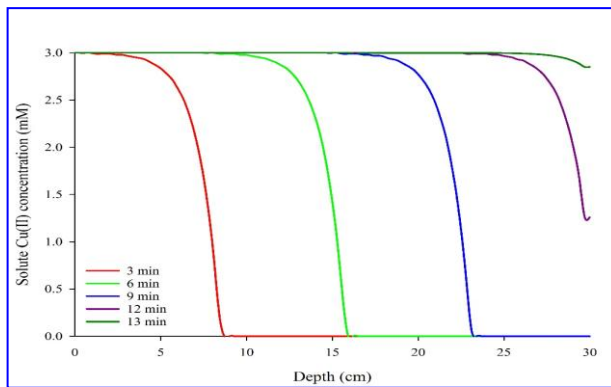


Figure 3. Cu(II) concentration distribution with soil depth at different time ($H = 30$ cm, $C_0 = 3.0$ mM, $F = 10$ mL/min)

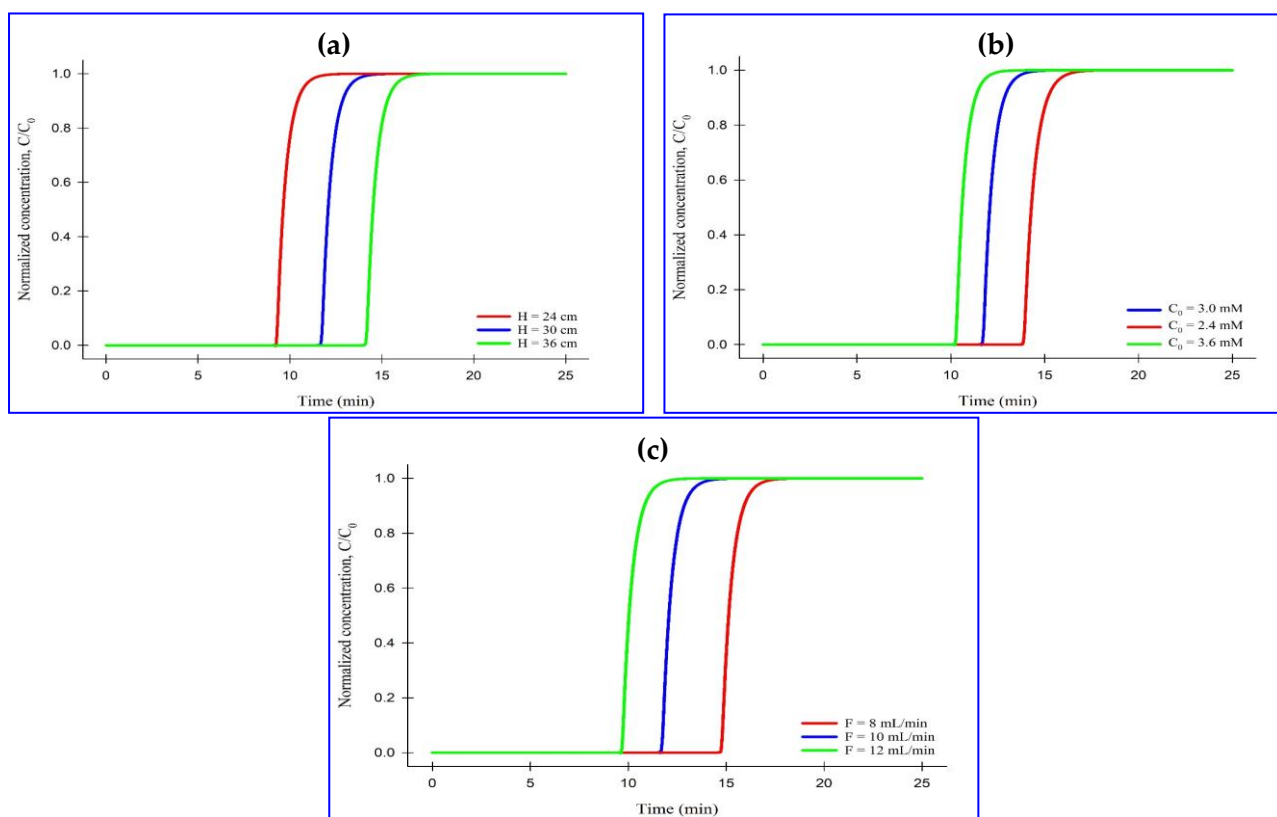


Figure 4. Breakthrough curves for the effect of (a) soil depth ($C_0 = 3.0$ mM, $F = 10$ mL/min), (b) inlet Cu(II) concentration ($H = 30$ cm, $F = 10$ mL/min), and (c) inlet Cu(II) flow rate ($H = 30$ cm, $C_0 = 3.0$ mM)

Comparison With Past Research

The results from this study were compared against two types of adsorbents for the same solute uptake, which are commercial activated carbons and biosorbent activated carbons (Toles & Marshall, 2002). The dynamic operational conditions of bed height, inlet concentration and inlet flow rate were taken, so that comparison can be done for the continuous dynamic behavior (i.e. exhaustion time). The comparison of equilibrium adsorption capacity (batch) and adsorption retention time (continuous) are given in Table 7.

Table 7. Comparison of batch and continuous results with past research

Materials	q_{cal} (mg/g)	Exhaustion time (min)	Reference
<i>Commercial GACs</i>			
Norit RO 3515	16.3491	126	Toles and Marshall (2002)
Norit C	19.0247	48	Toles and Marshall (2002)
Nuchar WV-B	10.1779	36	Toles and Marshall (2002)
<i>Almond shell GACs</i>			
AAS71	53.3498	114	Toles and Marshall (2002)
AS70	14.4668	66	Toles and Marshall (2002)
AAS70	55.0842	240	Toles and Marshall (2002)
<i>Agricultural soil</i>			
Kaolinite clay	2.0123	13	This study

* q_{cal} were calculated at concentration of 3.0 mM

The values observed for kaolinite clay soil was relatively low, indicates that kaolinite clay is not well-adsorb Cu(II) heavy metal when compared to organic adsorbents, such as GACs. This, most probably related to a lower cation-exchange capacity of kaolinite clay (Uddin, 2017), which attributes to the lower negatively charged sites on the surface, hence reducing the adsorption capacity of kaolinite clay towards heavy metal ions (Suraj et al., 1998).

CONCLUSION

The present study revealed that the investigated clay soil follow the monolayer adsorption isotherm type for Cu(II) uptake, with best fitted using Langmuir isotherm model. A one-dimensional solute transport model for single component heavy metal in clay soil was developed based on dispersed flow model of packed bed column, and Langmuir isotherm as adsorption model representing solute transport. Numerical simulations were computed in Aspen Adsorption V11, using implicit Euler as integration method, with 0.01 step size. The main findings obtained can be summarized as Cu(II) uptake by clay soil was confirmed as monolayer adsorption isotherm type, best fitted using Langmuir model with R^2 of 0.98. The q_{max} and K_L found were 2.015 mg/g and 1.016 L/mg, respectively, the dynamic retention of Cu(II) in clay soil was successfully modeled using Advection-Dispersion-Diffusion equation (ADDE) to determine the Cu(II) retention time in clay soil for a given set of conditions, the exhaustion time of Cu(II) in clay soil for soil depth of 30 cm, with inlet concentration of 3.0 mM and inlet flow rate of 10 mL/min was observed at minute 13, which relatively earlier exhaustion compared to other adsorbents, and natural clay soil has relatively low sorption capacity for Cu(II) uptake compared to organic adsorbent viz. activated carbons.

ACKNOWLEDGEMENTS

The authors want to fully acknowledge Universiti Malaysia Sabah (UMSGreat grant GUG0165-2/2017) for funding this work.

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