

Removal of Heavy Metals from Aqueous Solutions using Modified Irish Potato Leaf as Low Cost Biosorbent: Kinetic and Thermodynamic Studies

Abimbola A. Ogundiran M.Sc.^{1,2}; N.A. Adesola Babarinde Ph.D.²; Edwin A. Ofudje Ph.D.^{3*}; and Olusegun O. Ogundiran Ph.D.⁴

¹Department of Chemical Sciences, Tai Solarin University of Education, Ijagun, Ogun-State, Nigeria.

²Department of Chemical Sciences, Olabisi Onabanjo University, Ago- Iwoye, Ogun- State, Nigeria.

³Department of Chemical Sciences, Mountain Top University, Ibafo, Ogun State, Nigeria.

⁴Department of Chemistry, Tai Solarin College of Education, Omu-Ijebu, Ogun-State, Nigeria.

E-mail: eaofudje@mtu.edu.ng*

ofudjeandrew4real@yahoo.com

ABSTRACT

This study reports the kinetics and thermodynamics of the biosorption of six metal ions (Cd^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Pb^{2+} , and Co^{2+}) from synthetic wastewater unto base modified Irish potato leaf. The biosorbents were characterized using Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The effects of pH, contact time, initial concentration of metal ions, the mass of biosorbent, and temperature were investigated. Batch kinetic data were subjected to the Pseudo first-order, Pseudo second-order, intraparticle diffusion, and Elovich kinetic models.

The ceiling adsorption ability was found at a solution pH of 6, metal concentration of 10 mg.L^{-1} , adsorbent dosage of 1.0 gL^{-1} , and at 2 hrs contact time. The adsorption capacity was found to be in the order of $\text{Ni} > \text{Zn} > \text{Pb} > \text{Cd} > \text{Cr} > \text{Co}$. Kinetic study showed that the Pseudo second-order model was suitable to describe the experimental data having a correlation coefficient (R^2) ranges from (0.998 to 0.999). The value of the correlation coefficient (R^2) of the entire tested isotherms were compared and found out that the Freundlich model has better value and this signifies that this model best symbolizes the experimental data and thus best suited isotherm for the adsorption process in this study. FT-IR analysis revealed bands characteristic of hydroxyl groups at 3475.07 cm^{-1} , alkyl group at 2978 cm^{-1} and unsaturated carbonyl at 1651 cm^{-1} with a frequency slightly shifted as a result of the metal ions attachment to the biosorbent surface. Conclusively, the study showed that the prepared sorbent can be a preferable sorbent for the

confiscation of toxic metal ions being a cheap and eco-friendly alternative adsorption material.

(Keywords: biosorption, bioremediation, Irish potato leaf, kinetics, heavy metals, thermodynamics)

INTRODUCTION

Water is a harbinger to all forms of life, but pollution by heavy metals is increasing daily due to ever-increasing population and industrial activities. In recent years, the quest to find a solution to the persistence of toxic metals in the environment has become a worldwide issue.

A large volume of wastewater is daily generated. Some of the industries which release heavy metals contaminants are metal plating, tanneries, car radiator manufacturing, pharmaceutical, and mining industries (Feizi *et al.*, 2015; Choi *et al.*, 2016; Adeogun *et al.*, 2018). Heavy metals such as Ni, Cd, Pb, Cr, etc. are some of the pollutants present in the wastewater. Their inability to degrade biologically and the possibility to accrue in the food chain pose an important risk to the wellbeing of all kinds of living organisms (Mani & Kumar, 2014). Therefore, it becomes necessary to sequester these toxic metals from soils and wastewater.

Several techniques reported to have been used for heavy metals abstraction from the environment include membrane filtration solvent extraction, membrane separation, coagulation-flocculation, ion-exchange, electrochemical operations, adsorption, etc. (Obi and Njoku, 2015; Feizi *et al.*, 2015; Ihsanullah *et al.*, 2016; Choi *et al.*, 2016; Ofudje *et al.*, 2017; Barsbay *et*

al., 2018). Most of the techniques are costly and are inept in decreasing the concentration of contaminants in industrial wastewater especially in small scale industries. Adsorption has been studied over the years to be appropriate because it is cheap with ease of operation compared to other methods (Wang and Chen, 2009; Kim *et al.*, 2015).

Recently, there is an increase in the search for inexpensive adsorbents and many materials have been explored which include wool fiber and by-products of rice mill, coal, rice husk, potato peel, bael leaf, microbial biomass, straw, palm press fibre, sugarcane bagasse, coconut husk, soybean, cottonseed hulls, etc. (Feizi *et al.*, 2015; Choi *et al.*, 2016; Ofudje *et al.*, 2017; Adeogun *et al.*, 2018). The presence of functional groups such as hydroxyl, amide, sulfhydryl and, carboxyl on the surface of these adsorbents have been suggested to be responsible for adsorption of pollutants such as metal ions from wastewaters (Feizi *et al.*, 2015; Choi *et al.*, 2016; Ofudje *et al.*, 2017; Adeogun *et al.*, 2018).

In developing countries like Nigeria, agricultural wastes such as Irish potato leaves are frequently produced and due to improper waste management systems, these wastes are burned or left to rot in the soil. However, the utilization of these wastes materials in the treatment of aquatic systems such as industrial, agricultural, and municipal wastewaters will not only reduce environmental pollution caused by these waste materials but also add value to them.

There is little information about the efficiency of Irish potato leaves in the adsorption of heavy metals from aqueous solutions. This study therefore aimed at confirming the possibility of the removal of Cr, Ni, Cd, Zn, Co, and Pb from aqueous solution using base modified Irish potato leaves. The work will also investigate the sorption kinetic and equilibrium of these metals while using thermodynamic parameters to evaluate the effect of the chemical activation on the biosorbent performance.

MATERIALS AND METHODS

Preparation of Adsorbate

All the chemicals and reagents used in this study were of analytical reagent grade. Adequate amounts of metal compounds were dissolved in

de-ionized water (DIW) for the preparation of the stock solutions of concentration 1000 mg/L. Concentrations used in the studies were acquired by dilution of the prepared stock solution. All glassware was washed with soap, followed by 10% HNO₃, and then rinsed many times with DIW before use. Adjustment of pH was done using either 0.1 M HCl or 0.1M NaOH using pH meter.

Biosorbent Preparation

The samples of Irish potato leaves (IPL) were collected from local agriculture farmland after harvest in Jos Nigeria. The leaf was washed with tap water and dried under the sunlight for 3 days. It was then activated with 0.2 M NaOH. The base modified Irish potato leaves (bIPL) leaves were dried and stored in a desiccator for the study.

Batch Biosorption Experiments

All the studies were conducted in a batch system using a boiling tube in a thermostatic shaker at 25°C. Each tube was filled with 25 mL of metal solution and 0.5 g of Irish potato leaves. The effect of parameters on the uptake of metal ions, such as initial metal ion concentration (10–100 mg L⁻¹), pH of the aqueous solution (1–7), contact time (0–300 min), and temperature (25–50°C) was studied. At equilibrium, the residual concentration of the heavy metals in the solution was analyzed using Atomic Absorption Spectrometer (Analyst 700, Perkin-Elmer, USA) after separation of the biosorbent by centrifugation. The amount of metal adsorbed at equilibrium, q_e (mg g⁻¹), was calculated using the equation:

$$Q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentration of metal ions in the solution (mg.L⁻¹), respectively, V is the volume of metal solution (L), and m is the mass of the dry Irish potato leave (g). The percentage of metal removed (R , %) from the solution was computed as follows:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Each experiment was prepared in triplicate and the data were articulated as the mean of the triplicate results.

Details of all the parameters have been reported elsewhere (Ofudje *et al.*, 2017; Adeogun *et al.*, 2018).

Kinetic Model

The evaluations of kinetics of a system explain how the metal ions bind to the surface of the sorbent. The four kinetic models applied in this study are: Pseudo-first-order (PFO) Equation (3), Pseudo-second-order (PSO) Equation (4), Elovich Equation (5), and intraparticle diffusion (IpD) Equation (6) (Lagergren, 1898; Weber and Morris, 1963; Ho, 2004; Ofudje *et al.*, 2017):

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

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

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

$$Q_t = K_{id} t^{0.5} + C_i \quad (6)$$

Characterization

FT-IR spectral analysis was done out to determine the possible functional groups present in the modified sweet potato leaf. Infrared spectra of the raw and metal-loaded biomass were obtained using a Fourier transform infrared (FT-IR) spectrophotometer. Scanning electron microscope (SEM) analysis was achieved to investigate the morphology of the Irish potato leaves using Hitachi (Japan) S-3000H electron microscope.

RESULTS AND DISCUSSION

Effect of pH

Effect of initial solution pH on metal ions removal was studied from pH 1-7 and the results are presented in Figure 1. The result showed that the removal of the metal ions from the solution increased as the pH increases with maximum percentage removal of 73.21, 74.08, 59.26, 70.21, 61.85, and 60.05 % for Zn, Co, Cr, Cd, Pb, and Ni, respectively at a pH of 6.

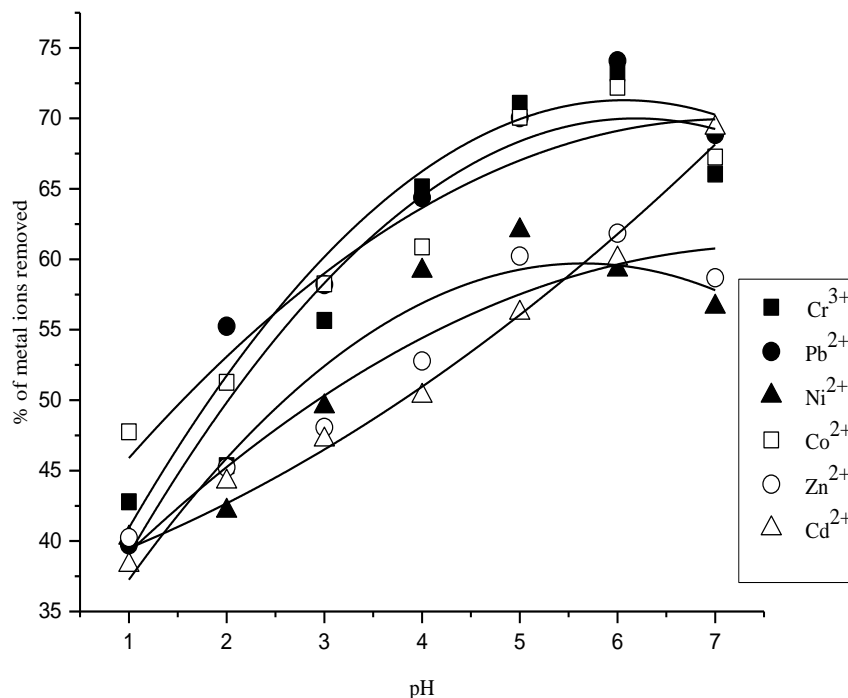


Figure 1: Effect of Initial Solution pH on Biosorption of Metal Ions onto bIPL

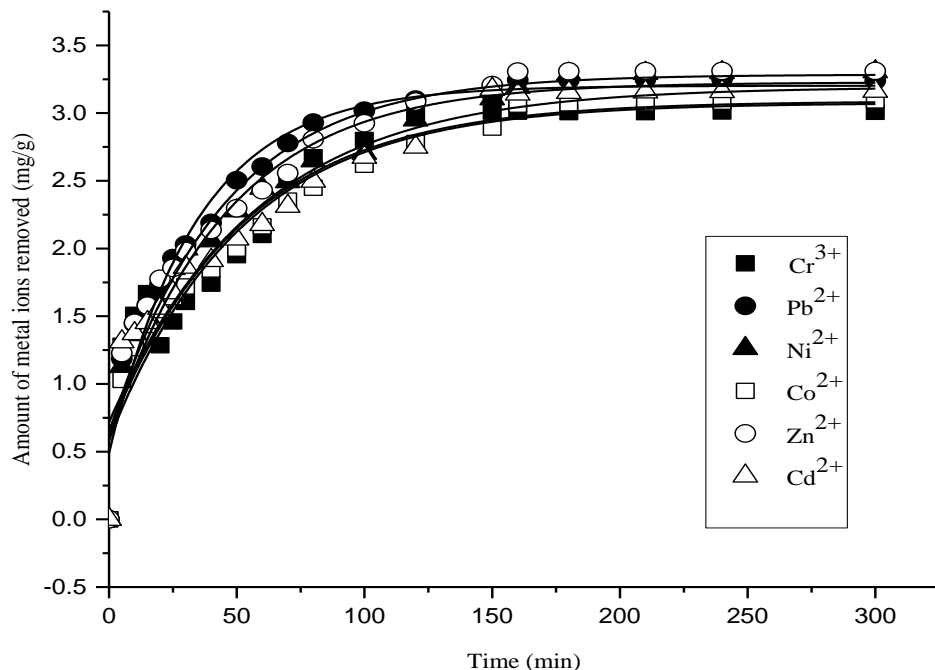


Figure 2: Time Profile for the Adsorption of Metal Ions onto the Leaf Biomass of bIPL.

At a pH below 6, the concentration of hydrogen ion was high and competed with the metal ions for the available sites on the biomass, which caused the metal ions to be repelled. But as the pH increased, the competition between the metal ions and H⁺ ion reduced greatly and the adherence of the metal ions increased considerably (Barsbay *et al.*, 2018).

Laroussi *et al.* (2019) used functionalized graphene oxide sheets to recover Cu(II), Ni(II) and Co(II) from aqueous solution and the results depicted that the adsorption capacities of these functionalized materials towards different metal ions increase with increasing pH in the range 4-6 and this they attributed to the protonation of the active sites of the adsorbents.

The effect of initial pH on the sorption of heavy metals by different adsorbents was reported by Morteza and Mohsen (2015) and it was noted that increase in pH resulted in increasing Cu sorption by all sorbents with maximum pH of 7, Cd sorption by potato, canola and walnut shell residues was obtained at pH 6, 6, and 7, Zn sorption by sunflower, potato, canola, and walnut shell residues occurred at pH 8, 7, 7, and 8, while Ni sorption by sunflower, potato, canola, and walnut shell powders was attained at pH of 8, 7, 8, and 6,

respectively. Furthermore, for the sorption of Mn by sunflower, potato, canola and walnut shell, percentage removed of 81.6, 79.8, 81.8, and 96.5 % was achieved from solution at pH 8, 7, 8, and 8, respectively. Generally, as pH increased, the surface of the biosorbent become deprotonated and thus leads to the increased removal of metal ions. However, at a solute pH higher than 6, the decrease observed in the uptake of the metal ions could be due to the formation of metal hydroxides.

Effect of Contact Time

The influence of contact time on the sorption of metal ions onto bIPL is shown in (Figure 2). The results showed that the amount of heavy metal ion removed from the solution increased with raise in the contact time from 5-300 min and reached a maximum after 120 min. At 120 min, adsorption of the metal ions approached equilibrium with maximum adsorption capacities of 3.31, 3.10, 3.01, 3.16, 3.24, and 3.31 mg/g for Zn, Co, Cr, Cd, Pb, and Ni, respectively.

Recently, Laroussi *et al.* (2019) reported that the time required to reach equilibrium in the adsorption of Cu(II), Ni(II) and Co(II) was found to be 9 h for Graphene oxide (GO), 8 h for GO modified by ethylenediamine (GO-EDA), 6 h for grafted chloroacetylchloride (GO-EDA-CAC) and 4 h for GO EDA-CAC grafted with bis(2-pyridylmethyl)amino groups (BPED) (GO-EDA-CAC-BPED) with maximum adsorption capacities of $3.464 \pm 0.100 \text{ mmol g}^{-1}$, $3.254 \pm 0.098 \text{ mmol g}^{-1}$ and $3.054 \pm 0.093 \text{ mmol g}^{-1}$, respectively.

In a study carried out by Morteza and Mohsen (2015), the equilibrium time of Cd sorption by sunflower, potato, canola, and the walnut shell was 120, 200, 600, and 200 min, Cu sorption time by sunflower, potato, canola, and walnut was 50, 80, 30, and 80 min, Ni sorption time by all sorbents was 120 min, sorption duration of Zn ions by sunflower, potato, canola, and walnut shell powders was reached 120, 600, 200, and 200 min, Fe sorption duration by sunflower, potato, canola, and walnut shell adsorbents was 120, 120, 120 and 20 min, while the sorption of Mn by sunflower, potato, canola, and walnut shell powders was reached at equilibrium time of 120, 200 and 200 min, respectively.

From the surveillance in this study, the adsorption system is assumed to have taken place in two separate steps: the first one being a quick phase of considerable adsorption and secondly, a slower

and quantitatively inconsequential one, and this kind of activities has been documented by Babarinde *et al.* (2013). The fast step lasts for an hour with metal ions adhering rapidly to the available and abundant active binding sites on the biosorbent, while the slow stage persists for quite a few hours. The steady habitation of these sites by metal ions to bIPL surface becomes slowed down, leading to the slow step and inefficiency of bIPL to remove the metal ions (da Costa *et al.*, 1991; Adebayo *et al.*, 2012).

Effect of Initial Metal Ion Concentration

The effect of initial metal concentration on biosorption was performed to investigate the dependence of the metal ions concentration on the adsorbent sorption capability. The plot for the effect of metal ion concentration is shown in Figure 3. The study revealed that the uptake of pollutants is dependent on their initial concentrations, and this raises with an increase in the initial concentration of metal ions. At lower concentration, the ratio of the binding active sites to metal ion concentration is high which enable all metal ions to adhere to the surface of the sorbent (Reddy *et al.*, 2014). However, as the concentration increased, the binding sites were saturated, thus causing a reduction in the percentage of metal ion removed from the solution.

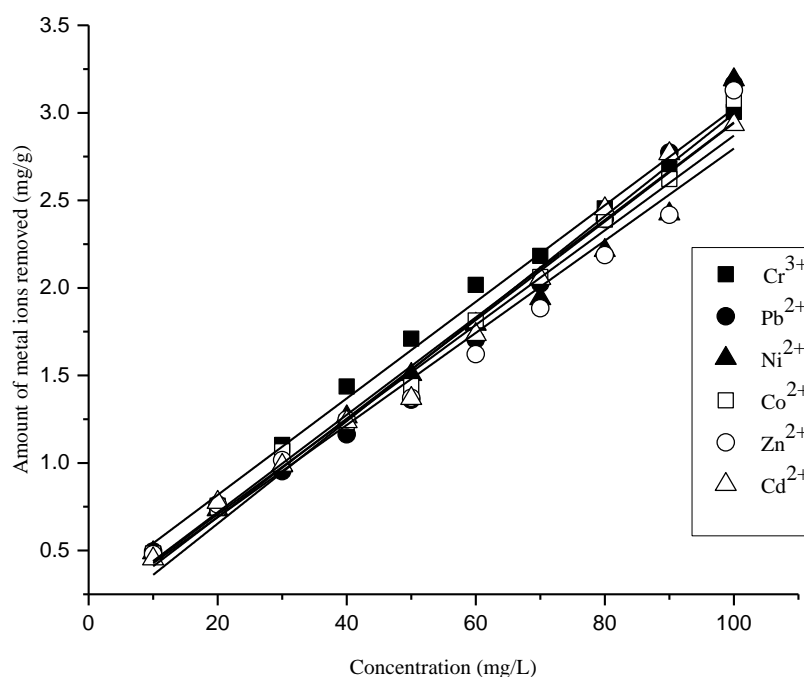


Figure 3: Effect of Initial Metal Concentration on the Biosorption of Metal Ions onto bIPL.

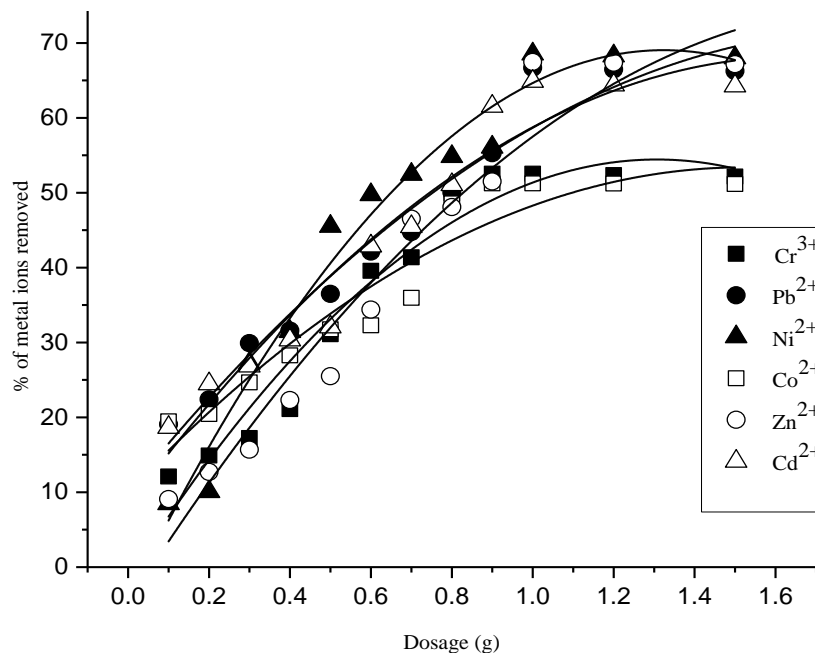


Figure 4: Effect of Dosage on the Biosorption of Metal Ions onto bIPL.

As discussed recently by Laroussi *et al.* (2019), when the initial concentration of metal ions increases from 50 to 250 mgL⁻¹, the maximum adsorption capacities of the various adsorbent tested increase and become nearly constant for a metal ion concentration higher than 250 mgL⁻¹. This view was supported by Zhang *et al.* (2016) and they observed that the increase in metal ion removal efficiency with initial concentration may be due to higher interaction between metal ions and the active sites located onto the surface of the adsorbents.

Effect of Biosorbent Dosage

The amount of metal ions sorbed by bIPL is influenced by its dosage. The effect of biosorbent dosage is represented in Figure 4. The percentage of metal ion sorbed increased as the mass of sorbent increased (Taşar *et al.*, 2014) and this is because the biosorption process depends on the available active sites as experienced when the dose of bIPL was increased from 0.1 to 1 g. An additional increase in the adsorbent dose did not result in considerable alteration in the elimination of the metal ions. This could be due to the congestion of contaminants at the binding sites on the adsorbent which eventually reduced the effectiveness of the sorbent.

Effect of Temperature and Thermodynamic Studies

It is expedient to study the effect of temperature on the biosorption of heavy metals. The uptake of contaminants onto base modified Irish potato leaves (bIPL) increased with an increase in temperature from 298 to 323 K. This suggests that biosorption of metal ions is endothermic. Whereas, an increase in adsorption efficacy as temperature increased may be due to the chemisorption process (Kara *et al.*, 2003). The thermodynamic activities of the sorption of the metal ions onto bIPL were determined using Gibb's free energy, ΔG° , enthalpy change (ΔH°), and entropy change (ΔS°). These parameters were evaluated from Equation (7) below (Adeogun *et al.*, 2018):

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

With R standing for the universal gas constant (8.314 J/Mol/K), T is temperature in Kelvin and K_c designates the thermodynamic equilibrium constant and is obtained from the below equation:

$$K_c = \frac{C_a}{C_e} \quad (8)$$

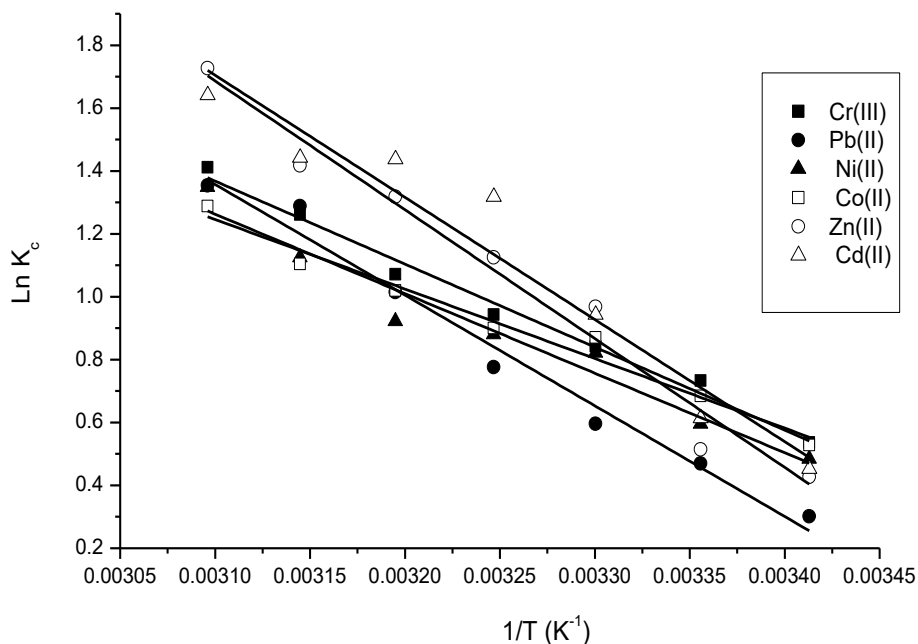


Figure 5: Thermodynamic Plots for the Biosorption of Metal Ions using Base Modified Irish Potato Leaf.

Table 1: Thermodynamic Parameters for Biosorption using Acid Modified Irish Potato Leaves.

	Temperature	Cr ³⁺	Pb ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺
ΔG° (kJ/mol)	293	-1305.89	-733.367	-1181.17	-1286.04	-1040.61	-1101.95
	298	-1816.48	-1162.54	-1477.28	-1695.43	-1275.13	-1521.74
	303	-2122.48	-1500.96	-2071.2	-2192.31	-2439.53	-2375.49
	308	-2414.68	-1986.91	-2254.39	-2305.27	-2880.59	-3374.27
	313	-2788.59	-2641.35	-2398.67	-2653.36	-3429.05	-3739.65
	318	-3333.92	-3406.71	-2974.12	-2918.69	-3746.88	-3814.76
	323	-3790.43	-3636.34	-3623.19	-3460.27	-4637.13	-4407.35
ΔH° (kJ/mol)		20.359	28.321	18.462	17.744	32.569	30.885
ΔS° J/Kmol)		73.45	98.196	66.43	64.523	113.93	108.85

With C_a representing concentration of adsorbate per litre and C_e is equilibrium concentration of solution (Sarin & Pant, 2006). The Gibb's free energy is also related to enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the Van't Hoff equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \quad (9)$$

From the slope and intercept of Van't Hoff's plot of $\ln K_c$ against $1/T$ (Figure 5) the values of ΔH° and ΔS° were estimated. The positive value of ΔH° indicates that the process is endothermic while the positive value of ΔS° shows increased randomness at solid solution interphase (Ali, and Alrafai, 2016). Also, the increase in the negative value of the change in Gibb's free energy (ΔG°) as temperature increased is an indication of the feasibility and spontaneous nature of the biosorption process.

Kinetic of Biosorption

The plots for studied kinetics are shown in Figure 6 and as shown in Table 2 the high value of the correlation coefficient of the Pseudo-first-order model suggests that the experimental data may support the PFO model to illustrate the adsorption kinetics of the metal ions. But on observing the differences between the experimental values, q_e , which were higher than the modelled values, therefore; it is assumed that the Pseudo-first-order model may not be sufficient to explain the kinetic for the experimental metal ions sorption by base modified Irish potato leaves.

Therefore, of the investigated kinetic models, the experimental values for Pseudo second-order correspond well with the calculated data (Table 2). Therefore, it can be recommended that the best fit is the PSO model for the adsorption of the metal ions. Hence, Pseudo second-order is the rate-

limiting step; it involves the exchange of electrons between the metal ions and different functional groups in the sorbent. The value of the Elovich constant shows that the process of biosorption is more than one mechanism. Similar results have been documented for the kinetic adsorption of different pollutants onto diverse adsorbents (Arshadi *et al.*, 2014; Meitei, and Prasad, 2014; Farnane *et al.*, 2018; Ksakas *et al.*, 2018).

Adsorption Isotherms

Results obtained from the equilibrium experiments were analyzed using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) isotherms as listed below (Freundlich, 1906; Langmuir, 1918; Temkin and Pyzhev, 1940; Dubinin *et al.*, 1947; Adeogun *et al.*, 2013).

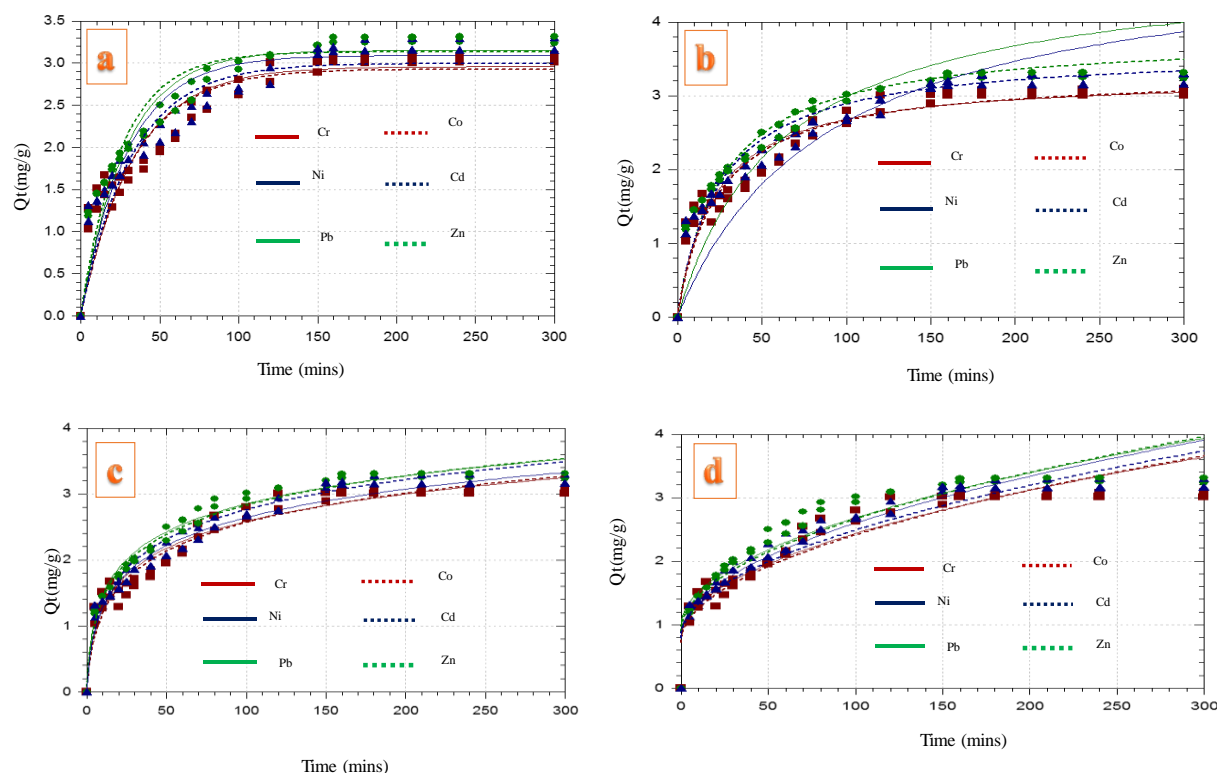


Figure 6: Kinetics Plots of (a) Pseudo-First-Order, (b) Pseudo-Second-Order, (c) Elovich, and (d) Intraparticle Plot for Biosorption of Metal Ions using Base Modified Irish Potato Leaf.

Table 2: Kinetic Model Parameters for the Metal Ions Biosorption onto Base Modified Irish Potato Leaves (bIPL).

Kinetic	Parameters	Cr	Pb	Ni	Co	Zn	Cd
PSEUDO-FIRST-ORDER	Q(cal)(mg/g)	3.266	3.811	3.613	3.298	4.811	4.017
	Q(exp)(mg/g)	3.008	3.239	3.306	3.094	3.312	3.162
	k ₁ (min ⁻¹)	0.0323	0.039	0.0033	0.0234	0.0435	0.0031
	SSE%	0.01818	0.03532	0.01985	0.01408	0.07343	0.04987
	R ²	0.958	0.978	0.983	0.981	0.975	0.963
PSEUDO-SECOND ORDER	Q(cal)(mg/g)	2.956	3.131	3.091	2.927	3.149	2.995
	Q(exp)(mg/g)	3.008	3.239	3.306	3.094	3.312	3.162
	k ₂ (g/mg min)	0.014	0.099	0.011	0.013	0.033	0.022
	SSE%	0.005	0.008	0.016	0.014	0.013	0.014
	R ²	0.977	0.983	0.981	0.982	0.981	0.983
ELOVICH	α (mg/g min)	0.431	0.637	0.421	0.344	0.501	0.418
	β (g/mg)	1.654	1.608	1.506	1.554	1.543	1.594
	R ²	0.921	0.987	0.978	0.982	0.977	0.981
INTRA PARTICLE DIFFUSION	Kp(mg/g min ^{1/2})	0.793	0.969	0.817	0.717	0.893	0.785
	C	0.164	0.171	0.178	0.168	0.177	0.174
	R ²	0.922	0.914	0.954	0.951	0.943	0.954

$$Q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (10)$$

$$Q_{eq} = K_F C_e^{1/n} \quad (11)$$

$$Q_e = Q_s e^{-\beta \varepsilon^2} \quad (12)$$

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \quad (13)$$

Details of all the parameters are as discussed elsewhere (Adeogun *et al.*, 213; Ofudje *et al.*, 2017). From Langmuir expression, the separation factor (R_L) can be deduced from equation 14 below:

$$R_L = \frac{1}{(1 + b C_o)} \quad (14)$$

Such that C_o (mg L⁻¹) stands for the initial pollutants concentration in which R_L values between 0 and 1 depicts favorable adsorption, R_L > 1 denotes unfavorable adsorption and R_L = 0 signify irreversible process (Adeogun *et al.*, 213; Ofudje *et al.*, 2017). According to the D-R isotherms, the Polanyi potential (ε) is given by:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (15)$$

where R (J mol⁻¹ K⁻¹), C_e (mg L⁻¹) and T (K) are as previously defined. The values of the constant β (mol² J⁻²) can be used to estimate the value of the mean free energy E (kJ mol⁻¹) of the adsorption process which is given as (Ofudje *et al.*, 2017):

$$E = (2\beta)^{-0.5} \quad (16)$$

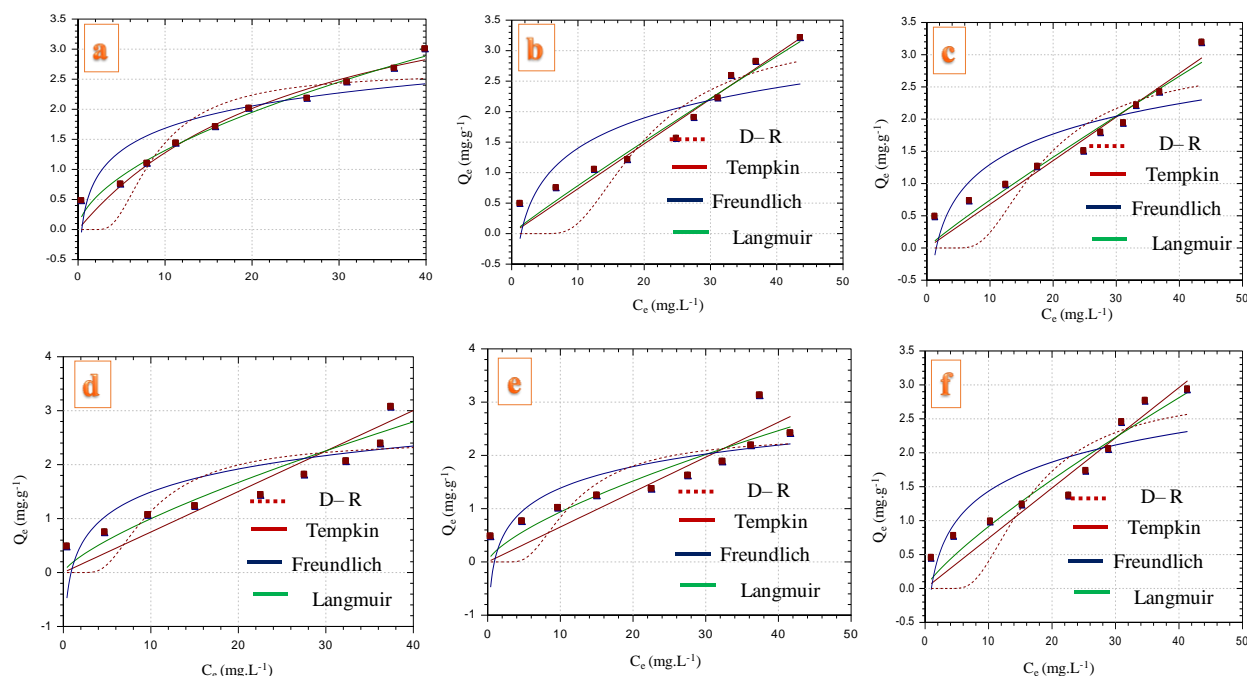


Figure 7: Isotherm Plots of (a) Cr(IV), (b) Pb(II), (c) Ni(II), (d) Co(II), (e) Zn(II) and (f) Cd(II) Ions by Base Modified Irish Potato Leaf.

Table 3: Isothermal Parameters of Base Modified Irish Potato Leaves (bIPL) for the Biosorption of Metal Ions.

Isotherms	Parameters	Cr(III)	Pb(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)
Langmuir	$Q_{max}(mg.g^{-1})$	4.745	3.327	3.401	3.975	2.654	3.889
	$R_L(L.mg^{-1})$	0.036	0.032	0.196	0.125	0.0125	0.126
	R^2	0.993	0.995	0.987	0.988	0.979	0.998
Freundlich	$K_f(L.g^{-1})$	0.355	0.089	0.089	0.18	0.188	0.141
	n	1.762	1.061	1.087	1.346	1.034	1.232
	R^2	0.996	0.996	0.997	0.997	0.998	0.998
Temkin	$A_T(L.mg^{-1})$	0.346	0.706	0.745	1.129	1.081	1.011
	$b_T(kJ.mol^{-1})$	453.91	346.19	381.52	402.8	425.93	400.16
	R^2	0.964	0.956	0.964	0.952	0.976	0.973
D-R	$Q_m(mg.g^{-1})$	2.614	3.349	2.894	2.438	2.366	2.906
	$E(kJ.mol^{-1})$	0.216	0.968	0.106	0.196	0.163	0.811
	R^2	0.975	0.978	0.955	0.913	0.944	0.974

Figure 7 shows the non-linear plots of Langmuir, Freundlich, D-R, and Temkin isotherms in the sorption of Cd^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Pb^{2+} , and Co^{2+} ions. The parameters of each of the models were obtained by the non-linear plots are summarized in Table 3.

The value of the correlation coefficient (R^2) of the entire tested isotherms were compared and found out that the Freundlich model has better value and this signifies that this model best symbolizes the experimental data and thus best suited isotherm for the adsorption process in this study. Although, judging from the value of all the

metal ions, ($R^2 > 0.9$), all the tested isotherms demonstrated good fitting. From the Freundlich isotherm, $1/n$ is a heterogeneity parameter. If a value of $1/n$ is below one, it indicates a normal adsorption process.

The smaller the values of $1/n$, the greater the expected heterogeneity and the Freundlich expression reduces to a linear adsorption isotherm when $1/n = 1$. If n falls between 1 and 10, it is an indication of a favorable adsorption process. However, $1/n$ greater than 1 suggests a cooperative adsorption process (Dalal *et al.*, 2017). As seen from Table 3, the values of n have ranged between 1.034 and 1.762 suggesting a favorable adsorption process. This was corroborated by the values of RL which lies between 0.0125 and 0.196 $L \cdot mg^{-1}$. Furthermore, the values of the monolayer adsorption capacity as obtained from the Langmuir isotherm is given as 4.745, 3.327, 3.401, 3.975, 2.654, and 3.889 $mg \cdot g^{-1}$ for Cr^{3+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} & Cd^{2+} ions respectively. The theoretical adsorption capacity, Q_m , and maximum adsorption energy E obtained from the D-R isotherm ranged between 2.366 and 3.349 $mg \cdot g^{-1}$ and 0.106 and 0.968 $kJ \cdot mol^{-1}$.

Characterization

The FT-IR investigation performed to evaluate the various functional groups present on the surface of the base modified Irish potato leaf is depicted in

Figure 8. The broad peak between 3200 and 3600 cm^{-1} is symptomatic of the presence of hydroxyl groups of macromolecular alliance (cellulose, pectin, etc.) (Arslanoglu *et al.*, 2008). The most significant vibration modes were the C–H stretching around 3000 cm^{-1} and the –CH deformation modes around 1460 cm^{-1} and 1365 cm^{-1} .

The CH_3 asymmetric stretching vibration occurred at 2978–2950 cm^{-1} . Carboxylic acid salts typically show a strong, characteristic asymmetric stretching absorption from the CO_2 group in the 1655–1550 cm^{-1} region. The peak at 1468 cm^{-1} can be assigned to the methylene C–H bend (Silverstein *et al.*, 1991).

The comparison showed that the bands characteristic to hydroxyl groups at 3475.07 cm^{-1} , alkyl group at 2978 cm^{-1} , and that characteristic to unsaturated carbonyl at 1651 cm^{-1} frequency were slightly shifted due to the attachment of the metal ions. The SEM images depicting the surface of the adsorbent surfaces before and after the adsorption process are shown in Figure 9. Before the adsorption process, the presence of porous structure was apparent, however, the occupation of the porous adsorbent surface by the deposits of the pollutants, even coverage on the surface of the adsorbent was noticed which may be as a result of the relations between the adsorbent surface and the metal ions.

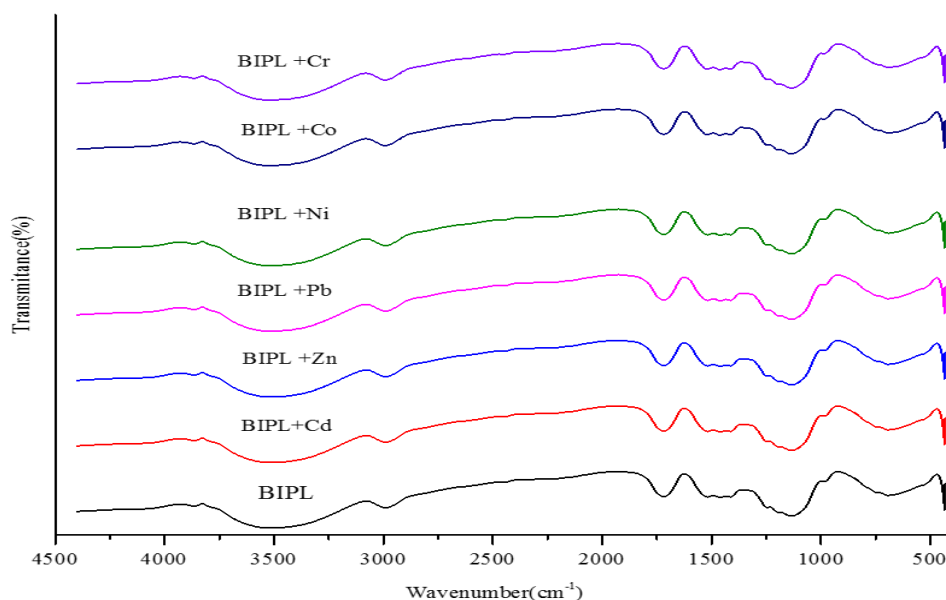


Figure 8: FT-IR Spectra of Free and Metal Bound Modified Irish Potato Leaf.

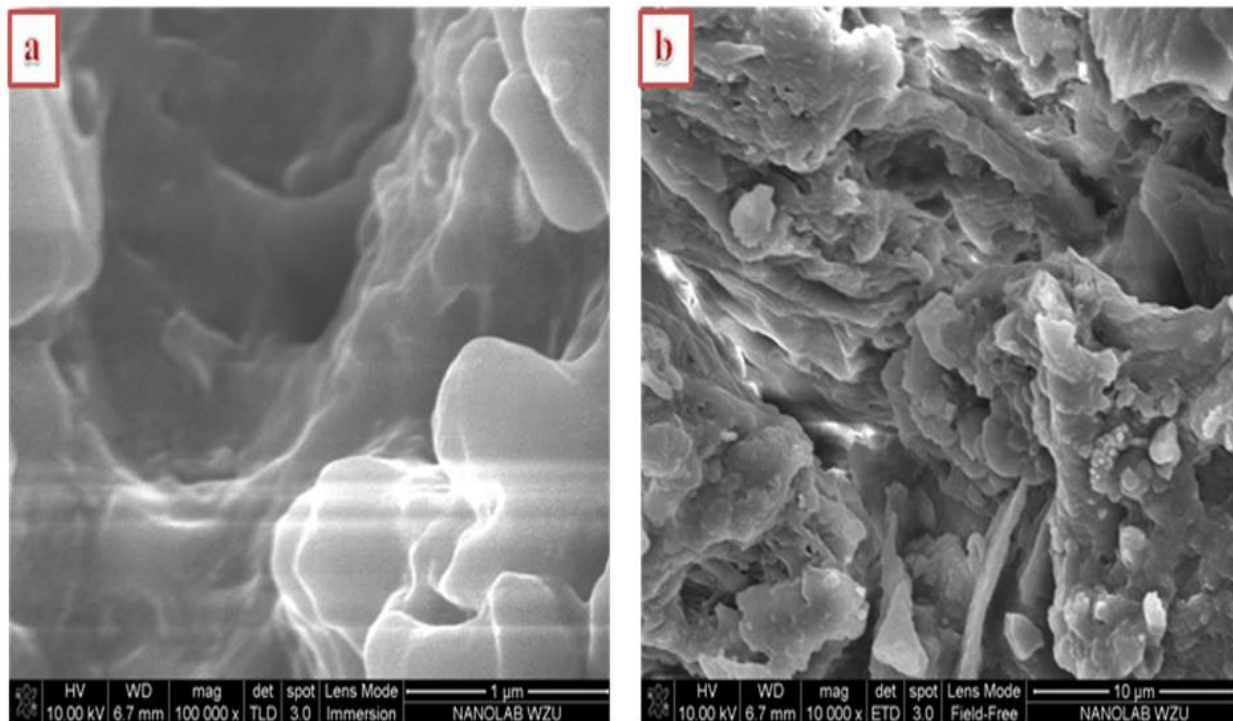


Figure 9: SEM Images of (a) Irish Potato Leaf Biomass before Adsorption (b) Irish Potato Leaf Biomass after Adsorption of Pollutant.

Table 4: FT-IR Spectra Characteristics of Modified Irish Potato Leaf after Biosorption of Metal Ions.

Metal ion	Absorption band (cm ⁻¹)			Functional groups
	Before	After	Difference	
Ni(II) Cr(III) Co(II) Cd(II) Pb(II) Zn(II)	3475	3403.07 3437.29 3439.24 3423.81 3440.29 3426.63	27.10 61.32 63.27 47.84 64.32 50.66	O-H Stretch O-H Stretch O-H Stretch O-H Stretch O-H Stretch O-H Stretch
Ni(II) Cr(III) Co(II) Cd(II) Pb(II) Zn(II)	2978	2967.99 2968.06 2968.04 2968.21 2960.41 2968.56	0.43 0.50 0.48 0.65 2.85 1.00	C-H Stretch C-H Stretch C-H Stretch C-H Stretch C-H Stretch C-H Stretch
Ni(II) Cr(III) Co(II) Cd(II) Pb(II) Zn(II)	1651	1664.70 1660.24 1661.41 1660.93 1660.27 1661.21	1.93 0.00 1.93 1.93 1.93 7.71	C=O Stretch C=O Stretch C=O Stretch C=O Stretch C=O Stretch C=O Stretch

CONCLUSION

The study revealed that the biosorption of Cr (III), Co(II), Zn(II), Ni(II), Pb(II), and Cd(II) by Irish potato leaf biomass was enhanced by the solution pH, biosorbent dose, contact time, temperature and initial metal ion concentration. The metal ions uptake process is best explained by a Pseudo-second-order model based on the assumption that the rate-limiting step may be a chemical adsorption process.

The investigation of the thermodynamic data showed a negative value of ΔG suggesting the process to be feasible, spontaneous, and therefore industrially relevant while the positive value of enthalpy change (ΔH) designates an endothermic process. The FT-IR studies of the base modified Irish potato leaf before and after being loaded by the metals disclosed that hydroxyl and carboxylate functional groups may have been involved in the sorption process as the intensities and wave numbers of these bands changed after the biosorption process. Hence the use of the leaf biomass of Irish potato can be employed as a good sorbent for the removal of metal ions from aqueous solutions and as an alternative sorbent for industrial effluent treatment.

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SUGGESTED CITATION

Ogundiran, A.A., N.A. Adesola Babarinde, E.A. Ofudje, and O.O. Ogundiran. 2021. "Removal of Heavy Metals from Aqueous Solutions using Modified Irish Potato Leaf as Low Cost Biosorbent: Kinetic and Thermodynamic Studies". *Pacific Journal of Science and Technology*. 22(2): 257-271.

