Kinetics, equilibrium and thermodynamics of heavy metal ion sequestration onto mango seed biomass (*Mangifera indica*)

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ABSTRACT

This study deals with the evaluation of biosorptive removal of nickel (II) by Mangifera indica seed. FTIR was used to determine the functional groups on Mangifera indica responsible for adsorption. Experiments have been carried out to find the effect of various parameters such as pH, adsorbent dosage, contact time, and temperature on the adsorption performance for the removal of Ni(II) ions. The experimental data were analyzed with four sorption kinetic models: the pseudo-first order, pseudo-second order, intraparticle diffusion as well as the Boyd models. Results showed that the adsorption kinetics followed the pseudo-second order rate equation. The mechanism of reaction was film-diffusion controlled. Langmuir, Freundlich and Dubinin–Radushkevich (D–R)models were used to describe the adsorption of Ni(II) ions on Mangifera indica seed. Biosorption equilibrium was better described by the Freundlich model (R^2 = 0.97). The monolayer biosoption capacity of Mangifera indica for Ni(II) ions concentration of 50 mg/L was 77.5 mg/g at 30 ± 1^oC. The thermodynamic parameters revealed that adsorption reaction using the Mangifera indica seed was spontaneous and endothermic for Ni(II) ions. The mean free energy, E, from the D-R, the ΔG and E_a values obtained showed that the adsorption process was physisorption. The present investigation showed that Mangifera indica can be utilized as a low cost and easily available biosorbent for Ni(II) ions removal.

Keywords: Adsorption isotherm, Kinetics, *Mangifera indica,* Models, Nickel

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INTRODUCTION

The contamination of the environment by heavy metals all around the world has been a major source of concern because of its toxic effect on man, animal and plant. The major source of heavy metal pollution is industry, including mining, metal plating, electric device manufacturing, tanneries, etc. [1, 2]. Heavy metals are generally more persistent in the environment than organic contaminants such as pesticides or petroleum byproducts. They can become mobile in soils depending on soil pH and their speciation. The exposure to nickel is known to inhibit oxidative enzyme activity. Acute poisoning causes nausea, vomiting, chest pain and rapid respiration [3].

Over the past few decades, many remediation techniques were applied all over the world to deal with the contaminated water bodies. Some of the different methods for removing heavy metal ions from aqueous solutions include ion exchange, solvent extraction, reverse osmosis, chemical precipitation and membrane filtration[4,5,6]. These methods are time consuming, expensive and relatively ineffective. Attention of researchers have been drawn

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in recent times to the use of biological methods such as biosorption for the removal of heavy metals in waste water. The main benefits of these methods include the ability to carry out the remediation insitu, the cost effectiveness and their environmentally benign nature.

*Mangifera indica*bark dust has been used to remove SO_2 from the air [7]. Unfruiting buds (battoor) of mango, *Mangifera indica L,* had been tested for the biosorption of multiple metal ions insingle metal system (SMS) and binary metal system (BMS) [8]. Sahare [9] used *Mangifera indica* bark to remove aqueous solutions of heavy metals.
This study investigated the use of *Mangifera indica* seed as an inexpensive and easily sourced biosorbent for the removal of Ni(II) from aqueous solution in a batch system. This involved the determination of the effect of pH, biomass concentration, initial metal concentration and contact time. Kinetic models such as pseudo-first order, pseudo-second order, intraparticulate diffusion and Boyd model were used to describe the biosorption process. Moreover, the batch equilibrium process was explained using Langmuir and Freundlich models. The effect of temperature on the adsorption of nickel by the biosorbent was also considered. To the best of our knowledge the use of *Mangifera indica* seed as a biosorbent has not been reported in literature.

EXPERIMENTAL SECTION

2.1 Biomass preparation
The *Mangifera indica* seed was washed with distilled water to remove any adhering dust and dried at 303 ±1 K for 24 h in an oven. It was then ground to fine powder using a blender and sieved to a constant size (1mm). It was stored in sterile, closed glass bottles and used as biosorbent without any further treatment.

2.2 Solution preparation
A stock solution of 1000 mg/L $NiSO_4\cdot6H_2O$ (analytical reagent grade) in double-distilled water was prepared. From the stock solutions 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L were prepared in 250 mL standard flasks. The initial pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a pH meter (A TOAV pH meter (HM30P) calibrated with standard buffer solutions.

2.3 Biosorption experiments
Batch biosorption experiments were carried out to determine the effect of pH, adsorbent dosage on nickel removal capacity of the *Mangifera indica*seed. The pH experiment was conducted by agitating 0.1 g of *Mangifera indica*seed with 100 mL of nickel solution of initial concentration 50 mg L^{-1} at different solution pH ranging from 2.0 to 7.0. The initial metal concentration (50-250 mg/L) and the biomass dose (100-500 mg) experiments were carried out using conical flasks tightly covered with clean aluminium foil on an orbital shaker for 5 h at a speed of 200 rpm and a temperature of 30 ± 1 ^{o}C. The concentrations of nickel in the solutions before and after adsorption were determined using Perkin-Elmer atomic absorption spectrophotometer (AAS).

2.4 Adsorption kinetics and equilibrium studies
Kinetic experiments were carried out in 250 mL conical flasks tightly covered with clean aluminium foil containing 100 L each of 50-250 mg/L of nickel solution to which 0.1 g of the biosorbent was added. All the experiments were performed at pH 6.0 for Ni(II) for 5 h. Samples were collected from the flasks at predetermined time intervals for analyses of the residual concentration of Ni(II) in the solutions. The residual amount of Ni(II) in each flask was determined using AAS. Similarly, the equilibrium experiments were conducted by adding to the 100 mg of *Mangifera indica* 100 mL each of nickel solution (50-250 mg/L) at 30 ± 1°C for 5 h. The concentrations of the nickel in the solutions before and after sorption were determined using AAS. The effect of temperature on biosorption was also carried out. Similar method to the equilibrium experiment was used except that the experiment was carried out at different temperatures of 303, 308, 313 and 318 K. The amounts of Ni (II) ions biosorption at equilibrium, q_e (mg/g), were calculated according to the following mass balance equation for the metal ion concentration

$$q_e = \frac{C_o - C_e}{m}V$$

(1)

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where q_e is the adsorption capacity at equilibrium, C_o and C_e are respectively initial and equilibrium concentrations of nickel (II), m is the mass of the adsorbent and V is the volume of the solution. The percent sorption capacity was calculated from the equation

$$\% \text{ sorption capacity} = \frac{(C_o - C_e)}{C_o} x100 \tag{2}$$

The experiments were carried out in duplicate.

RESULTS AND DISCUSSION

3. 1 FTIR analysis
The existence of the functional groups on the biosorbent surface and their responsibility for Ni biosorption were supported by FTIR technique. Fig. 1 shows the FTIR spectrum of *Mangifera indica.* The FTIR spectral analysis is vital in identifying the characteristic functional groups which are responsible for adsorption of metal ions. FTIR spectrum of *Mangifera indica* seed reflects distinct peaks at 1635.3, 1432.4 and 1090.8 cm^{-1} (Fig. 1). The peaks at 1635.3cm^{-1} is assigned to CO stretching of carboxyl or amide groups while the one at 1432.4 cm^{-1} is assigned to a C-H bend of alkane. FTIR spectrum also shows the shift in peak at 1097.2 cm^{-1} which may be attributed to the intensity of –P=O stretching vibration group with the sorbate. Thus FTIR spectra revealed that functional groups like –C=O and –P=O present on the *Mangifera indica* bark surface are involved in nickel adsorption.
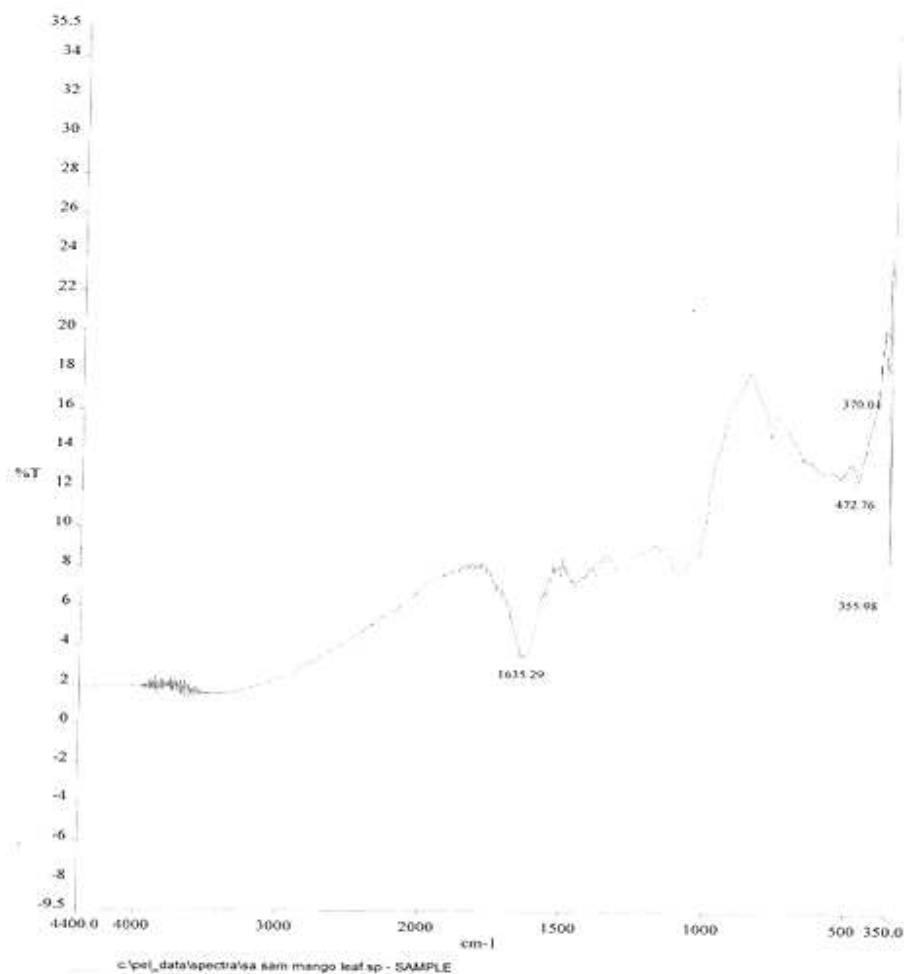

Fig.1. FTIR of *Mangifera indica* seed powder

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3.2. **Effect of pH**
The pH of the aqueous solution is one of the vital parameters which affect the biosorption of heavy metals. Solution pH affects the cell wall metal binding sites and the metal ion chemistry in water[10]. The effect of pH on the biosorption of nickel is depicted in Fig. 2.This study showed that there was an initial decrease in pH from 2 to 4.5 for Ni(II) biosorption and then a sharp increase in pH to a maximum at pH 6. The initial decrease in adsorption with increase in equilibrium pH indicated that there was an exchange between Ni^{2+} and H^+ ions for the surface sites. In other words, even though the surface of the biosorbent was negatively charged, the stiff competition for the surface site by H^+ persisted till pH 4.5, which decreased the attraction towards positively charged Ni^{2+}. In addition, biomass surface possesses positive charge when solution pH is less than the isoelectric point, and observes a reverse trend when the isoelectric point pH is more than the solution pH [11]. Thus isoelectric point less than 4.5 enabled *Mangifera indica* to possess a positive charge thereby decreasing the electrostatic attraction for nickel. At isoelectric point greater than 4.5, *Mangifera indica* possessed a negative charge thus increasing its uptake capacity for nickel. Similar decrease in adsorption with increase in pH was obtained by Ghokale [10]. Above pH 4.5 there was a sharp increase in pH up to a maximum of 6.0. Above pH 6.0 there was a decrease in pH which may be due to the precipitation of the metal hydroxide. Similar result obtained by [12] showed that insoluble metal hydroxide started precipitating from the solution at higher pH values which made true biosorption studies impossible.
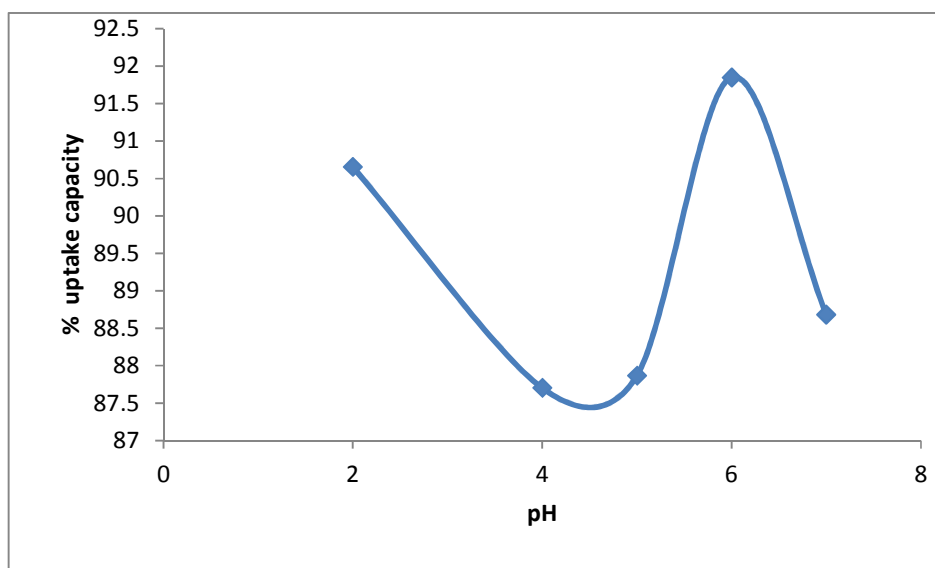

Fig. 2. Effect of pH on the adsorption of Ni (II) ion on *Mangifera indica*seed *at 30 ± 1 ᵒC*

3.3 Effect of biomass dose
The effect of the mass of biomass (*Mangifera indica*) on the biosorption of Ni(II)was determined at 30 ± 1^oC as shown in Fig. 3. The study showed a rapid increase in adsorption up to 0.13g. Beyond this value there was no significant adsorption and the system reached equilibrium. Thus increase in the biomass dose does not significantly increase the amount of Ni^{2+} adsorbed at different concentrations except at 200 mg/L where the amount adsorbed increased with increase in the mass of *Mangifera indica* from 0.2-0.5 g. A transient equilibrium was reached from 0.14 g to 2 g after which there was a slight decrease in adsorption. At biomass dose >0.3 g, adsorption increased gradually. The biomass dose was also studied with respect to different concentrations ranging from 50 mg/L to 250 mg/L. Fig. 3 showed that adsorption of nickel increases with increase in the initial metal concentration. At 50 mg/L the highest amount of Ni^{2+} removed by the varying mass of adsorbent was 45.0 mg/g, while at 250 mg/L, the highest amount removed was 217.7 mg/g.
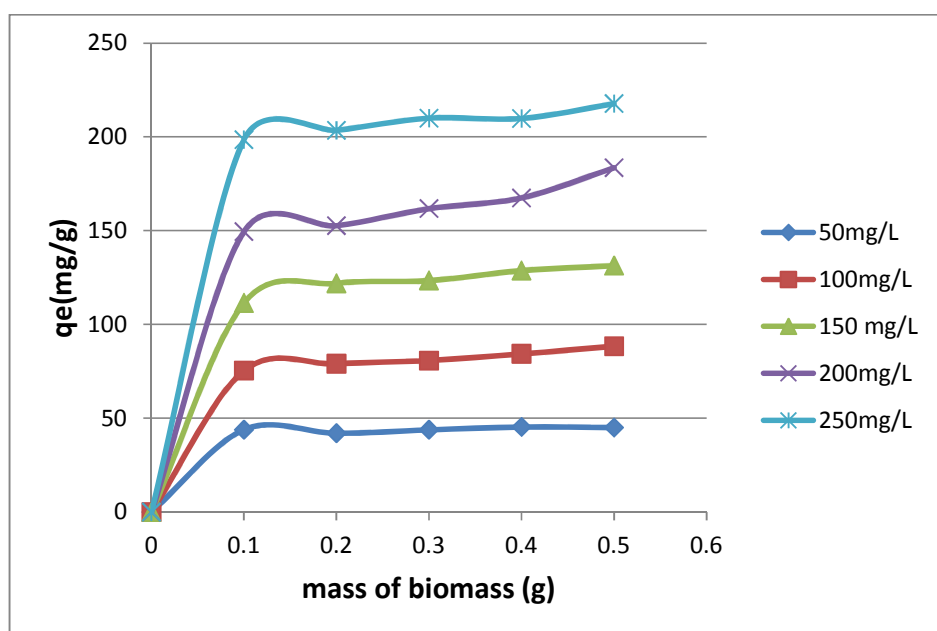
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Fig. 3 Effect of biomass dose on the biosorption of Ni(II) on *Mangifera indica* seed. Experimental conditions: pH 6, temperature, 30 ± 1°C

3.4 Effect of Contact Time

The effects of contact time and the equilibrium time on Ni(II) uptake capacity of *Mangifera indica* were carried out. The amount of metals biosorbed increased with contact time before it reached a plateau which was an indication of equilibrium (Figure not shown). In 1.0 h a large amount of the metal ions had bound to the adsorbent. The initial high amount of metal ions biosorbed was attributed to the availability of binding sites on the adsorbent. The rate of biosorption slowed as it approached equilibrium for the metal. The adsorption of Ni(II) increased gradually for concentrations of 50, 100, 150, 200 and 250 mg/L before equilibrium was reached. From the Figure (not shown) the higher the concentration of metal solution, the higher the amount of Ni(II) adsorbed by *Mangifera indica* seed powder. At initial concentrations of 50 and 250 mg/L the maximum amounts of nickel biosorbed were 49.02 and 241.4 mg/g respectively.

3.5 Kinetic modeling

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the resident time of adsorbate uptake at the solute interface including the diffusion process [13].The rate kinetics for the biosoption of Ni (II) on *Mangifera indica* seed powder was analyzed using kinetic models namely pseudo first order, pseudo second order and intra particle diffusion as well as Boyd.

3.5.1 Langergren pseudo-first order model

The linearized form of Lagergren pseudo-first-order model is given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

Where q_e (mg/g) and q_t are the biosorption capacities of the biosorbent at equilibrium and at any time t, respectively; k_1 is the langergren rate constant of the pseudo- first order biosorption (h^{-1}).

The plots of $\log(q_e-q_t)$ versus t (h) for different concentrations of nickel give straight lines (Figure not shown). From the plots, k_1 and q_e are determined from the slope and intercept respectively as shown in Table 1.

3.5.2 The pseudo second order model

The linearized form of the pseudo-second order chemisorptions of metal ions in solution is expressed as:

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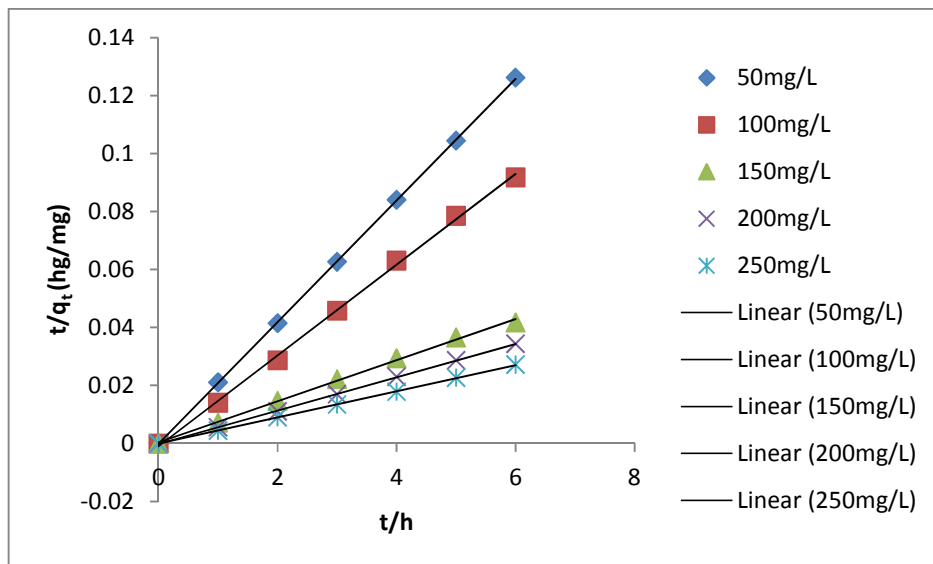$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_t} t \qquad\qquad\qquad\qquad (4)$$

Fig.4Pseudo-second-order kinetics for the biosorption of Ni (II) ions by *Mangifera indica*seed at30 ± 1ºC, pH= 6, C$_o$= 20 mg/L

wherek_2 (g/mg h) is the pseudo second order rate constant. If second-order kinetics is applicable, the plot of t /q_t versus t should show a linear relationship. The values of q_e and k_2 can be determined from the slope and intercept of the plot. Table 1 presents the rate parameters   obtained from the straight line plots of $\ln(q_e - q_t)$ versus t for the pseudo-second-order model (Fig. 4). The correlation coefficient for pseudo first order for Ni (II) ions was not suitable for describing the adsorption because the values of the $q_{e(calc)}$ are low compared to the $q_{e\,(exp)}$. According to the values of the correlation factors, R^2, in Table 1, the pseudo-second-order kinetic model showed satisfactory fit for Ni(II). The experimental equilibrium sorption capacities, $q_{e\,(exp)}$, obtained from the pseudo-second-order kinetic model were also in good agreement with the theoretical equilibrium sorption capacities at all concentrations studied for Ni(II) ions. These findings indicated that the pseudo-second-order kinetic model is more suitable to describe the Ni(II) biosorption onto *Mangifera indica*. In addition, the correlation coefficients showed very good fits for Ni(II) at all concentration ranges.

3.5.3 Intraparticle diffusion
The equation for the time dependent intraparticle diffusion described by Weber and Morris[14] is given by
$$q_t = K_p\, t^{0.5} + c \qquad\qquad\qquad\qquad (5)$$

whereq_t is the amount of metal ion adsorbed at time t and K_p is the rate constant of intra-particle diffusion and c is the intercept which gives information about the thickness of the boundary layers i.e, boundary effect increases with increase in the intercept.

If a linear graph that passes through the origin is obtained when q_t is plotted against $t^{0.5}$ then the intraparticle diffusion is the sole rate determining step [15]. The plots obtained(not shown) are linear but do not pass through the origin, which is an indication that intraparticle diffusion is not the sole rate determining step. The plots obtained are multilinear with three distinct regions indicating three different kinetic mechanisms.   The first stage is the transfer of Ni (II) ions onto the surface of *Mangifera indica* seed powder (external mass transfer or film diffusion (boundary layer)) and the rapid distribution of Ni (II) ions onto the outer surface of *Mangifera indica* because of the spontaneity of the biosorption process. The second stage is the transporting and subsequent gradual adsorption of Ni(II) ion (intra-particle mass transfer) onto the interior surface of *Mangifera indica*, followed by a plateau to equilibrium where the intraparticle diffusion starts to decrease due to the low concentration in solution phase as well as fewer available adsorption sites. Thus, intraparticle diffusion is involved in the adsorption process but may not be the controlling factor in determining the kinetics of the process. Mass transfer is a function of the diffusion

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mechanisms and their related equations as well as the coupling between liquid and solid phase [16]. Similar results were obtained by [16,17].The values of c was found to increase from 13.9 to 67.7 mg/g when the initial concentration of Ni(II) increased from 50 to 250 mg/L, indicating that the boundary layer thickness increased with increase in initial concentration of Ni(II) ions. The value of k_p decreased from 10.3 to 2.25 mg/g $h^{1/2}$ when the initial concentration of Ni(II) ions was increased from 50 to 400 mg/L.

Table 1 Comparison of pseudo–first order, pseudo-second order and intra-particle diffusion (Weber-Morris) kinetic models for the sorption of nickel (II) ions on *Mangifera indica* seed

Initial conc. (mg/L)	$q_{e\,(exp)}$ (mg/g)	First order kinetic model			second order kinetic model			Weber-Morris model
		$k_1(h)$	$q_{e(calc)}$ (mg/g)	R^2	k_2	$q_{e(calc)}$ (mg/g)		k_p (g(mgh)$^{-1}$)
50	47.8	0.53	5.82	1.000	4.38	47.6		10.3
100	66.46	0.03	2.10	0.999	0.23	63.7		8.11
150	137.8	0.29	1.85	0.998	0.13	138.7		6.61
200	176.7	1.05	2.05	1.000	0.16	172.4		2.91
250	223.6	0.06	1.21	1.000	0.20	222.2		2.25
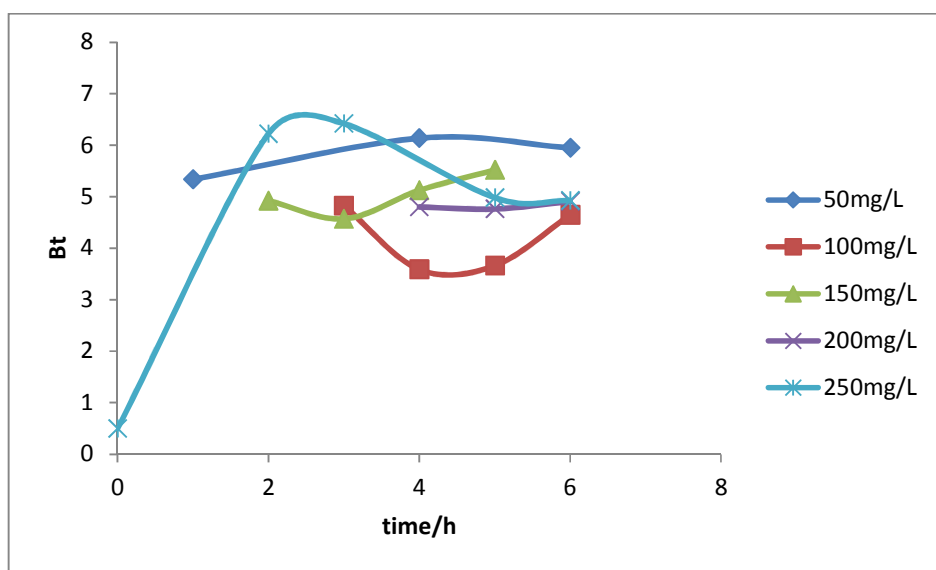
Fig.5. The Boyd kinetics showing the plot of βt against time for the adsorption of Ni^{2+} on *Mangifera indica*at 30 ± 1°C

The Boyd kinetic equation [18] was applied to distinguish between film diffusion and intraparticle diffusion and to identify the slowest step in the adsorption process. The Boyd expression is given by

$$U = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \ell^{(-n^2 \beta t)} \qquad (6)$$

where βt is a mathematical function of U and U is a representation of the fractional attainment of equilibrium at any time t given by Eq. (7):

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$$U = \frac{q_t}{q_e} \tag{7}$$

Where q_t and q_e are earlier defined in 3.4.1

Approximate values of βt can be obtained by the transformation of equation 6 to give

$$\beta t = -0.4977 - \ln(1 - U) \qquad \text{(for U >0.85)} \tag{8}$$

$$\beta t = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2}{3} U \right)} \right)^2 \qquad \text{(for U<0.85)} \tag{9}$$

The linearity of the plot of βt versus t could be used to determine the slowest step in the adsorption process. If the plots are linear and passes through the origin, then the slowest or rate limiting step in the adsorption process is intraparticle or pore diffusion. If the plot is nonlinear or linear but does not pass through the origin, then the adsorption process is controlled by film diffusion [19]. The Boyd plots for the adsorption of Ni^{2+} onto *Mangifera indica*seed at 50mg/L to 250mg/L are nonlinear (Fig. 5) suggesting that film diffusion controls the rate of the adsorption. Similar observations were reported by Hameed and Khaiary [20] for the adsorption of malachite green by rattan sawdust and Njoku and Hameed [19] for the adsorption of 2,4-dichlorophenoxyacetic acid on Corncob activated carbon.

3.6 Sorption isotherms

Several equilibrium isotherms originally used for gas phase sorption are available and readily used for gas phase equilibria [21]. Langmuir and Freundlich adsorption isotherms were used. Sorption isotherm provides a relationship between concentration of nickel in solution and the amount of nickel adsorbed on adsorbent when both the phases are at equilibrium [12]. The Langmuir model assumes monolayer adsorption. The linear form of the Langmuir isotherm equation is given by the following:

$$\frac{C_e}{q_e} = \frac{1}{Q_o a} + \frac{C_e}{Q_o} \tag{10}$$

whereq_e is the monolayer biosorption capacity of the biosorbent (mg/g); and ais the Langmuir constant (L/mol), and is related to the free energy of biosorption. A plot of C_e/q_eversus $C_e$for the biosorption of Ni (II) ions onto *Mangifera indica* (Fig. 6) gives a straight line of slope, $1/Q_o$, and intercept, $1/Q_o a$. The R^2 and Q_o values in Table 2 suggest that the Langmuir isotherm may be a suitable model and the maximum monolayer biosorption capacity was found to be 77.5 mg/g for Ni at % 50 mg/L and at a temperature of 30 ± 1 ^{o}C.

A dimensionless equilibrium parameter, E_L, proposed by [22] described the favourability of adsorption. It is expressed as

$$E_L = \frac{1}{(1 + aC_o)} \tag{11}$$

A favourable adsorption has its E_L value between 0 and 1, for unfavorable and linear adsorption $E_L > 1$ and $E_L = 1$ respectively, while the adsorption operation is irreversible if $E_L = 0$. Value of

E_L was found to be $2 \times 10^{-3}$for Ni**. This confirmed that *Mangifera indica* is favourable for the biosorption of Ni under conditions used in this study.

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Table 2 Langmuir and Freundlich isotherm for nickel (II) ion biosorption on *Mangifera indica* at 30 ± 1ºC

Langmuir				Freundlich			Dubinin–Radushkevich		
R^2	Q_o (mg/g)	K_L (L/mg)	E_L	R^2	K_F (mg/g)	n	q_m (mg g^{-1})	β (mol^{2}KJ^{-2})	E (KJ mol^{-1})
0.83	77.5	3.58	2×10^{-3}	0.97	0.21	1.66	5.10	0.09	3.37

The Freundlich isotherms can be used for adsorption on a heterogenous surface where the binding sites are not equivalent [23]. The equation is given by

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

(12)

where q_e is the equilibrium metal concentration on the biomass (mg/g); C_e is the equilibrium metal concentration in the solution (mg/L); K_F (L/g) and n (dimensionless) are Freundlich isotherm constants that indicate the extent of the biosorption, and the degree of nonlinearity between solution concentration and biosorption, respectively[24]. The Freundlich model plots for the biosorption of Ni(II) onto *Mangifera indica* biomass at 30ºC were presented in Fig. 7. The numerical value of the Freundlich constant, n,   for Ni is 1.66. Since the values of n is greater than unity, it indicates that nickel is favorably biosorbed by *Mangifera indica* at   the experimental temperature. Freundlich model fitted well for Ni(II) ions (R^2 = 0.97). The correlation coefficient of the Freundlich model is higher than that of Langmuir. This means that the former is better for explaining Ni(II) adsorption than the latter.
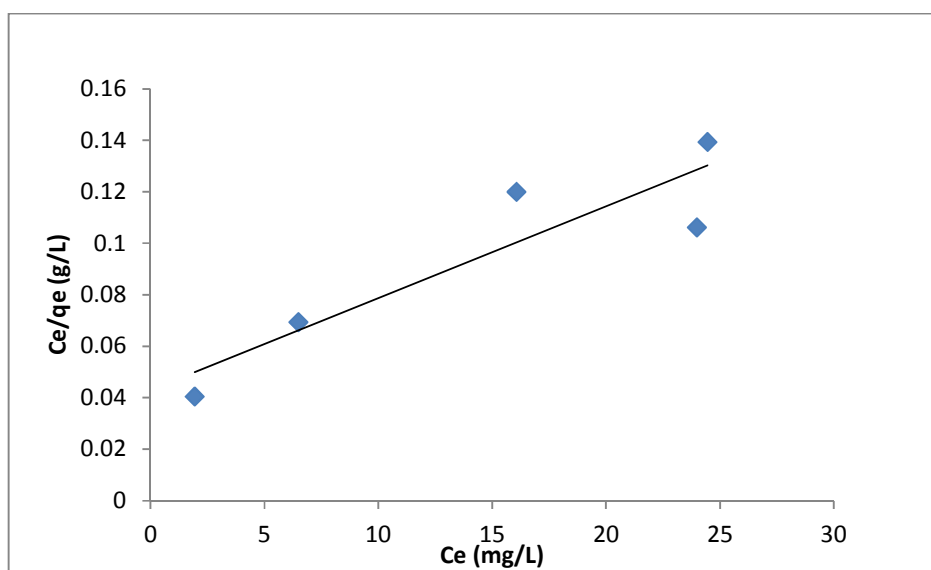
Fig. 6.Langmuir adsorption isotherm of nickel (II) ions on *Mangifera indica* at 30 ± 1ºC

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm, because it does not assume a homogenous surface or constant sorption potential [25]. The linearized form of the D–R equation is given by

$q_e = \ln q_m - \beta\varepsilon^2$ where $\varepsilon = RT \ln (1 + 1/C_e)$ (13)

q_e is the amount of metal ions adsorbed at equilibrium, β is a constant related to the adsorption energy, q_m is the theoretical saturation capacity, ε is the Polanyi potential. Table 1 gives the R^2 value for the plot of q_e against ε^2

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(Figure not shown). The q_m and β values were calculated from the slope and intercept of the plots and presented in Table 2. The mean free energy of biosorption, E, was obtained from the equation

$$E = 1\sqrt{-2\beta} \tag{14}$$

The mean biosorption energy was calculated and given in Table 2. These results suggest that the biosorption processes of heavy metal ions onto the studied *Mangifera indica* seed is likely to take place by physical mechanism because the sorption energy (3.37 kJ/mol) is below the 8 kJ/mol.
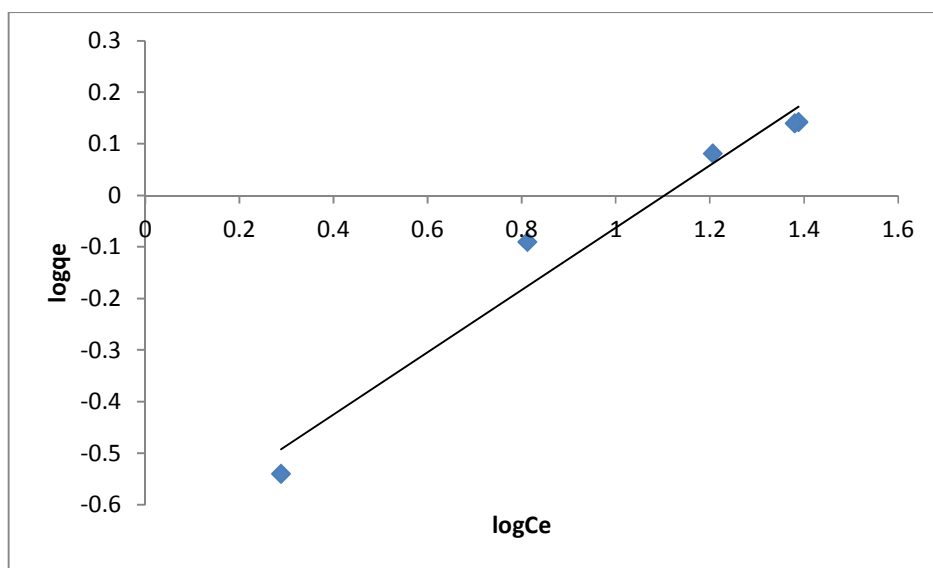

Fig. 7.Freundlich adsorption isotherm of nickel (II) ions on *Mangifera indica*at 30 ± 1°C

3.7AdsorptionThermodynamics

The calculation of the thermodynamic parameters is essential in order to determine the thermodynamic behaviour of the adsorption of the metal species on *Mangifera indica* seed. The thermodynamic parameters evaluated are the change in Gibb's free energy, ΔG, the enthalpy change, ΔH, and the entropy change, ΔS, and they can be obtained from the following equations:

$$K_d = \frac{q_e}{C_e} \tag{15}$$

$$\Delta G = -RT\ln K_d \tag{16}$$

$$\ln K_d = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

Where K_d is the distribution coefficient for the adsorption , q_e is the amount of metal species (mg) adsorbed on the adsorbent per liter of the solution at equilibrium and C_e is the equilibrium concentration (mg L^{-1}) of the metal species in the solution. T is the solution thermodynamic temperature (K) and R is the molar gas constant. ΔH and ΔS were calculated from the slope and intercept of Van't Hoff plots of ln $K_d$vs T^{-1} (eq.17). The results are shown in Table 3. Distribution coefficient (K_d) reflects the capability of the *Mangifera indica* to retain metal species molecules and is also used as a quantitative indicator of the mobility of the metal species in the solution.

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Table 3. Thermodynamic parameters for the adsorption of nickel on *Mangifera indica*

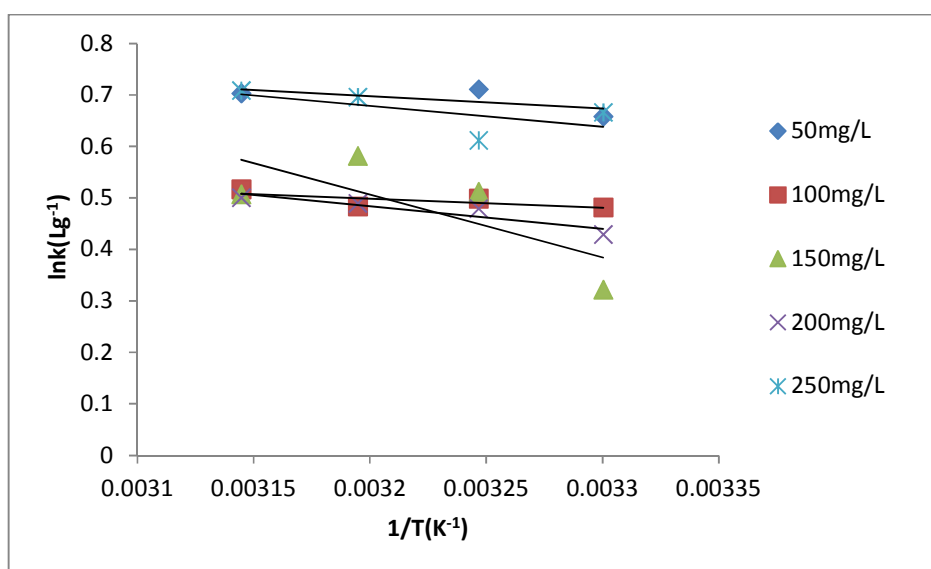| Metal Conc.(mgL^{-1})	ΔH (kJmol^{-1})	ΔS (Jmol^{-1}K^{-1})	$-\Delta G$ (kJmol^{-1})				E$_a$ (kJmol^{-1})
			303K	308K	313K	318K	
50	7.41	30.3	1.66	1.82	2.67	1.86	9.93
100	1.45	8.77	1.21	1.27	1.26	1.36	3.97
150	10.1	36.7	0.81	1.31	1.51	1.34	12.7
200	3.65	15.7	1.08	1.23	1.27	1.32	6.17
250	3.35	16.4	1.68	1.56	1.81	1.87	5.87

Fig. 8 Effect of temperature on the adsorption of Ni(II) ion on *Mangifera indica* at 30 ± 1°C, pH=7, C$_o$ = 20mg/L

Table 4 Adsorption results for Ni (II) ions by various sorbents from the literature

Sorbent	Adsorption Capacity (mg/g)	Temperature (^{o}C)	Reference
Dye loaded sawdust	17.9	-	[26]
Unmodified core fibre	1.83	-	[27]
G.thermoleovorans (G2)	21.0	25	[28]
Barley straw	35.8	23 ± 0.5	[29]
Teak tree bark composite beads	10.1	-	[30]
Jackfruit plant	6.13	-	[30]
Mangifera indica	77.5	30 ± 1	This study

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phase. According to [31] K_d is a useful parameter for comparing the adsorptive capacities of different adsorbent materials for any particular ion, when measured under same experimental conditions. At initial concentrations of 100, 200 and 250 mg/L, the magnitude of ΔG decreased with the rise in temperature for the biosorption of Ni(II) on *Mangifera indica*. Similar results were obtained for Ni(II) adsorption at 50 and 150 mg/L except at 318K where the value of ΔG increased. The negative values of ΔG confirmed the feasibility of the process and the spontaneous nature of sorption of Ni(II) on *Mangifera indica*. Generally, the change of free energy for physisorption is between -20 and 0 KJ mol^{-1}, but chemisorption is a range of -80 to -400 KJ mol^{-1} [32]. From the ΔG values obtained in Table 3, the adsorption process was physisorption. The positive values of ΔH obtained indicated that the sorption of Ni(II) on *Mangifera indica* was an endothermic reaction. The positive values of ΔS reflect the affinity of the adsorbent for Ni(II). In addition, the positive values of ΔS was an indication of the increasing randomness at the solid/liquid interface during the sorption of Ni (II).

Information on the mechanism of the ion exchange process can be obtained by determining the value of E_a. In general, the sorption process is classified to be film-diffusion controlled when E_a is below 16 kJ mol^{-1}, particle-diffusion controlled when E_a is 16–40kJ mol^{-1}, and chemical-reaction controlled when $E_a$is greater than 40 kJ mol^{-1} [33, 34]. The activation energies of Ni(II) adsorption at different concentrations (as shown in Table 3) were less than 16 kJ mol^{-1} which suggests that this adsorption is a film-diffusion-controlled process. This corroborated earlier result we obtained from Boyd kinetic equation. This also meant the involvement of weaker forces of attraction indicating physisorption.

Table 4 presents the comparison of the maximum amount of nickel removed by various adsorbents.

CONCLUSION

The biosorption of *Mangifera indica* seed biomass was studied in a batch system with respect to initial pH, biomass dose, kinetics and temperature. FTIR result showed that the functional groups on the surface of *Mangifera indica* responsible for adsorption are –C=O and –P=O. The solution pH played a significant role in affecting the biosorption capacity of *Mangifera indica* for nickel. The biomass exhibited maximum uptake at pH 6.0 for nickel. Pseudo –second order model best described the kinetics of the biosorption of Ni(II) while the adsorption mechanism was mainly by film diffusion. Biosorption equilibrium was better described by the Freundlich model. The thermodynamic parameters obtained showed that the biosorption was spontaneous and feasible. In addition, the sorption process was endothermic with increasing randomness at the solid/liquid interface.

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