Communication in Physical Sciences 2020, 6(1): 774-782

Decontamination of Pb^{2+}, Cd^{2+} and Ni^{2+} Polluted Water by Adsorption Unto Butterfly Pea (*Centrosema pubescens*) Seed Pod

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Received 18 November 2020/Accepted 26 November 2020/Published online: 27 November 2020

Abstract: *Heavy metal contaminations of water bodies by industrial and other wastes have been confirmed to exert significant role in the environment because of expanding risk factor such contamination can cause. In this study, batch adsorption method is adopted to removed Pb^{2+}, Cd^{2+} and Ni^{2+} from aqueous solution using butterfly pea pod. The adsorption data reflected strong dependency of the adsorption on temperature, adsorbent dosage, initial metal ion concentration, period of contact and other factors. The adsorption of the three metal ions proceeded through similar mechanism (i.e. physical adsorption) and the trend was supported by maximum adsorption capacity values (which were Pb(II), Cd(II) and Ni(II) ions was 10.52, 18.32 and 13.18 mg/g), free energy change data and sticking probability parameters. The adsorption was spontaneous and best fitted Langmuir, Flory Huggins, Freundlich and Dubinin-radushkevich adsorption models. Results of the present investigation revealed that butterfly pea pot is an excellent adsorbent for lead, cadmium and nickel ions.*

Key Words: *Contamination, water, heavy metals, remediation, adsorption, butterfly peas pod*

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1.0 Introduction

The presence of heavy metals ions in the environment has significant impact because of their toxicity and subsequent consequences (Eddy *et* al., 2004). Unfortunately, heavy metal generation and discharge to the environment is growing proportionally with increasing urbanization, industrialization, agricultural practices and other anthropogenic activities (Ngah *et al*., 2008: Guyo *et al*., 2015). Heavy metals are those metals whose density is greater than 5 g/cm^3 (Obahiagbon and Olowojoba, 2006). These include the cadmium, mercury, lead, nickel, iron, selenium and others. Unique property of these metals is that they are toxic above certain concentration (which vary from one heavy metal to another) (Babel and Kurniawan, 2003; Okoyeagu *et al*., 2020).

Cadmium, lead and nickel exist as divalent heavy metals whose toxicity regime has been widely reported. For example, cadmium ion accounted for the popular itai ita diseases that recorded global toxicity signal. Cadmium ion can replace calcium ion in bone, teeth and other organs and can lead to softening of bones and kidney failure (Fu and Wang, 2011). Nickel toxicity may lead to contact dermatitis, gastrointestinal disorder, headaches, lung fibrosis, cardiovascular diseases, lung and other forms of cancer, etc (Genchi *et al*., 2020; Nicholas *et al*., 2003). Lead ion exert its toxic effect on the blood and can manifest its taxological signs and symptoms in the central nervous system and the gastrointestinal tract disorder (Amadi *et al*., 2020). Chronic exposure to lead ion above 1 mg/L has been confirm to be precursor for mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and eventual death (Martin & Griswold, 2009).

In view of the known and established toxicity of most heavy metals in the environment, several approached have been designed and implemented as technologies for the removal of heavy metal ions from the environment especially, aqueous solution. Some conventional methods include ion exchange, filtration, chemical precipitation, complexation, adsorption, electrodeposition and reverse osmosis, etc (Anwar, *et al*., 2010; Foo and Hmeed 2009; Panida *et al*., 2014). Both natural and synthetic adsorbents have been studied by various researchers for the removal of heavy metal ions from dilute solutions [Panida *et al*., 2014: Feng *et al*., 2012].

However, the use of plant materials has been linked to ecofriendliness and optimum efficiency. Plant leaves (Odoemelam *et al*. 2018), seeds (Eddy, 2009) stem and roots and even their waste product have beeen successfully used to remove heavy metals from aqueous solution. The use of plant waste has given hope toward effective waste management. For example, Essien and Eddy (2015) reported the effectiveness of Sorghum waste (from Champion brewery industry) for the adsortion of some heavy metals. Okwunodulu and Eddy (2014) reported significant adsorption capacity of cola nitida waste biomass for the removal of lead, cadmium and nickel from aqueous solution. Similar findings have been reported by Uchechukwu *et al*., (2018) for thee removal of nickel, cadmium and lead ions from aqueous solution using kola nut pod husk. *Centrosema pubescens* is a legume and belongs to the family, *Fabaceae* and subfamily *Faboideae*, and tribe Phaseolae. Although it is a native of South America, it is widely cultivated in most tropical countries (including Nigeria) as a foliage plant. The seed pods of the plant are normally wasted and may attract disposal problem in some cases. This means technology toward possible re-use or recycling of the waste materials is a welcome and sound environmental management practice. Lead, nickel and cadmium are widely distributed in the environment and their concentrations have been observed to be increases at the rate that may posed future threat. Therefore, adoption of effective remediation plan towards the control of these heavy metal ions in industrial and other effluent is essential. Studies have shown that chemical constituent of an adsorbent materials has strong influence on their performance. Generally, the presence of suitable funtional groups in the adsorbent has been found to enhance adsorbent. *Centrosema pubescens* seed pod an agricultural waste contains polymeric groups like cellulose, pectin, proteins etc. that promotes sorption process through physical and chemical linkages (Anwar, *et al*., 2010).

This material has been found to have significant potential to remove heavy metals from contaminated soil (Kumar *et al*., 1995). However, their potential as adsorbent for the removal of heavy metals from aqueous solution has not been widely investigated. Therefore, the present study is aimed at using C*entrosema pubescens* seed pod as an adsorbent for the removal of heavy metal from aqueous solution.

2.0 Materials and Methods

All the reagents used were of analytical grades from Sigma-Aldrich and were used without further purification. Double de-ionized water was used in the preparation of all sample solutions. 1000 mg/L solutions of lead, cadmium and nickel were prepared as stock solutions from their salts $Pb(NO_3)_2$, $CdSO_4.8H_2O$ and $NiSO_4.6H_20$ respectively.

2.1 Preparation of the adsorbent

Samples of butterfly pea seed pod were obtained from Michael Okpara University of Agriculture botanical garden in Umudike, Abia state Nigeria. The pods were carefully removed, washed with de-ionized water, dried and crushed to powder form using a blender. The powdered samples were sieved to obtain 180 μm mesh size. The sieved samples were soaked in 0.3 M HNO_3, stirred for 30 minutes and allowed to stand for 24 h before filtering through Whatman no. 41 filter paper rinsed thoroughly with de-ionized water and sundried for 2 h. The adsorbent was kept in an oven at 105 ºC for 2 h and finally stored in a tight plastic container.

2.2 Batch adsorption experiments

Batch adsorption experiments were carried out by agitating the 250 mL volumetric flasks containing 0.05 g adsorbent and 50.0 cm^3 solution of the metal ions on a rotary shaker at 150 rpm for 60 min. The batch adsorption experiment for investigating the influence of adsorbent dosage was similar but the concentration, temperature and pH were held constant while the mass of the adsorbent was varied. Influence of temperature was investigated by keeping other factors constant except temperature. Batch adsorption experiment carried out by varying the initial concentration of the respective heavy metal ions at constant temperature, pH, contact time and adsorbent dosage was used to study the effect of initial heavy metal ion concentration. In each case, the percentage of heavy metal ion removed from the solution through adsorption was calculated using equation 1 while the equilibrium amount of metal ions adsorbed was calculated using equation 2

$$\%R = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \quad (1)$$

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{v}{m} \quad (2)$$

where C_0 is the initial concentration of the metal ion, C_e is the equilibrium concentration, V is the volume of solution and m is the mass of the adsorbent.

Concentration of metal ions in solution was analysed using Atomic Absorption Spectrophometer (Perkin Elmer Analysit 200). Calibration curves were prepared separately for nickel, cadmium and lead respectively. Each solution containing the respective metal ion was aspirated into the spectrophotometer. Concentration of the respective metal ion was determined through extrapolation after the absorbance has been read from the spectrophotometer.

3.0 Results and Discussion

3.1 Effect of adsorbent dosage

Fig. 1 shows the variation of amount of dye adsorbed with adsorbent dosage. From the plot, it is observed that the percentage removal increases with increase in adsorbent dosage. Adsorption of the three heavy metal ions seems to follow similar trend, which indicates that they also followed similar mechanics,

Several factors have been documented to influence preferential the extent of adsorption of ions on similar adsorbent. Some of these factors are charge of the ion, ionic radius, surface area, etc (Mobasherpour *et al*., 2012). However, lead, cadmium and nickel have similar charge. Their ionic radius are Pb(1.19A°) >Cd(II) (0.97A°)> Ni(II) (0.72A°). Ideally, the trend for adsorption under similar conditions should be in order of their decreasing ionic radius but from the results obtained in this study, the observed trend is Cd(II)>Pb (II) > Ni(II). This suggests that the adsorption of these ions unto the studies adsorbent depends on other factors apart from ionic radius. Generally, the larger the ionic radius, the stronger the adsorption of the ion since the hydration capacity of that ion is smaller, resulting in weaker binding of the ion and water phase. The preference of adsorption exhibited for Pb (II) and Cd (II) over Ni (II) and Cu (II) may be also due to the difference hydration energy. Trend similar to the one observed in this work has been reported by Ekuma *et al*., (2019).

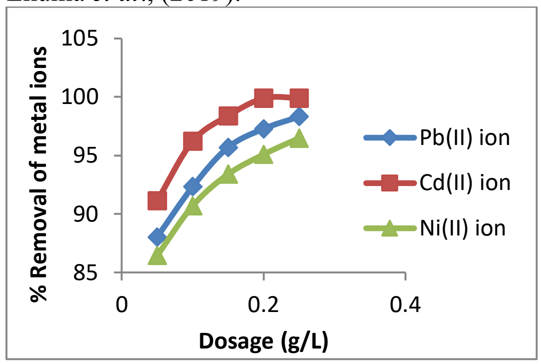

Fig.1: **Variation of percentage removal with dosage for the adsorption dose on the adsorption of metal ions onto butterfly pea seed pods**

2.2 Effect of initial metal ion concentration

Fig. 2 shows plots for the variation of equilibrium amount of nickel, lead and cadmium ions adsorbed with initial concentration.

The plot shows a linear relationship between the adsorbate and their respective concentrations. However, the adsorption of the three-metal ion is observed to be parallel to each other which indicate similarity in adsorption mechanism. The observed linear pattern can be attributed to the progressive increase in adsorption due to increase in the amount of metal ions diffusing unto the surface of the adsorbent. As long as the available adsorption site is not fully occupied, Adedirin *et al.* (2011a,b) observed similar trend for the adsorption of heavy metal unto microorganism while Donmez and Akin (2002) attributed the pattern to the exceeding gravity of initial concentration exhibiting greater driving force to overcome all mass transfer resistance of all molecules between the aqueous and solid phases (Donmez and Aksu, 2002). The results obtained indicate that surface saturation is dependent on initial metal ion concentration (Amadi *et al*., 2017). For reasons explained earlier, cadmium is the most adsorbed ion while nickel is least adsorbed.

2.3 Adsorption isotherm

Adsorption isotherms can give deep insight into the adsorption characteristics of the studied heavy metals and the adsorbents. This may include level of interaction, existent of mono or multiple layer of adsorption, degree of association and other properties (Gökcekus *et al*., 2011). Therefore, adsorption isotherms are critical models suitable for optimizing the adsorption process. The adsorption models represent the surface properties and affinity of the adsorbent.

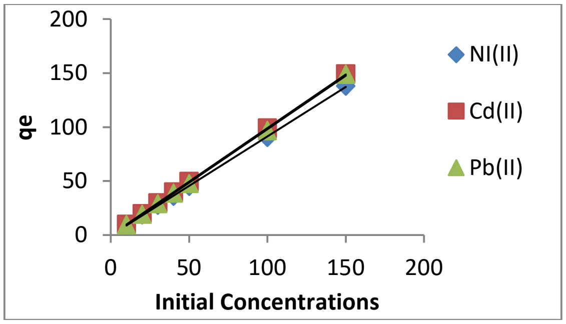

Fig 2: **Variation of equilibrium amount of heavy metal adsorbed with initial metal ion concentration for the adsorption of heavy metal ions onto butterfly pea**

The adsorption of the heavy metals ions was found to fit Langmuir, Fruendlich and Dubinin Radushkevich adsorption isotherms. The assumptions defining the Langmuir isotherm can be written according to equation 3 (Ali and Ahmed, 2014)

$$\frac{Ce}{q_e} = \frac{1}{q_m K_{ads}} + \frac{Ce}{q_m} \qquad (3)$$

where *Ce* is the metal ions equilibrium concentration (mgL^{-1}), q_m is the maximum adsorption capacity of the sorbent when the surface is completely covered with the metal ions (mgg^{-1}), and K_{ads}(L/mg) is the Langmuir adsorption constant (adsorption energy) representing the affinity between the sorbent and the metal ions (mgg^{-1}). The Langmuir isotherms for the adsorption of the studied heavy metals are shown in Fig. 3. The degree of linearity of the plots (measured by R^2 values) was very high, which indicated excellent fitness of the Langmuir model to the adsorption data. Langmuir adsorption parameters deduced from the plots are recorded in Table 1. The results indicated that the trend for the variation of q_m, k_{ads} and free energy (ΔG^0_{ads}) follows the trend similar to the order of adsorption (i.e, $Cd^{2+} > Pb^{2+} > Ni^{2+}$). These three parameters determine the strength of adsorption indicating that cadmium ion was the most adsorbed heavy metal ion while nickel was least adsorbed.

Another significant information that can be obtained from the Langmuir model is the separation factor (R_L) defined as, $R_L = \frac{1}{K_L C_0}$ (Ahalya *et al*., 2005) (4)

Based on calculated values of R_L, there are extreme cases that can be described. These are: (i) for favorable adsorption, $0 < RL < 1$ (ii) for unfavorable adsorption, $RL > 1$ (iii) for linear adsorption, $RL = 1$ (iv)for irreversible adsorption, $RL = 0$ (Gupta and Bhattacharyya, 2006).

Estimated values of R_L values for lead, cadmium and nickel ions were 0.012, 0.00047 and 0.0204 which indicate that the adsorption of the studied heavy metal ions is favourable.

Calculated values of free energy recorded in Table 1 were calculated using the Gibb Helmholtz equation 5

$$\Delta G^0_{ads} = -2.303RTlogk_{ads} \qquad (5)$$

where R is the gas constant and T is the temperature. The free energy changes are found to be negative and less than the threshold values require for the mechanism of chemical adsorption. Therefore, the adsorption of the studied heavy metal ion is spontaneous and consistent with the mechanism of physical adsorption.

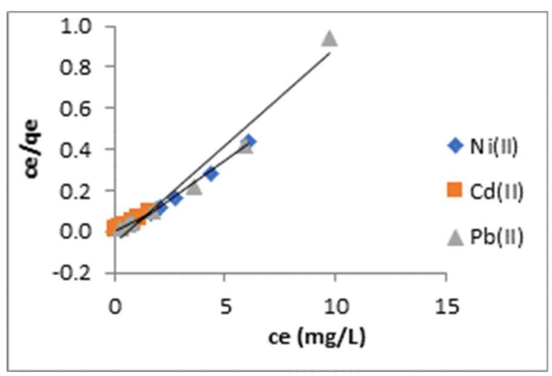

Fig. 3: Langmuir isotherm for the adsorption of lead, cadmium and nickel ions onto butterfly pea seed pod

Table 1: Langmuir parameter for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto butterfly pea seed pod

Metal ion	Slope	Intercept	q_m (mg/g)	K_{ads} (L/mg)	ΔG^0_{ads} (kJ/mol)	R^2
Pb^{2+}	0.0951	-0.0564	10.52	1.6854	1.32	0.9690
Cd^{2+}	0.0564	-0.0130	17.73	4.3385	3.70	0.9966
Ni^{2+}	0.0759	-0.0379	13.18	2.0026	1.75	0.9936

The Logarithm form of the Freundlich isotherm can be written according to equation 6 (Mohan & Singh, 2002),

$$logq_e = logK_F + \frac{1}{n}logC_e \quad (6)$$

Where qe is the amount of the metal ions adsorbed (mg/g), Ce is the equilibrium concentration of the metal ions in solution (mg/L), and K_F and n are constants which integrate the factors affecting the adsorption capacity and intensity of adsorption respectively. The value of 1/*n* varies with the sorbent heterogeneity and provides a criterion for determining the favourability of the adsorption process. There are four possible values for 1/*n* (Mckay *et al*., 1982): (i) for favourable adsorption, $0 < 1/n < 1$ (ii) for unfavourable adsorption, $1/n > 1$ (iii), for linear adsorption $1/n = 1$ (iv) for irreversible adsorption $1/n = 0$. The intensity of adsorption is an indication of the bond energies between metal ions and adsorbent, and the possibility of slight chemisorption rather than physisorption (Arivoli *et al*., 2007). The value of $1/n< 1$ and $n > 1$ for the metal ions suggest that adsorption are favourable and that chemisorption is much more favourable respectively. The Freundlich isotherm for the adsorption of the studied metal ions on the surface of the adsorbent is shown in Fig. 4 while Freundlich adsorption parameters are recorded in Table 2. From the presented results (Table 2), values of 1/n are less than unity, hence the adsorption of the studied heavy metal ions is favourable. Also calculated values of free energy changes indicated that the adsorption is spontaneous and follows physiosorption mechanism.

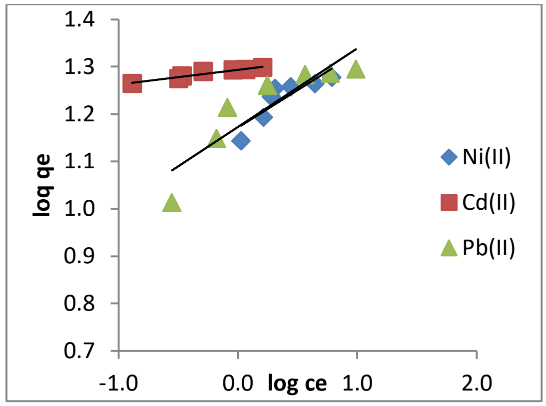

Fig..4: Freundlich isotherm for the adsorption of the metal ions onto butterfly pea seed pod

Table 2: Freundlich parameter for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto butterfly pea seed pod

Metal ion	Slope	$logK_F$	N	ΔG^0_{ads} (kJ/mol)	R^2
Pb^{2+}	0.1661	1.1731	6	-6.81	0.8062
Cd^{2+}	0.031	1.2936	10	-7.50	0.9423
Ni^{2+}	0.1583	2.1714	6	-12.30	0.7434

The Dubinin–Radushkevich (D-R) describes the adsorption on a single uniform pore and is mostly used to describe the mechanism of adsorption (Do, 1998). The linear form of D-R isotherm equation has the following form:

$$lnq_e = lnq_{DR} - k_{DR}\varepsilon^2 \quad (7)$$

where lnq_{DR} is the theoretical saturation capacity (mol/g), k_D (mol^2/J^2) is the activity coefficient which is related to the mean sorption energy. ε is the Polanyi potential expressed as,

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (8)$$

The adsorption energy is given as

$$E = \frac{1}{\sqrt{2K}}. \quad (7)$$

where q_D is the theoretical saturation capacity (mol/g), K_D (mol^2/J^2) is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential. The D-R constants q_{DR} and k_{DR} were calculated from the linear plots of lnq_e versus ε^2 (Fig.5) and the results are shown in Table 3. The saturation limit q_D may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate (Khan *et al*., 1995).

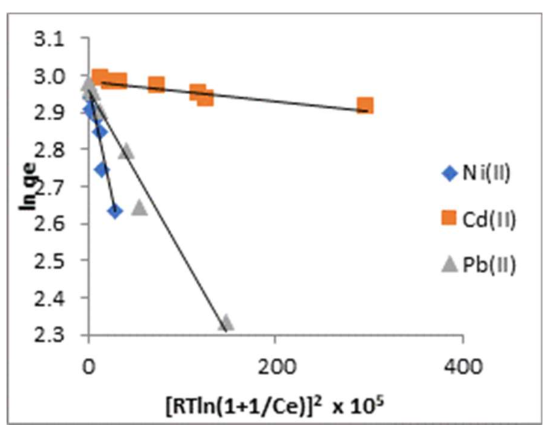

Fig. 5: D-K plots of metal ions on butterfly pea at constant temperature.

The adsorption is physisorption when the sorption energy is less than 8 kJ/mol and vice vera (Singha and Das, 2013). As shown in Table 1, the sorption energies are 10.5409 for Pb(II), 40.8248 for Cd(II), and 6.5094 J/mol for Ni(II) ions.

Table 3: Dubinin- Raduskevich adsorption parameter for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto butterfly pea seed pod

Heavy metal ion	K_{DR}	lnq_{DR}	E (J/mol)	R^2
Pb^{2+}	0.0045	19.3327	10.5409	0.9786
Cd^{2+}	0.0003	19.8122	40.8248	0.9210
Ni^{2+}	0.0018	19.3405	6.5094	0.9349

The graphical representation of the model for the metal ions adsorption onto the adsorbent is given in Figs. 5, while the characteristic constants are presented in Table 1. Flory- Huggins isotherm defines a multi-layer adsorption in connection with the presence of a heterogeneous pore distribution and expressed:

$$\left(\frac{\theta}{C_0}\right) = logK_{FH} + xlog(1-\theta) \qquad (9)$$

where x is the ions number occupying adsorption sites on the adsorbent and K_{FH} is the equilibrium constant (kinetic coefficient) in this model calculated and presented in Table 4.

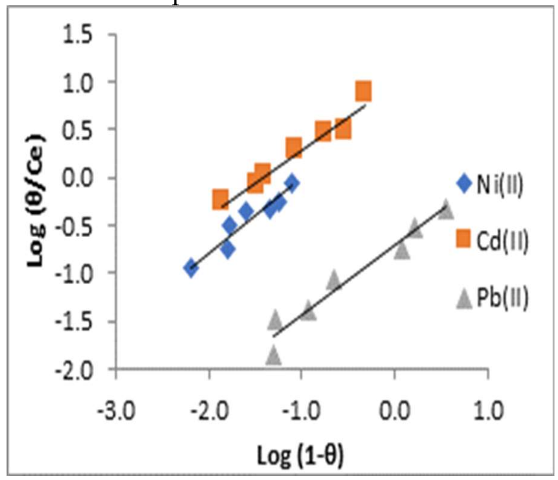

Fig.6. Flory-Huggins isotherm for the adsorption of the metal ions onto butterfly pea seed pod

The results of the experimental model were also described by Flory-Huggins
model where the values of the regression coefficients (R^2> 0.91) . Therefore, the retention of the metal ions onto butterfly pea is as a monolayer.

Table 4: Flory Huggins parameter for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto butterfly pea seed pod

Metal ion	K_{FH}	x	ΔG^0_{ads} (kJ/mol)	R^2
Pb^{2+}	8.0854	1.3138	-5265.16	0.9533
Cd^{2+}	66.0085	0.9926	-10554.66	0.9283
Ni^{2+}	3.5809	1.1000	-3213.24	0.8721

In order to further support the ascertain the predominant mechanism between physical and chemical adsorption, the values of the activation energy (Ea) and sticking probability (S*) were estimated using the modified Arrhenius type equation according to equation (10) (Ghaedi *et al*., 2013):

$$S^* = (1-\theta)e^{\frac{-E_a}{RT}}) \qquad (10)$$

From the logarithm of both sides of the equation, we have,

$$S^* = (1-\theta) - \frac{E_a}{RT} \qquad (11)$$

Therefore, a plot of logS* versus $\frac{1}{T}$ should be linear with slope and intercept equal to $-\frac{E_a}{R}$ and $(1-\theta)$ respectively. Generally, values of sticking probability link the adsorbate and adsorbent and lies in the range 0 < S* < 1. The parameter (S*) indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinite. The surface coverage (θ) can be calculated from equation 12

$$\theta = (1 - \frac{Ce}{Co}) \qquad (12)$$

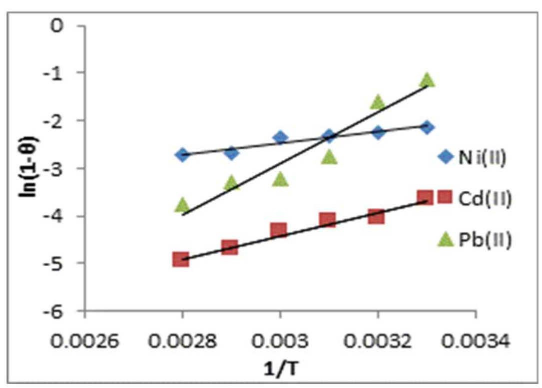

Fig. 6: Sticking probability plot for the adsorption of Ni^{2+}, Pb^{2+} and Cd^{2+} metal ions onto butterfly pea seed pod at various temperatures.

The activation energy and sticking probability are shown in Table 5, from a plot of $\ln(1-\theta)$ vs. $\frac{1}{T}$ (shown in Fig 6). The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies (<40 kJ mol^{-1}) are characteristics for physical adsorption, while higher activation energies (>40 kJ mol^{-1}) suggest chemical adsorption (Chakraborty *et al*., 2011). The activation energy obtained for the adsorption of metal ions onto adsorption indicates that the adsorption process is physisorption.

Table 5: Sticking probability parameters for the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto butterfly pea seed pod

Metal ion	$S^* \times 10^{-3}$	Ea (kJ/mol)	R^2
Pb^{2+}	0.749	44430.02	0.9249
Cd^{2+}	19.555	20301.96	0.9765
Ni^{2+}	2.309	9969.32	0.9200

4.0 Conclusion

The adsorption equilibrium of the metal ions onto butterfly pea was studied in a batch mode operation for the parameters initial metal ion concentration, temperature, and adsorbent dosage. The results showed that adsorption of the metal ions increased with increase in initial metal ion concentrations and temperature while it decreased with increase in adsorbent mass. The adsorption equilibrium isotherms were analyzed by Langmuir, Freundlich, D-R and Flory-Huggins isotherm equations. All results obeying isotherm models were choosing in this study but more favourable for Langmuir which provided the best correlations for the metal ions onto butterfly pea. As a result of the thermodynamic evaluation of metal ions adsorption, the obtained negative ΔG values revealed that the adsorption of metal ions onto butterfly pea was thermodynamically feasible and spontaneous during the adsorption process.

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Conflict of Interest

The authors declare no conflict of interest