

Sequestration of Co^{2+} , Zn^{2+} and Cd^{2+} by Base Modified Sweet Potato Leaf: Kinetics, Equilibrium and Thermodynamic Studies

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Abstract: *The use of base modified sweet potato leaf (BSPL) was demonstrated as an effective adsorbent for the removal of cobalt, zinc and cadmium ions using the batch adsorption process. The biosorption properties of the adsorbent for metal ions were evaluated for sorption time, initial concentration of the contaminants, pH, sorbent dosage and temperature. Maximum uptakes of metal ions were attained after 100 minutes for Zn^{2+} and Cd^{2+} ions and at 150 minutes for Co^{2+} ions. Kinetic analysis of the adsorption data revealed that the biosorption data were best described by the Pseudo-second-order model ($R^2 > 0.95$). It was also apparent that the data best fitted the Langmuir model, which yielded a maximum adsorption capacity of 3.879, 4.069 and 4.368 $\text{mg}\cdot\text{g}^{-1}$ for Zn^{2+} , Cd^{2+} and Co^{2+} respectively. Analysis of calculated thermodynamic parameters affirms that the biosorption process is feasible, spontaneous and endothermic. Evaluated entropy change (ΔS) for the adsorption processes were 162.12, 171.93 and 174.93 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for Co^{2+} , Zn^{2+} and Cd^{2+} ions respectively which is in agreement with the expected randomness of the system. Prominent infra red absorption bands which could be involved in the adsorption process included $-\text{OH}$, $-\text{NH}_2$, $\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{C}-\text{O}$ functional groups, while SEM analysis showed agglomeration of round particles shapes on the surface structure of the biomass. Thus, base-modified sweet potato leaves can be used as an excellent adsorbent to sequester toxic metal ions from wastewater.*

Keywords: *Pollution remediation biosorption, sweet potato leaf, heavy metals, kinetics,*

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1.0 Introduction

Heavy metals are among the most widely known and significant constituents of most environmental pollutants because of their

toxicity and non-biodegradable nature (Jaishankar *et al.*, 2014). Processes releasing heavy metal ions to the environment span from domestic, agricultural, natural and industrial activities (Zhang *et al.*, 2011; Ivanets *et al.*, 2014; Ofudje *et al.*, 2018). The toxicity of heavy metals is of great concern because they are a precursor to various illnesses and disorders once the specific limits are exceeded (Veli and Alyüz 2007, Ofudje *et al.* 2018). Zinc which makes up about 0.0075 % of the Earth's crust is an essential trace element for humans animals, plants and microorganisms (Prasad, 2008, Cherasse and Urade, 2017). Its major application is in corrosion-resistant zinc plating of iron. Zinc deficiency in children causes growth retardation, diarrhea, delayed sexual maturation and infection susceptibility (Hambidge and Krebs 2007). Despite zinc, its established biochemical role in humans, excessive intake of zinc can be harmful. For instance, excessive intake of zinc can lead to the suppression of copper and iron absorption (Fosmire 1990). Fosmire (1990) also reported that intake of 100–300 mg level of zinc may interfere with the utilization of iron and copper and can adversely affect cholesterol. Cobalt is also an essential element because it is vital to the metabolism of all animals and is a key constituent of cobalamin, i.e, Vitamine B₁₂ (Yamada 2013). However, cobalt intake above the tolerance limit has been reported as a precursor to vomiting and nausea, vision problems, heart problems and thyroid damage (Yamada 2013). Unlike zinc and cobalt, cadmium is the sixth most poisonous substance, whose health impacts include Janegitz *et al.* 2011, Adeogun *et al.* 2018 renal dysfunction, hypertension, bone degeneration, liver damage, and lung insufficiency (Janegitz *et al.* 2011, Adeogun *et al.* 2018). are the major consequences of exposure to fumes or dust of cadmium metal or cadmium oxide, r Also, chronic exposure to

cadmium may lead to emphysema and associated renal disturbance (Iqbal *et al.*, 2007).

There are different numbers of methods that can be used to remove heavy metal ions from aqueous solution, among which are electrolysis, ion exchange, chemical precipitation, membrane separation, and adsorption (Veli and Alyüz 2007, Zhang *et al.*, 2011, Ivanets *et al.*, 2014, Ofudje *et al.*, 2018). Among the listed, adsorption has received considerable attention because the process is highly efficiency, environmentally friendly and can be easily implemented at low costs (Zhang *et al.*, 2011, Ivanets *et al.*, 2014). The most widely used adsorbent for waste remediation is activated carbon; however, due to the high cost of production, its availability in most developing countries is a major challenge (Ofudje *et al.*, 2018). Several studies have reported on the development and applications of adsorbents that are cheap, eco-friendly and with competitive adsorption capacity. However, most of them are confronted with some levels of incoherency for some adsorbate, lack of tolerance to high temperature and a high degree of selectivity (ref). Consequently, research on the development of newer is preferably concentrated on finding suitable adsorbents that are less toxic and inexpensive for selective or broad applications in the removal of pollutants (including heavy metal ions) from wastewater and other sources. Some of the solid adsorbent for the removal of heavy metals includes modified phosphate dolomite (Ivanets *et al.* 2014), hydroxyapatite (Ofudje *et al.* 2018), clay (Veli and Alyüz 2007), fish scale (Janegitz *et al.* 2011), peanut (Witek-Krowiak *et al.* 2011), palm shell (Kadir and Puade 2013) and scale of croaker fish (Nkiko *et al.* 2013).

Given the existing knowledge gap, the present work is designed to investigate the suitability of base modified sweet potato leaf as an



adsorbent for the removal of Zn^{2+} , Co^{2+} and Cd^{2+} from aqueous solution. f. The effects of time, initial concentration of metal, solution pH and adsorbent dosage on the adsorption behavior were evaluated, while data obtained were evaluated using kinetic modeling, adsorption isotherms, and thermodynamic studies. The surface of the biomass was investigated using Fourier transform infrared (FT-IR).

2.0 Materials and Methods

All chemicals used were of analytical grade. Aqueous solutions of various concentrations of Co^{2+} , Zn^{2+} , and Cd^{2+} ion were made by dissolving the respective amount of analytical grade metal nitrate salts, $Co(NO_3)_2 \cdot 3H_2O$ (Merck-Germany), $Zn(NO_3)_2 \cdot 6H_2O$ (Fluka, Germany) and $Cd(NO_3)_2 \cdot 4H_2O$ (Fluka, Germany) in distilled water. Desired concentrations were achieved from the stock solutions following subsequent dilution.

2.1 Preparation of sorbent

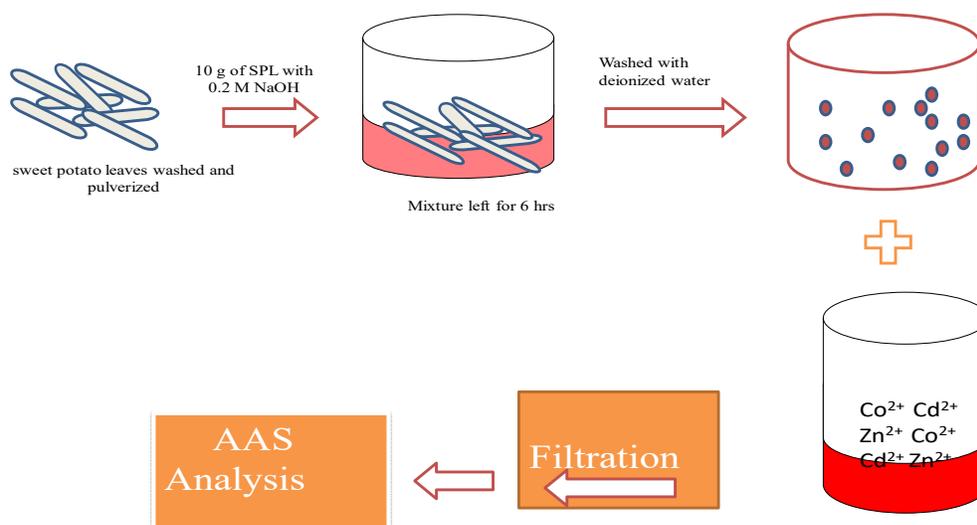


Fig. 1: Flow chart for preparation of BSPL for metals adsorption.

2.3 Characterizations of the adsorbent

A scanning electron microscope (Hitachi, Japan, S-3000H) was used to evaluate the

sweet potato leaves (SPL) were collected after harvest from farmland at Isade village near Ilese Barack, Ogun State, Nigeria. The leaves were properly rinsed with tap water, dried and later cut into pieces of approximately 0.5 cm. The dried leaf samples were further washed with distilled water and dried to constant weight.

2.2 Activation of the adsorbent

10 g of the dried sweet potato (SPL) were weighed into a beaker containing 0.2 M sodium hydroxide solution. The mixture was magnetically stirred for 2 h and then left for about 6 h, to enhance the activation. The leaves were rinsed with deionized water to wash off the base. Rinsing was done several times until no trace of the base was observed. The pre-treated sorbents were then dried and stored in an airtight container and referred to as base modified sweet potato leaves (BSPL) for further use. The schematic representation for the preparation of the adsorbent is shown in Fig. 1.

surface morphology of the modified leaves. Fourier transform infrared (FT-IR) spectra were recorded from 400 to 4000 cm^{-1} on



SENSOR 27 spectrometer (Bruker, Germany) using KBr pellet technique.

2.4 Batch adsorption experiment

The base modified sweet potato leaf was used as adsorbents for the removal of Zn^{2+} , Co^{2+} and Cd^{2+} via the batch process. The batch sorption process was done as reported elsewhere (Odoemelam *et al.*, 2018). The percentage of metal ion removal and the number of metal ions adsorbed by the sorbent were estimated using equations 1 and 2 (Eddy, 2009),

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

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

where q_e is the amount of adsorbate adsorbed, C_0 is the initial concentration in mg/L, C_e is the equilibrium concentration in mg/L, 'V' is the volume in litre and 'm' is the mass of the adsorbent.

3.0 Results and Methods

Fig. 2 shows the FTIR spectra of unloaded and metal loaded leaves respectively. The broad bands between 3405 and 3640 cm^{-1} (before and after biosorption) indicate the presence of hydroxyl and amino groups. The peaks observed between 2931 and 3010 cm^{-1} (before and after biosorption) were assigned to the stretching vibrations of C–H bond. The presence of the peaks between 1780 and 1792 cm^{-1} (before and after biosorption) is an indication of C=O bonds of carboxylic acid. The peaks at 1655 cm^{-1} (before biosorption) and 1644 cm^{-1} (after biosorption) corresponded to the presence of C=C stretching. Furthermore, the bands observed between 1065 cm^{-1} and 1082 cm^{-1} (before and after biosorption) corresponded to the C–O stretching. Thus prominent peaks which could be involved in the adsorption process include –OH, –NH₂, C=C, C=O and C–O functional groups.

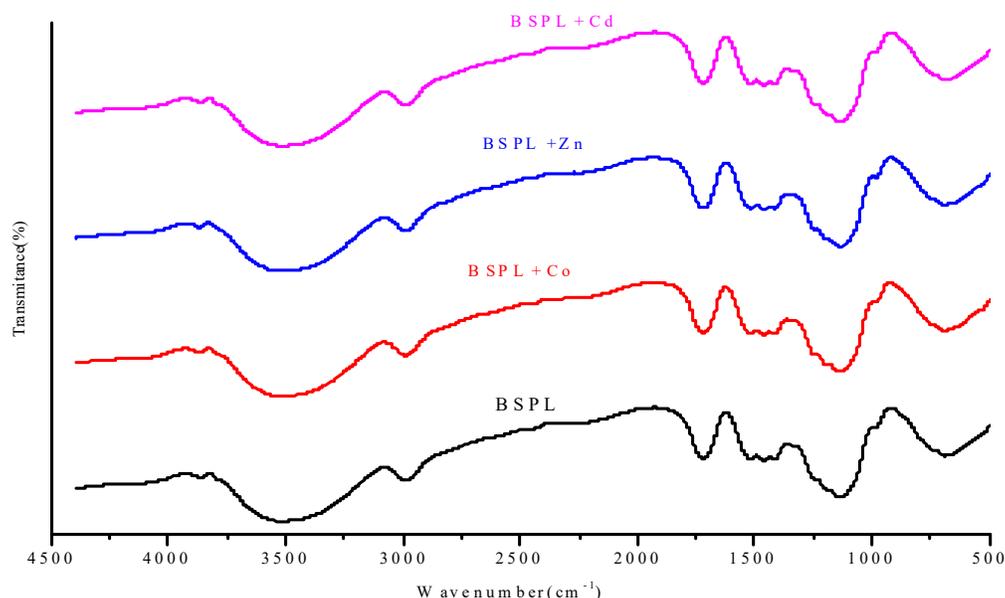


Fig. 2: FT-IR spectra of base modified sweet potato leaves before and after biosorption

Some works reported by Ali *et al.* (2016) and by Seo-Yun and Hee-Jeong (2017) indicated that the carboxylic acid functional group has

the highest adsorption capacity towards heavy metals because it can dissociate in an aqueous solution to give COO^- and H^+ . At a certain



pKa value, COO^- dominates. Consequently, the anionic form of carboxylic acid can effectively adsorb cationic heavy metals. Thus, heavy metal adsorption by biomass mechanism can be described based on the

electrostatic attractions between these functional groups on the surface of the adsorbent materials the positively charged heavy metals (Ofudje, *et al.*, 2013; Ali, *et al.*, 2016; Seo-Yun and Hee-Jeong, 2017).

Table 1: Metal ion characteristic parameters

	Atomic Number	Electronegativity	Hydration energy (kJ/mol)
Zn^{2+}	30	1.65	-2044
Cd^{2+}	48	1.69	-1806
Co^{2+}	27	1.88	-2054

Fig. 3 shows plots for the variation of the amount of metal ions adsorbed with time. It can be seen from the plots that the adsorption of the metal ions depends on the period of contact. Adsorption is observed to increase with time. Complete removal of Cd^{2+} and Zn^{2+} was observed after 100 minutes of contact while complete removal of Co^{2+} was achieved after 150 minutes. Therefore the adsorbent shows some levels of selectivity to metal ions. The observation can also be related to the hydrated ionic radii as the kinetics of metal ions slowed down as the ionic radii decreased. The maximum amount of Co^{2+} , Cd^{2+} and Zn^{2+} adsorbed were 4.008 mg.g^{-1} , 3.916 mg.g^{-1} and 2.860 mg.g^{-1} respectively which indicated that the adsorption favours Co^{2+} more than other metal ions. . It can be inferred from the plots that the uptake of the metal ions increased significantly within the first 5 to 30 minutes of contact until the optimum time was recorded, after which, the rate of adsorption tends to be stabilized. The number of available and active adsorption sites for a given system is fixed. Once sufficient time and other favourable factors are attained, almost all the adsorption sites would be occupied. Therefore, in the absence of desorption, the adsorption rate would remain steady as seen in the Figure. However, if there is desorption, the adsorption rate will decrease and the plots will slope downward as long as the rate of desorption

becomes greater than the rate of adsorption. Other factors such as a decrease in the concentration of the metal ions have also been proposed to explain the adsorption trend similar to what is observed in this study concerning time (Veli and Alyüz 2007, Adeogun *et al.* 2018, Ofudje *et al.* 2018). According to the adsorption capacity, the selectivity sequence of these heavy metals using base modified sweet potato leaf adsorbent was given as $\text{Co} > \text{Cu} > \text{Cd}$. According to literature reports, the adsorption behaviour of heavy metal ions can better be understood using their parameters which include atomic number, electronegativity, hydration enthalpy and many more (Minceva *et al.* 2008, Chaabane *et al.* 2019). In this present study, therefore, the affinity of Co^{2+} , Cd^{2+} and Zn^{2+} towards the adsorbent was investigated by examining the characteristic properties of these metals as presented in Table 1. Based on electronegativity, it is assumed that the sorption of heavy metals onto solid surfaces is more effective with metals having higher electronegativity and will readily adsorb metal ions (Minceva *et al.* 2008, Chaabane *et al.* (2019). Consequently, the sequestration selectivity series obtained in this work is in line with changes in the electronegativity of the heavy metal ions Co^{2+} (1.88) > Cd^{2+} (1.69) > Zn^{2+} (1.65).

3.1 Effect of initial metal ion concentration



It was observed from Fig. 4 that the amount of metal ions adsorbed increased with the initial metal concentration until around 60 – 70 mg.L⁻¹. Above this concentration, there was no substantial increase in the amount of metal ions adsorbed. The amount adsorbed increased from 0.414 mg/g at 10 mg.L⁻¹ to 3.030 mg.g⁻¹ at 60 mg/L for Zn²⁺, 0.472 mg.g⁻¹ to 3.32 mg.g⁻¹ for Cd²⁺, and from 0.763 mg.g⁻¹ to 3.975 mg.g⁻¹ for Co²⁺, respectively. The

increase in the adsorption of the pollutants with initial metal ions could be a result of an increase in the driving forces (Ghoneim et al. 2014). As reported by Chaabane et al. (2019), the higher interaction that exists between the active sites located on the surface of the adsorbent and the metal ions explains the increase in metal ion adsorption with the metal ions concentration.

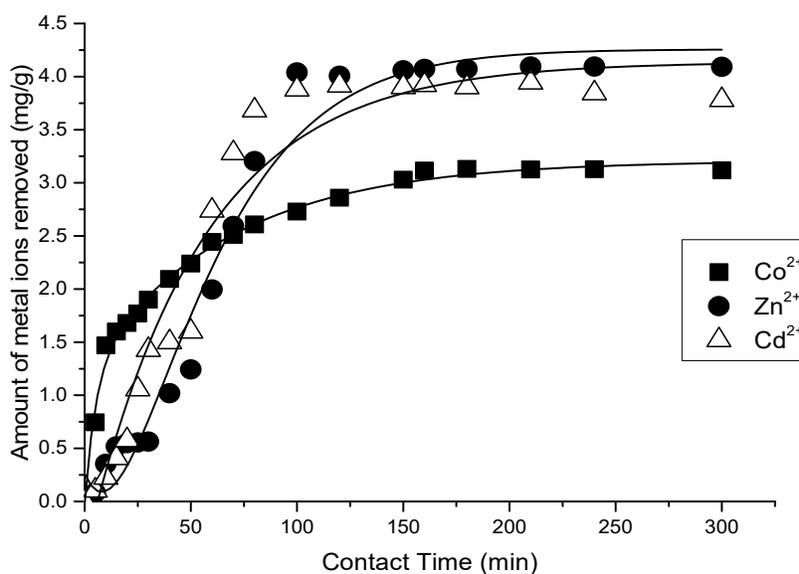


Fig. 3: Variation of concentrations of Co²⁺, Zn²⁺ and Cd²⁺ adsorbed by modified sweet potato leaves with time

However, at a concentration above 70 mg.L⁻¹, uniform adsorption is mainly attributed to the overload of adsorption sites by the metal ions which are due to an increase in the number of ions competing for available binding sites in the biomass (Ghoneim et al. 2014).

3.2 Effect of sorbent dosage

The dependence of metal adsorption on the adsorbent amount was investigated by varying the amount of BSPL (0.1–1.5 g) and the results are presented in Fig. 5. From the plots it shows that the amount of metal ions adsorbed increased with higher BSPL dosages with maximum metal ions adsorption of 4.090, 4.270 and 4.323 mg.g⁻¹ for Zn²⁺, Cd²⁺

and Co²⁺ ions respectively which was achieved at an adsorbent dosage of 0.8 g. A higher adsorbent dosage provides a higher surface area for the removal of metal ions due to the formation of greater adsorption sites (Bilge and Sevil 2009). As discussed by Seo-Yun et al. (2017), the amount of the heavy metal adsorbed increased with an increase in the amount of adsorbent used and this was attributed to an increase in the surface area of the adsorbent where heavy metals can be adsorbed which increases the probability of adsorbing the heavy metal ions onto the adsorbent surface. Thus, the order of Sequestration of the heavy metal ions obtained



based on the impact of adsorbent dosage is $\text{Co}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$.

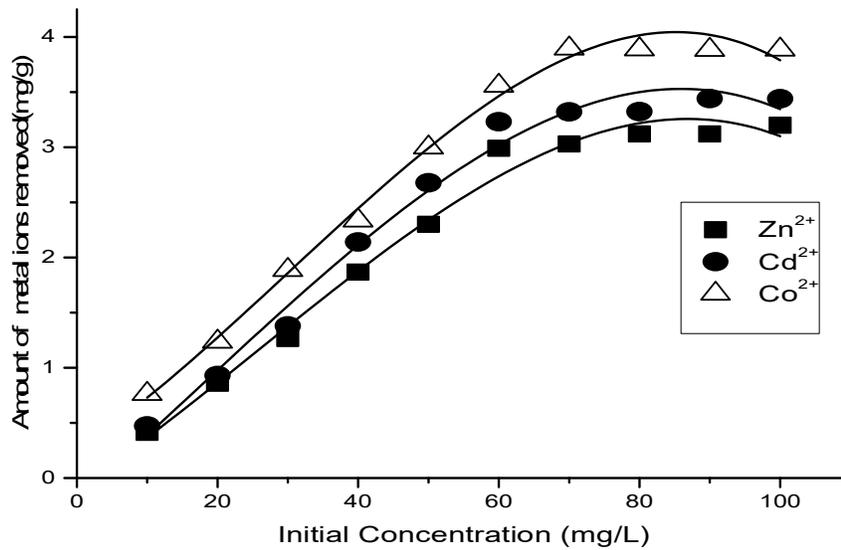


Fig. 4: Effects of initial metal ions concentration on the biosorption of Co^{2+} , Zn^{2+} and Cd^{2+}

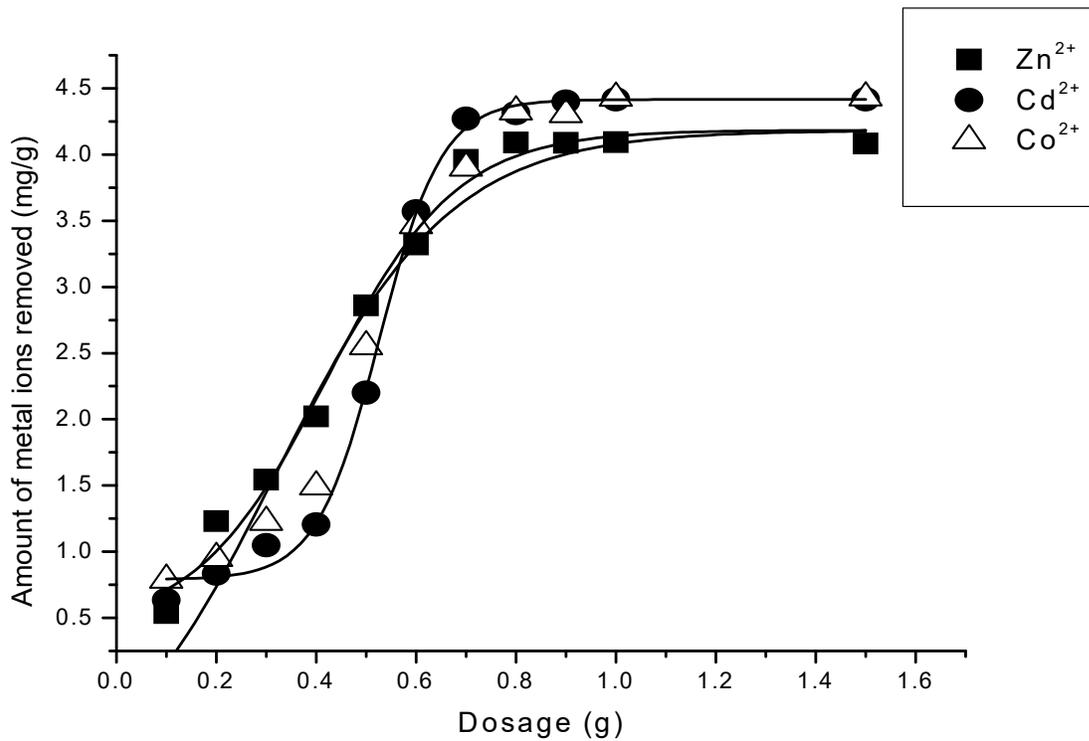


Fig. 5: Effect of sorbent dosage on the biosorption of Co^{2+} , Zn^{2+} and Cd^{2+}



3.3 Effect of pH

To investigate the role of pH on the sorption of Co^{2+} , Zn^{2+} and Cd^{2+} ions by BSPL, pH ranges of 1–7 were used as shown in Fig. 6. The adsorption of metal ions has been demonstrated to be dependent on the solution pH since it plays a vital role in the surface charge of the adsorbent and the degree of ionization (Ahmady-Asbchin et al. 2008). Results from this present study showed that the metals adsorption percentage increased to (85%, 69%, 65%) for Co^{2+} , Cd^{2+} and Zn^{2+} respectively at solution pH 5.5 - 6 and then showed a decrease at pH 7 and above. At lower pH, there was a clear competition for the adsorbent sorption sites between the metal ions and proton in the solution which resulted

in a decrease in the uptake of the pollutants at lower solution pH. This is because the functional groups present on the surface of the adsorbent are more protonated under acidic conditions, hence potential binding sites are less available for the adsorption of metal ions (Opiso et al. 2009, Adeogun et al. 2018, Ofudje et al. 2018). However, as the solution pH increases, deprotonation occur which makes the binding sites much more available for the sorption of the metal ions. The decrease in the adsorption process at a higher pH value above 7.0 is due to the formation of hydroxide ions in solution and as such the metal ions react with OH^- ions which lead to precipitation as a metal hydroxide at a high pH value (Farooq et al. 2010).

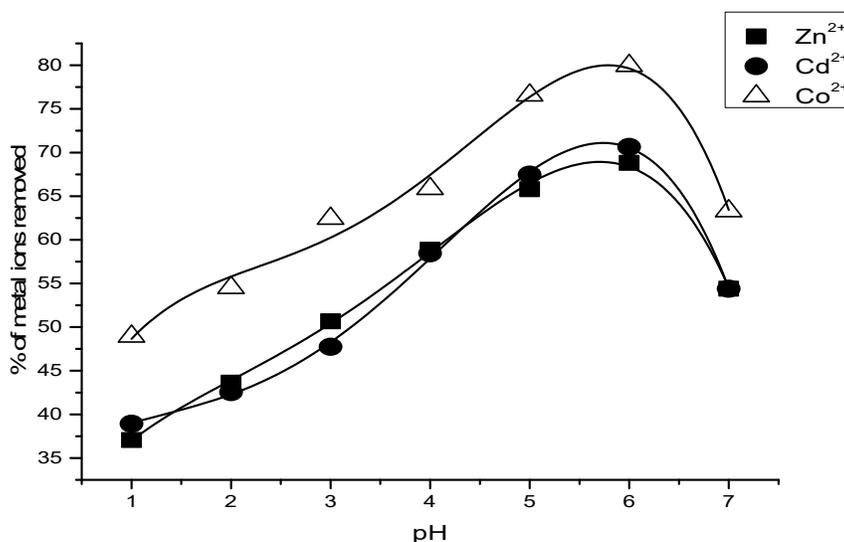


Fig. 6: Effect of solution pH on the biosorption of Co^{2+} , Zn^{2+} and Cd^{2+}

3.4 Kinetic Studies

The kinetics investigation of the adsorption process which describes the rate of the uptake of the metal ions by BSPL was analyzed using different kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models as represented in equations (3 to 6) respectively (Lagergren 1898, Weber and Morris 1963, Adeogun et al., 2018, Ofudje et al., 2018).

$$Q_t = Q_e (1 - e^{-k_1 t}) \tag{3}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{4}$$

$$Q_t = \frac{1}{\beta} \ln(\alpha \beta * t) \tag{5}$$

$$Q_t = K_p t^{0.5} + C_i \tag{6}$$

where all the physical constants had been previously discussed somewhere else



(Adeogun *et al.*, 2018). The best fit between the pseudo-first- and second-order kinetics models were evaluated by the sum of error squares (SEE, %) given by equation 7 (Adeogun *et al.*, 2018):

$$\% \text{ SSE} = \sqrt{\frac{((Q_{(\text{exp})} - Q_{(\text{cal})}) / Q_{\text{exp}})^2}{N - 1}} \times 100 \quad (7)$$

where N is the number of data points. The smaller the %SSE values and the higher the values of R², the better the curve fitting.

The plots of the different kinetic models for the adsorption of Co²⁺, Zn²⁺ and Cd²⁺ ions by BSPL are shown in Fig. 7, while the adsorption data are listed in Table 2. The correlation coefficient (R²) obtained, show that the Pseudo-second-order kinetic model best described the adsorption process of the three metal ions. The calculated values of Q_e

obtained from the Pseudo-second order plots, capered favourable with the experimental data better than those from the Pseudo-first-order model. Also, the values of the %SSE from the Pseudo-second-order model were smaller than calculated for the Pseudo-first-order The kinetic data for the adsorption of Co²⁺, Zn²⁺ and Cd²⁺ by BSPL was also analyzed using the intra-particle diffusion model as shown in Fig. 7c, and in Table 2 (where the calculated parameters are recorded). The values of the intra-particle diffusion rate constant K_p obtained for Zn, Co and Cd are 0.833, 0.552 and 0.214 mg.g⁻¹ min^{1/2} respectively, while the intercepts C_i of the curve showed a multilinear which means that the intra-particle diffusion is not the rate-limiting step (Adeogun *et al.*, 2018, Ofudje *et al.*, 2018).

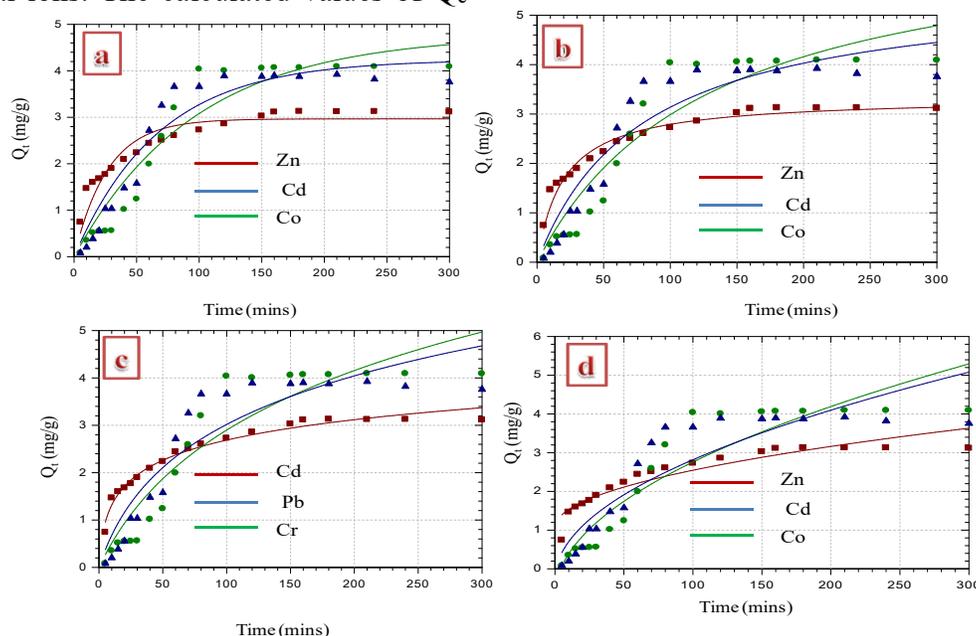


Fig. 7: Kinetics plots of: (a) Pseudo-first order, (b) Pseudo-second-order and (c) Elovich, and (d) Intra-particle kinetic models for the biosorption of Co²⁺, Zn²⁺ and Cd²⁺ onto BSPL.

Table 2: Kinetics Parameters for the Adsorption of Metal ions by BSPL

Kinetic	Parameters	Zn	Co	Cd
Pseudo-First-Order	Q _(cal) (mg.g ⁻¹)	3.343	6.855	5.625
	Q _(exp) (mg.g ⁻¹)	2.975	3.090	3.323
	k ₁ (min ⁻¹)	0.015	0.011	0.015



	SSE%	0.114	0.195	0.172
	R ²	0.873	0.938	0.873
Pseudo-Second-Order	Q _(cal) (mg.g ⁻¹)	2.966	4.778	4.24
	k ₂ (g.mg ⁻¹ min ⁻¹)	0.034	0.001	0.002
	SSE%	0.013	0.034	0.018
	R ²	0.996	0.997	0.996
Elovich	α (mg.g ⁻¹ min ⁻¹)	0.449	0.057	0.083
	β (g.min ⁻¹)	1.595	0.427	0.59
	R ²	0.992	0.95	0.945
Intra particle diffusion	K _p (mg.g ⁻¹ min ^{-1/2})	0.833	0.552	0.214
	C	0.169	0.332	0.304
	R ²	0.929	0.932	0.914

3.5 Adsorption Isotherms

The data obtained from equilibrium studies were tested for their fitness to the Langmuir (equation 8), Freundlich (equation 9), Temkin (equation 10), and Dubinin–Radushkevich (equation 11) *adsorption* isotherms (Freundlich, 1906, Langmuir, 1918, Temkin and Pyzhev, 1940, Dubinin *et al.*, 1947)

$$Q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{8}$$

$$Q_{eq} = K_F C_e^{1/n} \tag{9}$$

$$Q_e = Q_s e^{-\beta \epsilon^2} \tag{10}$$

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \tag{11}$$

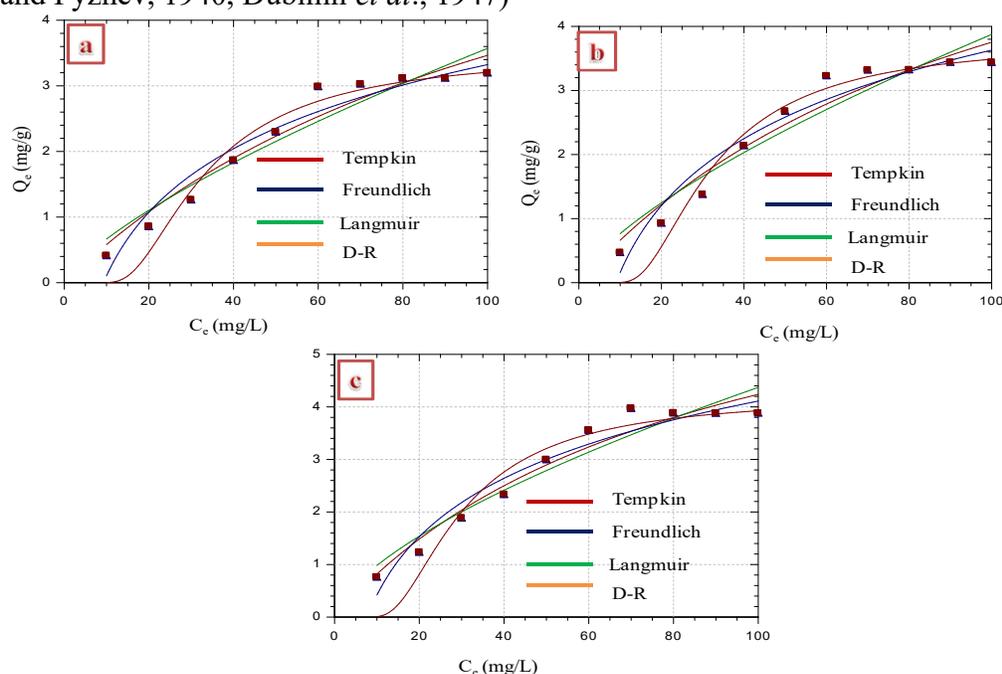


Fig. 8: Graphs of Langmuir, Freundlich, Temkin and D-R isotherms for the adsorption of (a) Co²⁺, (b) Zn²⁺ and (c) Cd²⁺ onto BSPL



From the Langmuir equation, Q_o and b represent the adsorption capacity and energy of adsorption respectively while the separation factor (R_L) was obtained from equation 12 (Eddy *et al.*, 2022)

$$R_L = \frac{1}{(1 + bC_o)} \quad (12)$$

where C_o (mg L^{-1}) is the initial adsorbate concentration with the values of R_L between 0 and 1 representing favourable adsorption, $R_L > 1$ implies unfavourable adsorption and $R_L = 0$ represents an irreversible process (Odoemelam *et al.*, 2018).

From the Freundlich isotherm model, K_F and n are the isotherm parameters representing adsorption capacity and intensity, respectively. However, α_T and b_T are the equilibrium binding constant (L g^{-1}) and heat of adsorption (J mol^{-1}) (in the Temkin isotherm) respectively. In the D-R isotherms, Q_s represents the saturation capacity (mol g^{-1}), the Polanyi potential (ϵ) is given by the relation, $\epsilon = \ln(1 + \frac{1}{C_e})$, where R ($\text{J mol}^{-1} \text{K}^{-1}$), C_e (mg L^{-1}) and T (K) are as previously

described. The values of the constant β ($\text{mol}^2 \text{J}^{-2}$) can be used to determine the mean free energy E (kJ mol^{-1}) of the adsorption process per molecule of the pollutants as the solid is transferred from the solution onto the surface of the adsorbent. The expression in equation 12 relates β to the mean free energy of adsorption of the adsorbate.

$$E = (2\beta)^{-0.5} \quad (13)$$

Fig.8 shows the Langmuir, Freundlich, D-R, and Temkin isotherms for the adsorption of Co^{2+} , Zn^{2+} and Cd^{2+} ions, while their physical parameters are presented in Table 3. It is indicative that the non-linear fits using the four isotherms were good for studying the adsorption process of the metal ions onto BSPL with R^2 values for the Langmuir, Freundlich, D-R, and Temkin isotherms given as (0.996, 0.984 and 0.984), (0.996, 0.995 and 0.991), (0.974, 0.978 and 0.977) and (0.958, 0.966 and 0.954) for Zn^{2+} , Cd^{2+} and Co^{2+} ions respectively.

Table 3: Isotherms Parameters of Metal ions Adsorption by BSPL

Isotherms	Parameters	Zn	Cd	Co
Langmuir	$Q_{\max}(\text{mg.g}^{-1})$	3.879	4.069	4.368
	$R_L (\text{L.mg}^{-1})$	0.053	0.106	0.09
	R^2	0.996	0.984	0.984
Freundlich	$K_F (\text{L.g}^{-1})$	0.518	0.793	0.753
	N	1.566	1.811	1.759
	R^2	0.996	0.995	0.991
Temkin	$A_T (\text{L.mg}^{-1})$	0.698	1.9	2.647
	$b_T (\text{kJ.mol}^{-1})$	1895.3	2409.9	2475.11
	R^2	0.974	0.978	0.977
D-R	$Q_m(\text{mg.g}^{-1})$	3.305	3.419	3.471
	$E (\text{kJ.mol}^{-1})$	0.382	0.556	0.502
	R^2	0.958	0.966	0.954



The Langmuir maximum adsorption capacity of the adsorbent for Zn^{2+} , Cd^{2+} and Co^{2+} ions were 3.879, 4.069 and 4.368 $mg.g^{-1}$ for respectively. The values of the separation factor (R_L) were found to be in the range of 0 to 1; which is an indication that the adsorption is favourable. The D-R isotherm plots are presented in Fig. 10 while the associated parameters deduced from the plots are recorded in Table 3. The theoretical adsorption capacity, Q_m and the maximum adsorption energy E evaluated from the plots were 3.305, 3.419 and 3.471 $mg.g^{-1}$ and 0.382, 0.556 and 0.502 $kJ.mol^{-1}$ for Zn^{2+} , Cd^{2+} and Co^{2+} ions respectively which suggest a physisorption adsorption process (Ofudje et al. 2018).

3.6 Thermodynamic Study

The effect of temperature on the adsorption of Co^{2+} , Zn^{2+} and Cd^{2+} ions by BSPL was evaluated and applied to evaluate thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The values of the enthalpy changes (ΔH) and entropy change (ΔS) were estimated from the slope and

intercept of plots developed from the Van't Hoff equation (Adeogun *et al.*, 2012):

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

where K_C is the equilibrium constant which expresses the relationship between the amounts of metal ions adsorbed (Q_e) in $mg.g^{-1}$ and the equilibrium concentration (C_e) in $mg.L^{-1}$. The distribution ratio (K_c) was calculated using equation (15):

$$K_C = \frac{q_e}{C_e} \quad (15)$$

The standard free energy change of the adsorption process was obtained using equation 16 (Uchechukwu *et al.*, 2015):

$$\Delta G^\circ = -RT \ln K_C \quad (16)$$

where ΔG° is the standard free energy change (J/mol), R is the ideal gas constant (8.314 J/mol /K) and T is the absolute temperature (K). The plots of $\ln K_C$ against $1/T$ for the adsorption of the studied metal ions are presented in Fig. 9, while calculated thermodynamic parameters are as presented in Table 4.

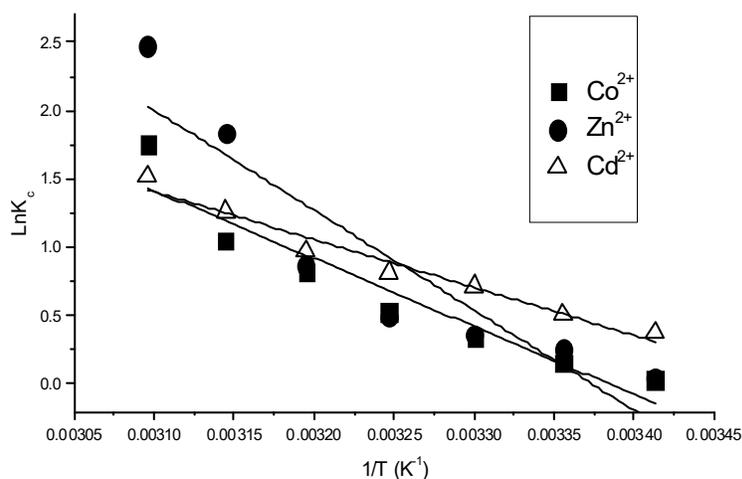


Fig. 9: Thermodynamic plot for the adsorption of Co^{2+} , Zn^{2+} and Cd^{2+} adsorption using BSPL



Table 4: Thermodynamic parameters for the biosorption of Co²⁺, Zn²⁺ and Cd²⁺ onto BSPL

	Temperature	Co ²⁺	Zn ²⁺	Cd ²⁺
	293	901.734	868.506	1448.24
	298	-397.26	-638.76	-739.8
$\Delta G^\circ(\text{kJ}\cdot\text{mol}^{-1})$	303	-852.46	-916.88	-1116.3
	308	-1358.5	-1276.4	-1297.2
	313	-2133.4	-2255.9	-1841.7
	318	-2765.4	-3078	-2372.4
	323	-4709	-5155.1	-5459
$\Delta H^\circ(\text{kJ}\cdot\text{mol}^{-1})$		48.341	51.192	51.453
$\Delta S^\circ \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$		162.12	171.93	174.93

The positive values of enthalpy change (ΔH) indicate that the adsorption is endothermic. The free energy change, ΔG , was found to have rise, which indicated the spontaneous nature of the adsorption process. The entropy change (ΔS) for the adsorption processes calculated are 162.12, 171.93 and 174.93 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for Co^{2+} , Zn^{2+} and Cd^{2+} respectively. The positive value of ΔS indicates that randomness increased in the system solid/solution interface during the adsorption process (Adeogun et al. 2012, Nkiko et al. 2013).

4.0 Conclusion

The study on the removal of Co^{2+} , Zn^{2+} and Cd^{2+} ions from aqueous solution by base modified sweet potato leaf was performed in a batch process under different experimental conditions. The biosorption process was found to depend on parameters such as sorption time, initial pollutant concentration, solution pH, sorbent dosage and temperature. The kinetic data fitted both Pseudo first and pseudo second-order kinetic models. The adsorption also fitted the Langmuir, Freundlich, Temkin and D-R isotherms. The thermodynamic parameters (free energy, enthalpy and entropy

changes) showed that the adsorption is feasible, spontaneous and endothermic. The prominent peaks which could be involved in the adsorption process are $-\text{OH}$, $-\text{NH}_2$, $\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{C}-\text{O}$ functional groups. It is therefore apparent that base modified sweet potato leaf may be applicable as sorbent for the biosorption of the metal ions from wastewater.

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