Bulletin of Environment, Pharmacology and Life Sciences
Bull. Env. Pharmacol. Life Sci., Vol 8 [11] October 2019 : 88-94

Online ISSN 2277-1808
Journal's URL:http://www.bepls.com
CODEN: BEPLAD
Global Impact Factor 0.876
Universal Impact Factor 0.9804
NAAS Rating 4.95

ORIGINAL ARTICLE **OPEN ACCESS**

Thermodynamics of Cadmium adsorption in the major Pineapple (*Ananas comosus*) Cultivated soils of Kerala

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ABSTRACT
A clear discernment of the adsorption equilibrium and thermodynamics is needed to unfold the adsorption process in the soil. Current study was conducted to assess the adsorption mechanism of Cadmium (Cd) onto different types of soil such as sandy clay loam (SCL), loamy fine sand (LFS), sandy clay (SC) and sandy loam (SL) through a series of batch experiments. Experimental data were found have a better fit to Freundlich isotherm for SCL,LFS and SL at 25°C and Langmuir isotherm for SC. The adsorption data had a better fit to Langmuir isotherm for SCL, SC and SL at 40°C and Freundlich isotherm for LFS. The thermodynamics parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were also evaluated. The values of ΔS° for Cd in different soils were negative and ranged from 58.79 $Jmol^{-1}K^{-1}$ and 7.3$Jmol^{-1}K^{-1}$. The ΔG° values were found to be positive for all types of soils and it ranged from 2.2$kJmol^{-1}$ to 17.52$kJmol^{-1}$. The values of enthalpy change (ΔH°)of Cd sorption varied from 0.0024 $kJmol^{-1}$to 0.0013 $kJmol^{-1}$.The positive values of ΔG° indicated that the adsorption of Cd onto the soil is a non-spontaneous process and the negative value of ΔH° stipulates the exothermic nature. The negative value of ΔS° indicated less disorder in the soil-Cd system. Thermodynamic results also indicated a weak or moderate adsorption of Cd onto the soils and may pose potential threat to the ground water by way of leaching through soil with percolating water.
Keywords: *Cadmium, Adsorption, Langmuir, Freundlich, isotherms and Thermodynamics*

Received 28.06.2019 Revised 22.07.2019 Accepted 21.09. 2019

INTRODUCTION

Soil is a dynamic environment in which all terrestrial life depends for their existence. Plants and microbes perform the intermediary role of assimilating the necessary elements in the soil making them available to other organisms. Soil is a heterogeneous medium having the ability to absorb, adsorb, exchange, oxidise minerals and metals leading to a healthy condition of the soil. Understanding of physical, chemical and biological processes and responses in the soil is more important today than ever before. Both natural and anthropogenic activities altered the soil, moreover heavy metals and other toxicants directly or indirectly affect the ecosystem. Soil contamination usually occurs with waste water irrigation [1]and the indiscriminate use of fertilizers and biocides. Study reports point out that phosphatic fertiliser is a source for Cd, Cr, Co, Ni, Pb& V in agricultural soil [2][3]. In addition to potential environmental risk[4]Cd causes kidney damage in grazing animals [5] as well as damage to the lungs, bones, cardiovascular system, liver, and reproductive system in human beings. Adsorption is the effective way of removing toxic contaminants from soil and aquatic systems. Different adsorbents such as wood ash, rice husk and clay soil[6] were usedto unfasten heavy metalsin waste water treatment. Low coast adsorbent such as termite mound [7], Ground nut husk powder [8] and Activated Carbon [9] were used for the removal of heavy metals from waste water. Several factors which determines the adsorption of Cd in the soil includes pH, CEC, particle size, organic matter and temperature [10]. Factors controlling the mobility and availability of trace metals include pH and types of soil [11].Current study focuses on the distribution of Cd in SCL, FLS, SC and SL soil and its adsorption behaviour at different temperatures (25°C and 40°C).

MATERIAL AND METHODS

2.2 Study area and Soil samples

Soils having different texture such as sandy clay loam (SCL), loamy fine sand (LFS), sandy clay(SC) and sandy loam (SL) from the major pineapple cultivated areas of central Kerala were selected for the study. Surface soil samples (0-20 cm) were collected and were air dried and sieved

Materials and analytical techniques

Particle size distribution was determined by hydrometer method. Soil pH, organic carbon (OC) and total Cd was determined by standard protocols[12].Stock solutions of Cadmium (Cd) were prepared from $CdCl_2$. All working solutions were prepared by diluting the stock solution using 0.01 M $CaCl_2$. The concentration of Cadmium ion solutions were measured by Atomic Absorption Spectrophotometer (Varian-240).

Batch adsorption experiment was conducted in 50 ml centrifuge tube by weighing 1gsoil followed by 25 ml of Cd solution of varying initial concentrations (2.5,5,10,20,40,60,80, 100 and 120 mgL^{-1}).The samples were shaken for 3 h at two different temperatures 25°C and 40°C and was adjusted to soil pH using 0.01 M $Ca(OH)_2$ or 0.01 M HCl. After centrifugation at 3000 rpm for 15 min, the supernatant liquid phase was filtered and Cd concentration was measured by atomic absorption spectrophotometer. The adsorbed Cd quantity(q_e , mgg^{-1})was calculated by the following equation.

$$q_e = \frac{V(C_i - C_e)}{M} \quad (1)$$

Where C_i and $C_e(mgL^{-1})$are the initial and final concentrations of (Cd). *V(L)* is the volume of metal solution and *M (g)* is the mass of (soil) used.

Adsorption isotherms

In order to understand the mechanism of interaction of Cd to soil, equilibrium adsorption isotherms were used. The experimental adsorption equilibrium data of Cd were fitted by Langmuir and Freundlich isotherm models explained by the following equation.

$$q_e = \frac{q_{\max} \times k_L \times C_e}{(1 + k_L C_e)} \quad (2)$$

$$q_e = k_F \times C_e^{1/n} \quad (3)$$

Where q_e (mgg^{-1}) is the specific equilibrium amount of (Cd) , $C_e(mg\ L^{-1})$ is the equilibrium concentration of Cd, q_{max} $(mg\ g^{-1})$ is the maximal adsorption capacity ,$k_L(Lg^{-1})$ and $k_F(Lg^{-1})$ is the empirical constants that indicates the extent of adsorption and *n* is the adsorption effectiveness .

Adsorption isotherms were plotted by using R software ver.3.2.3.In order to resolute the best isotherm for the Cd adsorption, data analysis was conducted using non-linear mathematical expression for the models. The fitness of the model was assessed based on the value of AIC (Akaike information criterion) because of its strong propensity with small data points and provide reliable results[13]. The model with minimum AIC value was selected as the best fit model[14].

Adsorption Thermodynamics.

The Cd adsorption mechanisms by different types of soil were assessed by using thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$[15]. It was calculated by the isotherm constants (k_L or k_F) adopting the van't Hoff's Equation (4,5,6).Thermodynamic consideration of an adsorption process was necessary to conclude whether the process is spontaneous or not. According to thermodynamic law, changes in free energy ($\Delta G°$) of adsorption is calculated by following equations

$$\Delta G^0 = -RT \ln K^0 \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

Where K^o is the thermodynamic equilibrium constant without units, *T* is the absolute temperature in Kelvin, *R* is the Universal gas constant (8.314 $Jmol^{-1}K^{-1}$). Enthalpy change *($\Delta H°$)*is calculated as

$$\Delta H^0 = -\ln(\frac{K_1}{K_2}) \times R(\frac{1}{T_2} - \frac{1}{T_1}) \quad (6)$$

Where K_1 and K_2 are the thermodynamic equilibrium constant at a temperature of 298 K (T_1) and 313 K(T_2) respectively. Entropy change $\Delta S°$ of adsorption is calculated by the equation.

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \quad (7)$$

RESULT AND DISCUSSION

Physico-chemical parameters

Physico-chemical parameters such as pH, organic carbon (OC),total Cd concentration,clay%, silt %, sand % of SCL, LFS, SC and SL samples are shown in table 1.

Table 1: Physico-chemical characterisation of soil

Samples	pH	OC%	Clay %	Silt %	Sand %	Soil Type	Total Cd (mg/kg)
SCL	5.3	1.2	31.2	2.45	66.4	Sandy Clay Loam	60
LFS	5.2	2.8	9.76	7	83.2	Loamy Fine Sand	120
SC	5.9	1.4	36.2	0.6	63.2	Sandy Clay	60
SL	4.2	0.8	17.8	9	73.2	Sandy Loam	80

The results showed that the Soil pH of SCL, LFS, SC and SL samples were found to be 5.3,5.2,5.9 and 4.2 with percentage of organic carbon1.2%, 2.8, 1.4 and 0.8 % respectively. Total cadmium residing in the soil samples under study ranges from 60 to 120mgkg^{-1}.

Adsorption isotherms

Adsorption of Cd onto SCL, LFS, SC and SL soils were evaluated using non-linear forms of Langmuir [16] and Freundlich isotherm [17] parameters are shown in table 2 and table 3 at 25º C and 40ºC respectively.

Table 2:Langmuir and Freundlich equation parameters for adsorption of Cd onto SCL, LFS, SC and SL at 25°C

	Langmuir isotherm			Freundlich isotherm			
Adsorbent	q_{max} (mgg^{-1})	k_L(Lg^{-1})	AIC of Langmuir	k_F (Lg^{-1})	n	AIC of Freundlich	Fitted Adsorption model
SCL	-3.414	-0.0009	-3.43	0.001	0.83	-8.37	Freundlich
LFS	0.89	0.009	-6.65	0.013	1.28	-10.83	Freundlich
SC	-0.02	-0.01	-22.54	0.008	1.34	0.88	Langmuir
SL	0.121	-0.078	0.38	0.0008	0.83	-11.53	Freundlich

Table 3:Langmuir and Freundlich equation parameters for adsorption of Cd onto SCL, LFS, SC and SL at 40° C

	Langmuir isotherm			Freundlich isotherm			
Adsorbent	q_{max} (mgg^{-1})	k_L(Lg^{-1})	AIC of Langmuir	k_F(Lg^{-1})	n	AIC of Freundlich	Fitted Adsorption model
SCL	1.52	0.002	-21.49	0.04	3.03	-7.84	Langmuir
LFS	0.36	0.06	-11.72	0.04	2.23	-18.1	Freundlich
SC	0.23	0.02	-16.07	0.01	1.87	-12.7	Langmuir
SL	0.04	0.42	-19.03	3.4	6.2	-11.89	Langmuir

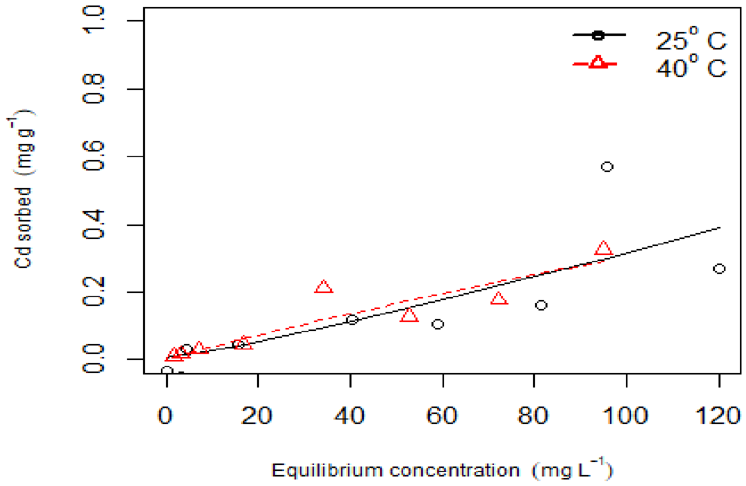

Figure 1: Fitted adsorption isotherm of Sandy clay loam soil at 25°C(Freundlich)and at 40°C (Langmuir).

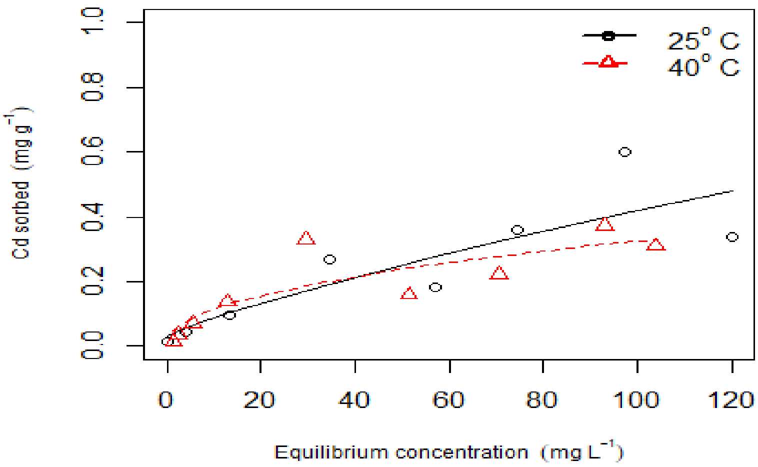

Figure 2: Fitted adsorption isotherm of loamy fine sandy soil at 25°C(Freundlich)and 40°C (Freundlich).

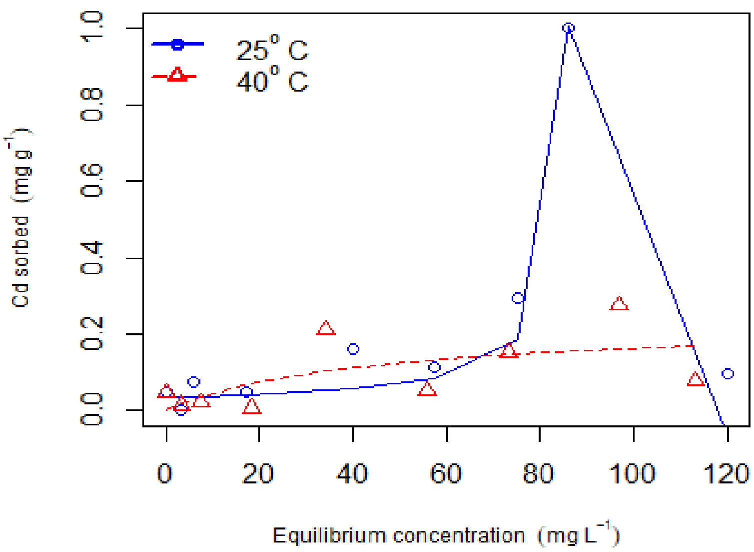

Figure 3: Fitted adsorption isotherm of Sandy clay soil at 25°C(Langmuir)and 40°C (Langmuir).

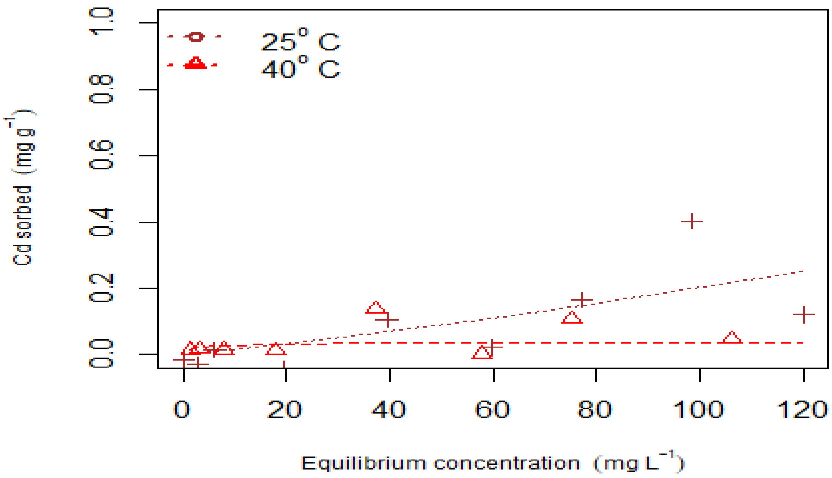

Figure 4: Fitted adsorption isotherm of Sandy loam soil at 25°C(Freundlich)and 40°C (Langmuir).

Adsorption isotherm data obtained for SCL at 25ºC are given intable 2 andshows that the$q_{max}$was -3.414 mg g^{-1} with k_L value -0.0009 Lg^{-1}. The Freundlich parameters k_F(0.001 Lg^{-1})and n (0.83) revealed the less adsorption capacity and the unfavourable adsorption. AIC values of Langmuir and Freundlich isotherm was -3.414 and -8.37 and the lower AIC values confirms that Freundlich model better explains the adsorption process (Fig 1).At 40°C,q_{max} from Langmuir isotherm was found to be 1.52$mgg^{-1}$and k_L value is 0.002Lg^{-1}. It was found that in SCL soil, adsorption of Cd increases with temperature and lower AIC value (-21.49) endorses the best fitting nature of Langmuir isotherm model than Freundlich model (-7.84).
In LFS Freundlich isotherm model fits better at both temperatures(Fig 2) than Langmuir isotherm. At 25°C, the n value1.28 indicates that adsorption was favourable and k_F value was found to be 0.013Lg^{-1}.Lower AIC value (-10.83) found to be for Freundlich adsorption isotherm confirms that the Freundlich model fit more than Langmuir isotherm model (-6.65).At 40°C, values of n and k_F are 2.2 and 0.04Lg^{-1} respectively and the adsorption is favourable and it increases with temperature. Lower AIC value (-18.1) confirms the best fitting nature of Freundlich isotherm than Langmuir (-11.72).
In SCsoils, Langmuir fits better than Freundlich at both temperatures (Fig 3). In SC at 25°C, q_{max} and k_L values were found to be -0.02$mgg^{-1}$and -0.01 Lg^{-1} respectively. Lower AIC valueof Langmuir isotherm than Freundlich indicates a better fit for the former model for these soils. At 40°C,$q_{max}$and k_L values were 0.23 mgg^{-1} 0.02 Lg^{-1}. .It was found that adsorption of Cd decreases with increase in temperature. Lower AIC value (-16.07) confirms that Langmuir model fits better than the Freundlich isotherms (-12.7) in these soils.
For SL Freundlich model fits better at 25°C (Fig 4), n value is 0.83 shows less adsorption(not favourable adsorption) and value of k_F was 0.0008Lg^{-1}. Lower AIC values were found to be -11.53 for Freundlich isotherm than Langmuir (0.38).At 40°C$q_{max}$and k_L value were found to be 0.04mgg^{-1} and 0.42Lg^{-1}that confirms lesser adsorption. Lower AIC value (-19.03) endorses the best fitting nature of Langmuir isotherm model than Freundlich model (-11.89). Lability of the adsorbed Cd [18] and reversibility of sorbed Cd [19] was more as compared with other heavy metals. Thus it poses a potential threat to ground water pollution and plants..

Table 4: Thermodynamic parameters obtained for the adsorption of Cd onto SCL, LFS, SC and SL of soil at 25ºC and 40ºC

Soil type	Temperature(K)	$\Delta G°$ ($kJmol^{-1}$)	$\Delta H°$($kJmol^{-1}$)	$\Delta S°$($Jmol^{-1}K^{-1}$)
SCL	298 313	16.24 15.62	-0.0013	-54.5 -49.9
LFS	298 313	10.77 8.3	-0.0024	-36.16 -26.53
SC	298 313	11 9.8	-0.0013	-36.94 -31.35
SL	298 313	17.52 2.2	-0.0021	-58.79 -7.3

Adsorption Thermodynamics

Consideration of thermodynamic parameters viz, free energy ($\Delta G°$), change in enthalpy ($\Delta H°$) and change in Entropy ($\Delta S°$) furnish an insight into the process of Cd sorption in the soils given in (table 4). $\Delta G°$ for Sandy clay loam at 25°C and 40°C were 16.24 $kJmol^{-1}$ and 15.62$kJmol^{-1}$ respectively. For loamy fine sand $\Delta G°$ at 25°C and 40°C were found to be 10.77 $kJmol^{-1}$ and 8.3$kJmol^{-1}$.Sandy clay soil gave a $\Delta G°$ values of 11 $kJmol^{-1}$and 9.8$kJmol^{-1}$ at 25°C and 40°C respectively. $\Delta G°$ value for Sandy loam was found to be 17.52$kJmol^{-1}$and 2.2$kJmol^{-1}$ at 25°C and 40°C.The positive $\Delta G°$ values indicated that the adsorption of Cd onto these soils were a non-spontaneous process. $\Delta H°$ values were found to be -0.001$kJmol^{-1}$(SCL),-0.0024 $kJmol^{-1}$(LFS), -0.0013 $kJmol^{-1}$(SC) and-0.0021$kJmol^{-1}$ (SL). The negative $\Delta H°$ values point out that the adsorption of Cd on to the soil is exothermic in nature. Similar results were reported in earlier studies [20]and show that nearly54.3 % of the applied Cd on to an Ultisol (highly weathered soil) was adsorbed by at 10°C as compared with that at25°C and 40°C. The increase in temperature can contribute a great escaping tendency of the solute from the solid to the solution phase. $\Delta S°$ for SCL at 25°C and 40°C were - 54.5 $Jmol^{-1}K^{-1}$ and -49.9$Jmol^{-1}K^{-1}$ respectively. For LFS$\Delta S°$ at 25°C and 40°C was found to be -36.16$Jmol^{-1}K^{-1}$ and -26.53$Jmol^{-1}K^{-1}$. SC soil showed $\Delta S°$ values of-36.94 $Jmol^{-1}K^{-1}$ and -31.35$Jmol^{-1}K^{-1}$ at 25°C and 40°C respectively. $\Delta S°$ value for SL was found to be -58.79 $Jmol^{-1}K^{-1}$ and -7.3$Jmol^{-1}K^{-1}$ at 25°C and 40°C respectively. The values of $\Delta S°$ for Cd in the studied soils were negative and it indicated a lesser disorder in the soil-Cd system. Results also indicate a weak or moderate adsorption of Cd on to the soils.

CONCLUSION

Soil types such as SCL, LFS, SC and SL were evaluated by its physico-chemical and adsorption potential towards Cd at 25ºC and 40ºC. The adsorption data was analysed using Langmuir and Freundlich adsorption isotherm models. The results showed that at 25°CFreundlich isotherm was found to provide a better fit to SCL,LFS and SL soils and Langmuir isotherm for SC soil. On the contrary, the adsorption data had a better fit to Langmuir isotherm for SCL, SC and SL and Freundlich isotherm for LFS at 40°C. Careful investigation and consideration of thermodynamics parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ revealed that the positive value of $\Delta G°$ indicated the adsorption of Cd on to the soil is a non-spontaneous process. The negative value *of* $\Delta H°$ indicated an exothermic nature of the adsorption process. The negative values of ΔS° indicated less disorder in the studied soil-Cd system. Results also stipulate a weak or moderate adsorption of Cd onto the soils and may pose threats to the ground water and pineapple fruit heavy metal contamination.

ACKNOWLEGDGEMENT

Grateful to Cochin University of Science and technology for the financial support and to the department of soil science, Kerala Forest Research Institute for the research facilities.

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CITATION OF THIS ARTICLE

K.A Samitha, R Sivalingam, S Sandeep and R Mary Lopez. Thermodynamics of Cadmium adsorption in the major Pineapple (*Ananas comosus*) Cultivated soils of Kerala .Bull. Env. Pharmacol. Life Sci., Vol 8 [11] October 2019: 88-94