

## Dynamics, Mechanistic and Equilibrium Studies for the Biosorption of Nickel on Palm Tree Leaves

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### ABSTRACT

Adsorption of heavy metals on biological sorbents, activated carbon and synthetic resin particles is a common separation technique. In this study, the biosorption of nickel ions from aqueous solution by palm tree leaves was investigated as a function of shaking time, nickel ions concentration and equilibrium pH. Competitive adsorption of nickel on palm tree leaves with EDTA and citric acid was also investigated.

Batch adsorption experiments revealed that the biosorption of nickel on palm tree leaves was strongly pH dependent, and maximum nickel sorption was found to occur at equilibrium pH of 6.0. Dynamics studies showed that: the initial uptake of nickel on palm tree leaves was rapid, equilibrium was established within 30 minutes, and the data followed the pseudo-second order reaction. The equilibrium sorption data of nickel on palm tree leaves at solution pH 6.0 were described by two-parameter isotherm models such as the Langmuir, Freundlich, and D-R models and three-parameter models such as Redlich-Peterson and Sips isotherm models. Ion-exchange, adsorption-complexation and intraparticle diffusion mechanisms were found to be involved in the biosorption process.

The Effect of ions interference on the biosorption of nickel on palm tree leaves showed that the sorption of nickel on palm tree leaves was adversely affected by the presence of chelating agents such as EDTA and citric acid.

**KEYWORDS:** Biosorption, Nickel, Palm tree leaves, Isotherms.

### INTRODUCTION

Heavy metals such as nickel, copper, lead and zinc are present in nature and industrial wastewater. Due to their mobility in natural water ecosystems and their toxicity even at low concentrations, the presence of these metals in surface water and groundwater is considered one of the major inorganic contamination problems. Nickel and its compounds are carcinogenic and may constitute danger to

human beings and other lives. Nickel is listed by the USA Environmental Protection Agency as one of the 129 pollutants found in wastewaters that constitute serious health hazards. The maximum permissible concentration of nickel in effluents in the U.S. is 2 ppm (Abu Al-Rub et al., 2002). Industrial wastewaters containing nickel ions are common, since nickel is used in a vast number of industries, such as electroplating, batteries manufacturing, mine, inorganic and dye industries and metal finishing.

Removal of heavy metals can be accomplished by many techniques. These include chemical precipitation

(Mauchauffée and Meux, 2007; Esalah et al., 2000), carbon adsorption (Abdulkarim and Abu Al-Rub, 2004), ion exchange (Corami and Mignardi, 2008; Samara et al., 2005), electro dialysis (Samara et al., 2007; Ottosen et al., 2005) and membrane separation (Muthukrishnan and Guham, 2006). The selection of a particular technique depends mainly on waste type and concentration effluent concentration, and the economics. However, these techniques have several disadvantages such as the high operating cost, low selectivity, incomplete removal and the possibility of generating toxic slurries that are difficult to treat (Abu Al-Rub et al., 2003).

In addition to these traditional wastewater detoxification treatments, biosorption processes, which utilize low-cost biosorbents to remove pollutants from wastewaters, are considered as a potentially attractive alternative to conventional methods of metal recovery from solutions. A broad range of biosorbents including bacteria (Gonçalves et al., 2007; Madhaiyan et al., 2007; De and Ramaiah, 2007), algae (El-Naas et al., 2007; Abu Al-Rub et al., 2006; Abu Al-Rub et al., 2004), yeast (Wang and Chen, 2006), fungi (Melgar et al., 2007; Zafar et al., 2007; Conveegaram et al., 2007), activated sludge (Hammaini et al., 2007), sheep manure (Abu Al-Rub et al., 2003; Kandah et al., 2003; Kandah et al., 2002; Abu Al-Rub et al., 2002), palm tree leaves (Abu Al-Rub, 2006), peat (Qin et al., 2006; Brown et al., 2000), bark (Nehrenheim and Gustafsson, 2008), peanut hulls (Brown et al., 2000) and rice husk (Chuah et al., 2005; Ricardo et al., 2004; Wong et al., 2003), have been recognized to be efficient in removing heavy metals from aqueous solution. In addition, these biosorbents showed high sorption efficiency of heavy metals from diluted solutions and the possibility of metal recovery.

Earlier studies demonstrated that palm tree leaves were efficient biosorbents for zinc removal from aqueous solutions. This efficiency can be attributed partially to the presence of different functional groups, such as hydroxyl, carboxylic and phenolic on the leaves of these trees (Abu

Al-Rub, 2006).

In this study, the use of palm tree leaves as biosorbents for the removal of nickel ions from aqueous solution was investigated. Batch sorption experiments were conducted and the nickel ions biosorption on palm tree leaves was investigated with respect to equilibrium pH, equilibrium metal ion concentration and process kinetics. The adsorption equilibrium was modeled using different isotherm models. The pseudo-second order kinetics in addition to the Weber and Morris equation and diffusion models were used to analyze the dynamics of biosorption of nickel ions on palm tree leaves. The Effect of ions interference of EDTA or citric acid on the biosorption of nickel on palm tree leaves will also be investigated.

## MATERIALS AND METHODS

### Preparation of Biosorbent

Fresh biosorbent of palm tree leaves was collected from one palm tree. They were washed a few times with distilled water to remove any impurities and dried for 24 h at 60 °C in the oven. The biosorbent was ground and sieved. A fraction of average particle size (1.2–1.4 mm) was used in this study. The main functional groups on the biosorbent such as carboxyl, lactones, lactols and phenols groups, were found by the Boehm's titration method as follows (Abu Al-Rub, 2006). Table 1 lists the different functional groups available on palm tree leaves used in this study.

**Table 1. The functional groups on the palm tree leaves (Abu Al-Rub, 2006).**

Functional Group	Meq H <sup>+</sup> /g palm tree leaves
Carboxyl	0.85
Lactones and Lactols	2.8
Phenols	0.65

### Chemicals

The solutions containing nickel(II) ions were prepared by diluting 1000 ppm of stock solutions of nickel(II) to

the desired concentrations. Stock solutions were prepared using analytical reagent grade of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in deionized water. Solution pH was adjusted by dilute hydrochloric acid and dilute sodium hydroxide solutions.

### Effect of pH on Nickel Speciation

The effect of pH on nickel speciation was studied both using different nickel concentrations at constant pH

and using constant nickel concentration of 100 ppm at different pH values. The concentration of nickel ions in the aqueous solution was measured after 24 h using Varian atomic absorption spectrophotometer.

### Metal Sorption Studies

A batch equilibrium method was used to determine the sorption of nickel ions by palm tree leaves. A set of 250 ml

**Table 2. Adsorption isotherms parameters for the biosorption of nickel ions on palm tree leaves at  $T = 25^\circ\text{C}$ ,  $\text{pH} = 6.0$  and mass of palm tree leaves = 0.08 g.**

Model	Parameter	Value
Langmuir	$q_{mon}$ (mg/g)	24.1
	$K_L$ (l/mg)	0.0559
	CFEF (mg/g)	0.29
Freundlich	$K$ (l/mg) <sup>1/n</sup> (mg/g)	3.79
	$n$	2.7
	CFEF (mg/g)	1.29
D-R	$q_D$ (mg/g)	22.42
	$B_D$ (mol/kJ) <sup>2</sup>	0.0025
	$E$ (kJ/mol)	14.10
	CFEF (mg/g)	0.22
Redlich-Peterson	$K_1$ (mg/g)(l/g)	0.896
	$K_2$ (l/g) <sup>B</sup>	0.0189
	B	1.11
	CFEF (mg/g)	0.05
Sip	$q_{mon}$ (mg/g)	23.91
	$K_L$ (l/mg)	0.0499
	$n$	0.13
	CFEF (mg/g)	0.21
pH Langmuir-type model	$A_1$ (mg/g)	2.83
	$A_2$	0.36
	$\beta$ (l/mg)	0.045
	CFEF (mg/g)	0.12

**Table 3. Investigation of ion exchange mechanism (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).**

Nickel bound (meq/g)	Cation released (meq/g)			$(R_{b/r})$
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	
0.034	$9.7 \times 10^{-3}$	$1.2 \times 10^{-3}$	$5.6 \times 10^{-3}$	2.0

Erlenmeyer flasks containing 50 ml of metal solution and a mass of 0.08 g of palm tree leaves were used in the experiments. Equilibrium isotherms were obtained by agitating 0.08 g of palm tree leaves with 50 ml of nickel ion solution for a predetermined time in a water bath shaker at 25°C. For adsorption isotherm studies, different nickel ion concentrations were used (0-400 ppm). Kinetics studies were carried out with 100 ppm initial nickel ions concentration and mass of palm tree leaves of 0.08 g. Samples were taken at periodic time intervals and then the nickel solution was separated from the sorbent by centrifugation (2000 x g, 10 min) and the supernatant was collected. The concentration of metal ions was determined using a Varian atomic absorption spectrophotometer. All experiments were carried out in triplicate and were also reproduced on different days. The nickel ions sorbed by the biomass was calculated using the equation:

$$q = \frac{(C_0 - C_e)V}{w}; \tag{1}$$

where  $q$  is the amount of nickel sorbed by biomass (mg/g),  $C_0$  the initial concentration of nickel (mg/l),  $C_e$  the concentration of nickel at equilibrium (mg/l),  $V$  the initial volume of nickel solution (l) and  $w$  is the dry mass of the palm tree leaves (g).

### Ions Interference Experiments

The effect of ions interference of EDTA or citric acid on the biosorption of nickel on palm tree leaves was also investigated. The studies were carried out at constant initial nickel ion concentration of 100 ppm and varying

EDTA or citric acid initial concentration. All the experiments were conducted at 25°C and using the same procedures used in the single ion adsorption experiments.

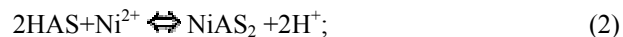
## RESULTS AND DISCUSSION

### Effect of pH

Most of the previous studies on biosorption of heavy metals have shown that pH was the most important parameter affecting the biosorption process. These studies have shown that pH has significant effects on speciation, solubility and biosorption capacity of heavy metals (Samara et al., 2007; Ottosen et al., 2005; Melgar et al., 2007; Zafar et al., 2007; Conveegaram et al., 2007). Figs. 1 and 2 show the effect of pH on nickel ions in aqueous solutions. Fig. 1 shows that for 100 ppm nickel concentration, precipitation of nickel starts at pH 6.2 where 98.8% of nickel exists in ionic form (Ni<sup>2+</sup>) and about 1.2% precipitates. At pH 8.5, only 70.2 % of nickel exists in ionic form. At pH 6.0, there was no nickel precipitation. The effect of nickel concentration on percentage of nickel in ionic form at pH 6.0 is shown in Fig. 2, which shows that about 98.9% of nickel in a solution of 350 ppm nickel concentration will be in ionic form.

Figure 3 shows the effect of pH on the biosorption of nickel ions on palm tree leaves. As can be depicted from this figure, the biosorption of nickel was strongly affected by equilibrium pH. At pH 3.0 or lower, little biosorption occurred, where almost no uptake was obtained at pH 2.0. A sharp increase in nickel uptake was observed at pH 4.0. No significant increase in nickel uptake was observed at pH values above 6.0. The low biosorption capacity at pH

values lower than 3.5 can be attributed to hydrogen ions that compete with nickel ions on the sorption sites; at lower pH, and due to protonation of the binding sites resulting from a high concentration of protons, the negative charge intensity on the sites is reduced, resulting in the reduction of the binding of nickel ions. This can be also explained using the following equation which can be used to describe the binding of metal ions in the solution with the biomass:



where AS represents the active sites of the biosorbent. This equation suggests that a competition between nickel and  $\text{H}^+$  ions for the active biosorption sites occurs at lower pH values. In addition to this competition between nickel and  $\text{H}^+$  ions on the active sites of the biosorbent, it is known that at low pH, some of the functional groups, such as the carboxylic groups, cannot bind the metal ions in the solution.

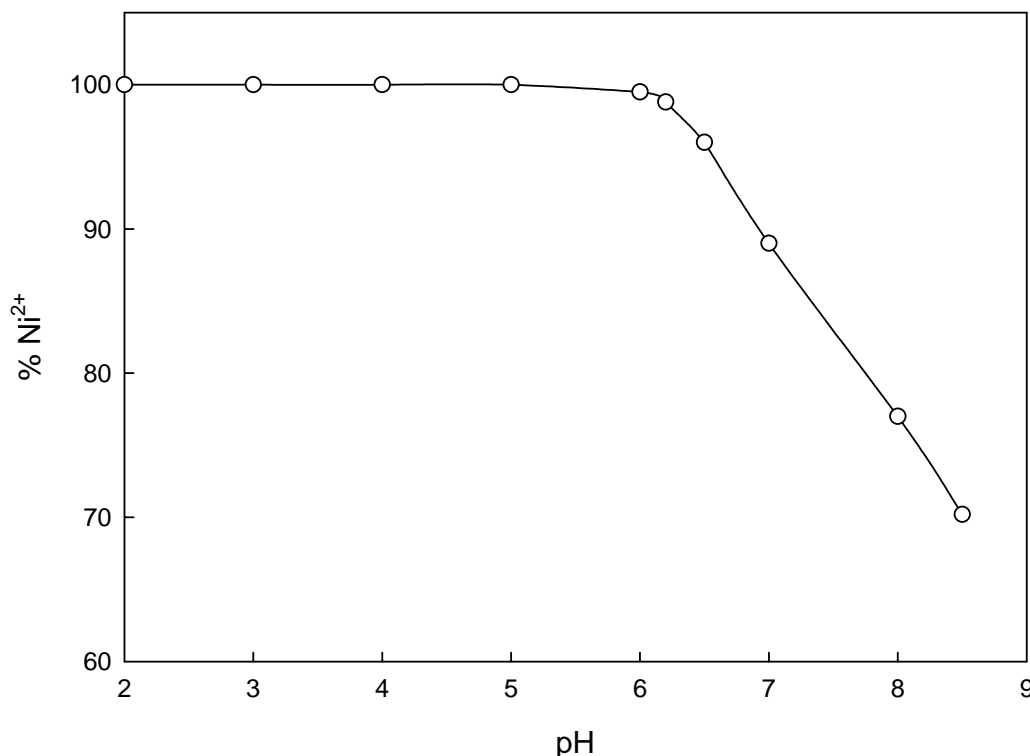


Fig. (1): Effect of pH on nickel speciation (initial nickel ions concentration = 100 ppm).

Increasing pH results in a net negative charge on the biomass surface and the ionic state of ligands such as carboxyl, lactones and lactols groups will be such that so as to promote the binding with the metal cations.

#### Adsorption Equilibrium

The efficiency of nickel ions biosorption on the palm tree leaves was ascertained by the biosorption equilibrium isotherms at nickel ions initial concentrations of 0–400

ppm. The palm tree leaves exhibited efficient nickel removal capacity as shown in Figure 4, which indicates that nickel biosorption onto palm tree leaves was proportional until it reached the equilibrium concentration of 363.3 ppm, corresponding to a nickel uptake of 22.93 mg/g. Afterward, there was no further increase of Ni ions removal.

In the design of sorption processes, models that describe the adsorption isotherm data are needed. Three

two-parameter adsorption models; namely Langmuir, Freundlich and Dubinin–Radushkevich models, and two three-parameter adsorption models; namely: Redlich-Peterson and Sips isotherm models will be used to analyze the data in this study. In addition to these models, the effect of pH on the biosorption of nickel on palm tree leaves will be analyzed using a Langmuir-type model.

The Langmuir isotherm model given by the equation:

$$q_e = \frac{q_{mon} K_L C_e}{1 + K_L C_e} \quad (3)$$

is considered one of the most widely used models to describe and analyze adsorption equilibrium isotherms. The adjustable parameters  $q_{mon}$  and  $K_L$  are the Langmuir constants which are related to the amount of adsorption corresponding to monolayer coverage or adsorption capacity and the energy of adsorption, respectively. This model is valid for monolayer sorption onto a surface with a finite number of identical sites and uniform adsorption energies, where there are interactions between the adsorbed molecules.

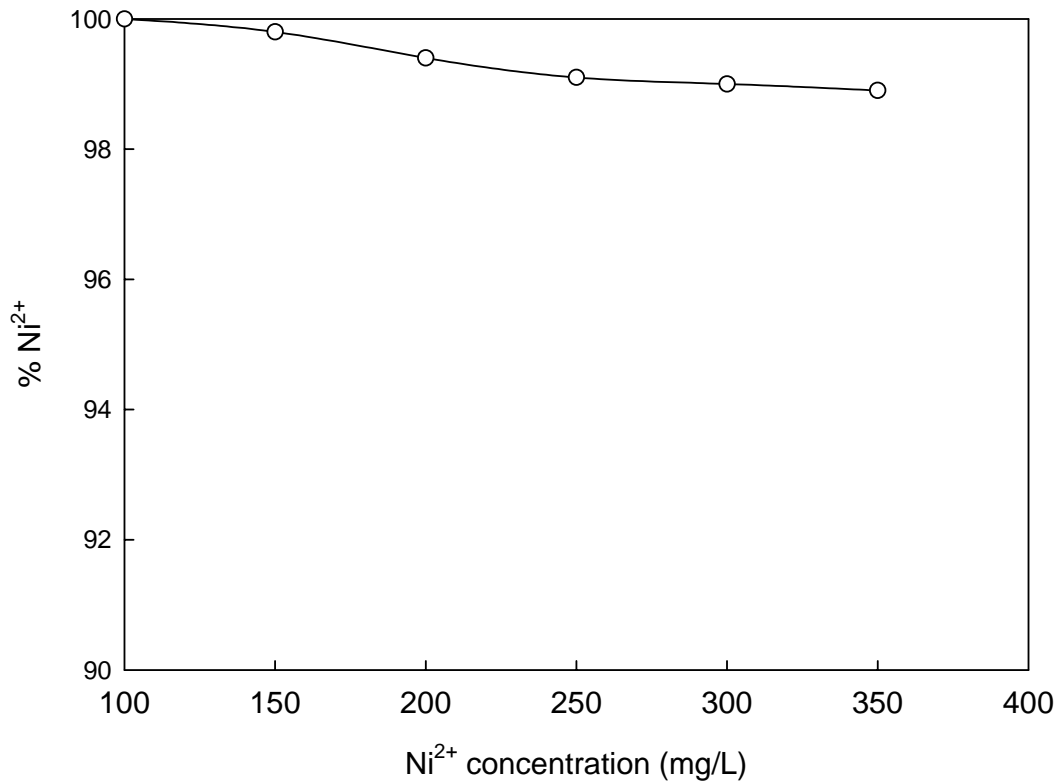


Fig. (2): Effect of pH on nickel speciation for different nickel concentrations (pH=6.0).

The Freundlich isotherm model given by the equation:

$$q_e = KC_e^{1/n} \quad (4)$$

is another widely used isotherm to describe adsorption data. This empirical model is based on the assumption that sorption occurs on heterogeneous surfaces. However, it does not provide any information on the monolayer

adsorption capacity. The adjustable parameters  $K$  and  $n$  are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively.

The final two-parameter isotherm model to be used is the Dubinin-Radushkevich (DR) isotherm which is given by the equation (Abu Al-Rub, 2004):

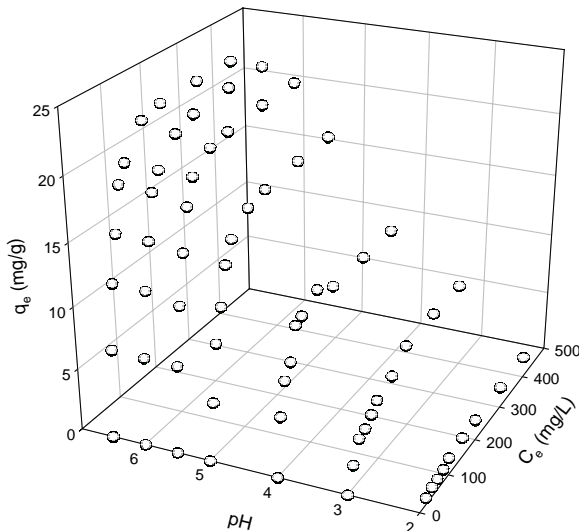
$$q_e = q_D e^{\left( -B_D \left[ RT \ln \left( 1 + \frac{1}{C_e} \right) \right]^2 \right)} \quad (5)$$

where  $q_D$  and  $B_D$  are the DR constants which are related, respectively, to the maximum adsorptive capacity and the mean free energy of adsorption per mole of the adsorbent as it is transferred to the surface of the solid from infinite distance in the bulk fluid;  $E$ , where  $E$  can be calculated using the relation (Dubinin, 1960):

$$E = 1/(2B_D)^{0.5} \quad (6)$$

The Sips model, given by the equation:

$$q_e = \frac{q_{mon} (K_L C_e)^{1/n}}{1 + (K_L C_e)^{1/n}} \quad (7)$$



**Fig. (3): Effect of pH on nickel removal (initial nickel ions concentration=100 ppm, mass of palm tree leaves=0.08g).**

where  $q_{mon}$ ,  $K_L$  and  $n$  are the Sips constants, is an example of three-parameter adsorption isotherm equations, proposed to improve the fit of the two-parameter adsorption isotherm models. At low sorbate concentration, this model assumes the form of the Freundlich model, while at high concentrations it predicts a constant, monolayer sorption behavior similar to that of the Langmuir isotherm.

Another three-parameter model used to analyze

adsorption data is the Redlich-Peterson (R-P) isotherm model, which is given by the equation:

$$q_e = \frac{K_1 C_e}{1 + K_2 C_e^B} \quad (8)$$

where  $K_1$ ,  $K_2$  and  $B$  are the R-P constants. It should be noticed that for values of  $B$  equal to one, the R-P equation reduces to the Langmuir equation.

The Composite Fractional Error Function (CFEF), defined by the equation below, was used as a non-linear error function to determine the parameters of these models (Ho et al., 2002):

$$CFEF = \min \sum_{i=1}^P \left[ \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \quad (9)$$

The parameters of the above-mentioned models along with the values of CFEF are listed in Table 2. The values of CFEF indicate that the five isotherm models could fit the biosorption of nickel ions on palm tree leaves.

The effect of pH on nickel biosorption on palm tree leaves can be modeled using the Langmuir-type model (Ma and Tobin, 2004):

$$q_e = \frac{q_c(pH)\beta C_e}{1 + \beta C_e} \quad (10)$$

This model encompasses the effect of pH on biosorption via the monolayer sorption capacity. The dependency of monolayer sorption capacity on pH can be simulated using the exponential form (Ma and Tobin, 2004):

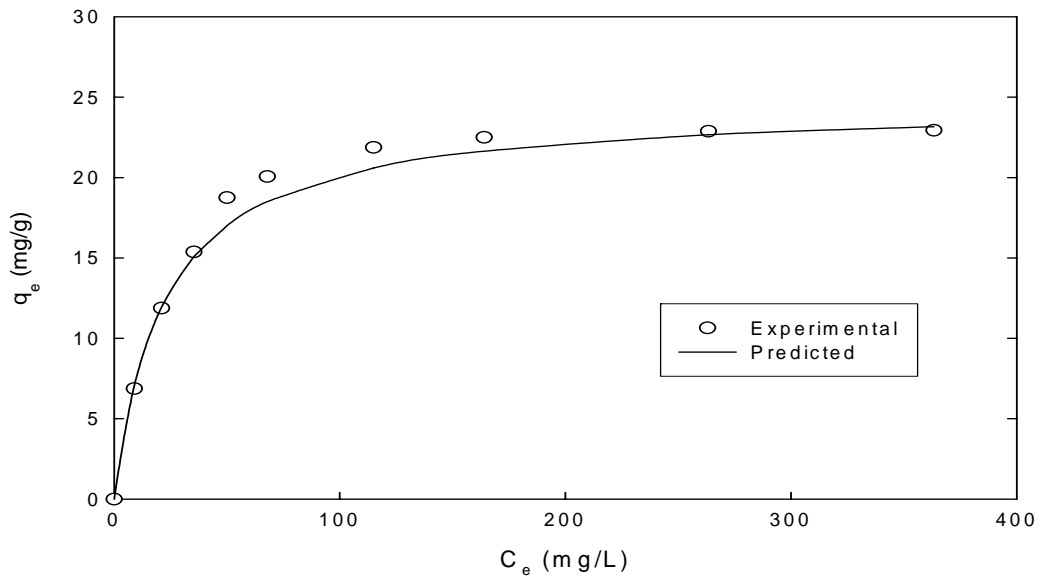
$$q_c = A_1 e^{A_2 pH} \quad (11)$$

The isotherm experimental data at different equilibrium pH values were fitted by CFEF non-linear regression (Eq. 9) to evaluate the adjustable parameters of equations (10) and (11), and the results are tabulated in Table 2. These parameters were used to predict the nickel biosorption on palm tree leaves at pH 6.0 as shown in Figure 4 which indicates that the proposed model could predict well the experimental data.

**Dynamics and Mechanistics of Nickel Biosorption on Palm Tree Leaves**

The relationship between shaking time and nickel biosorption by palm tree leaves is presented in Fig. 5. Figure 5 shows that the rate of nickel biosorption on palm tree leaves is high at initial stages, and gradually decreases to become almost constant after a period of 30 min. This observation is in agreement with the

findings of a previous study for the biosorption of zinc on palm tree leaves (Abu Al-Rub, 2006). Numerous kinetic and dynamics models have been proposed to elucidate the mechanism of biosorption of pollutants, e.g., heavy metals. The mechanism of biosorption depends on the physical and/or chemical characteristics of the biosorbent as well as on the mass transport process. In order to



**Fig. (4): Experimental and predicted isotherms of nickel ions biosorbed on palm tree leaves (pH = 6.0 and mass of palm tree leaves = 0.08 g).**

investigate the mechanism of nickel biosorption on palm tree leaves, different kinetic and mass transfer models are discussed below.

**Kinetics Models**

The biosorption of nickel ions on palm tree leaves can be theorized to be according to the following two reactions (Ho and Mckay, 2000; Weber and Morris, 1963):



or

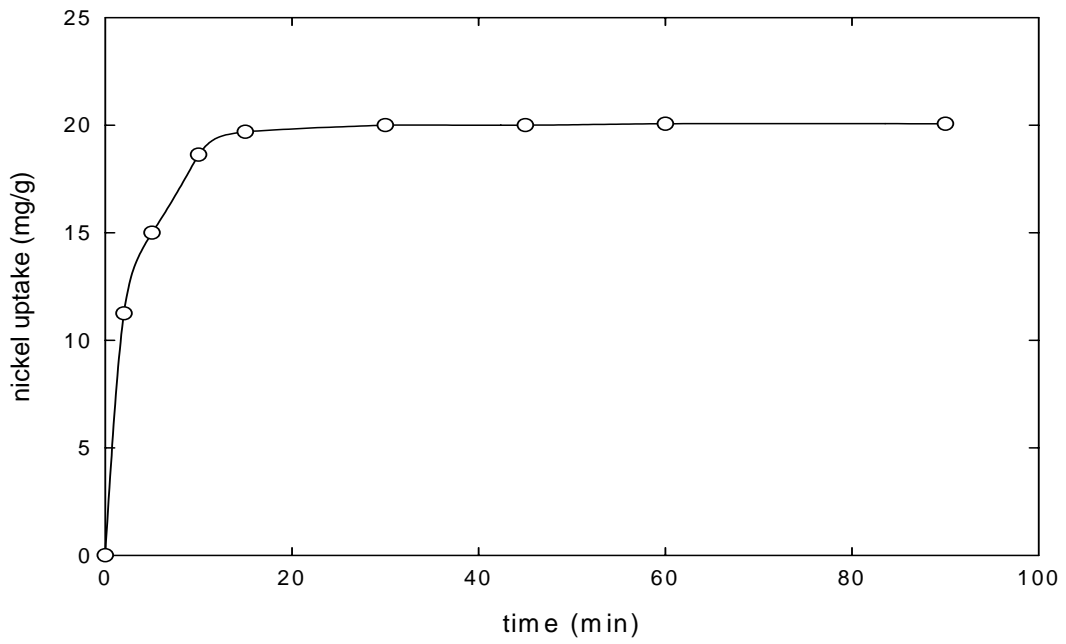


Assuming that the sorption capacity of nickel ions on palm tree leaves is proportional to the number of active sites occupied on the palm tree leaves, then the pseudo-second order is given by (Ho and Mckay, 2000; Weber and Morris, 1963):

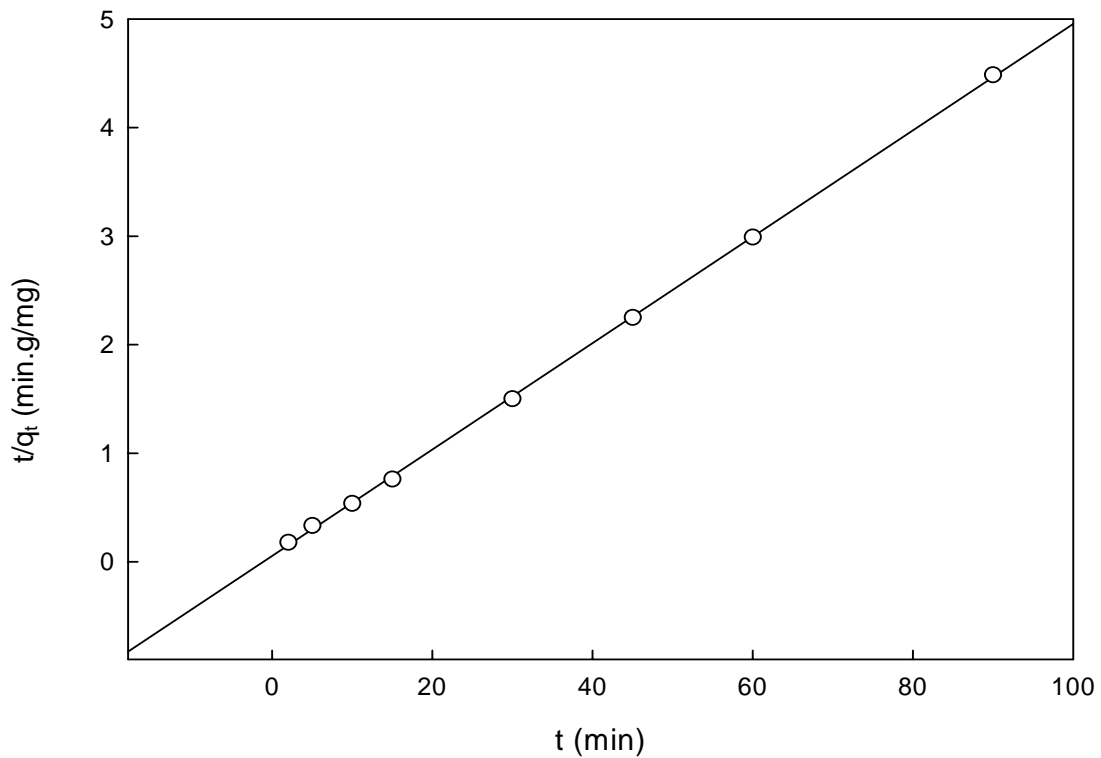
$$\frac{dq_t}{dt} = k(q_e - q_t)^2; \tag{14}$$

where  $k$  is the equilibrium rate constant of pseudo-second order sorption kinetics (g/mg.min),  $q_t$  is the amount of sorbate on sorbent at time  $t$ (mg/g) and  $q_e$  is the equilibrium uptake(mg/g). Equation (14) can be solved with the boundary condition:  $q = 0 @ t = 0$ , to give:





**Fig. (5):** Effects of shaking time on nickel removal (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).



**Fig. (6):** Kinetics of biosorption of nickel on palm tree leaves (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).

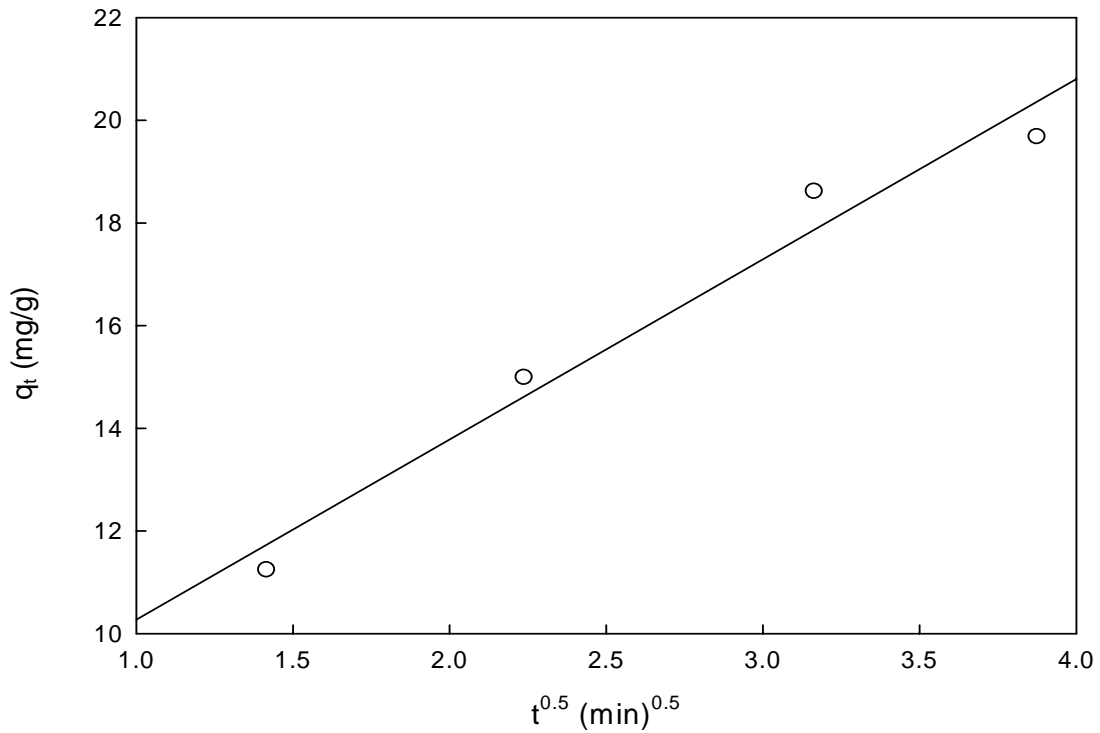


Fig. (7): Investigation of the contribution of intraparticle diffusion in the biosorption process of nickel on palm tree leaves: Application of the Weber and Morris equation (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).

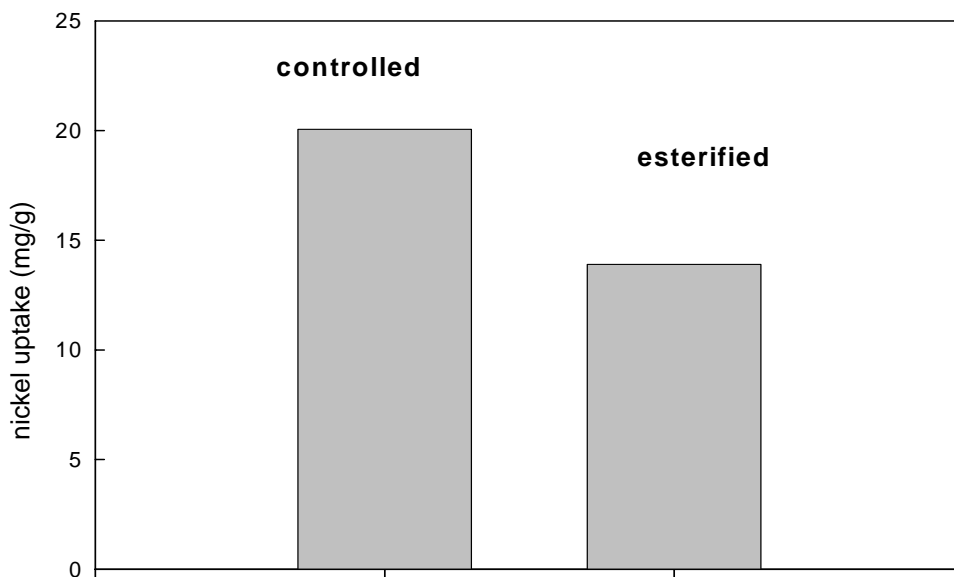
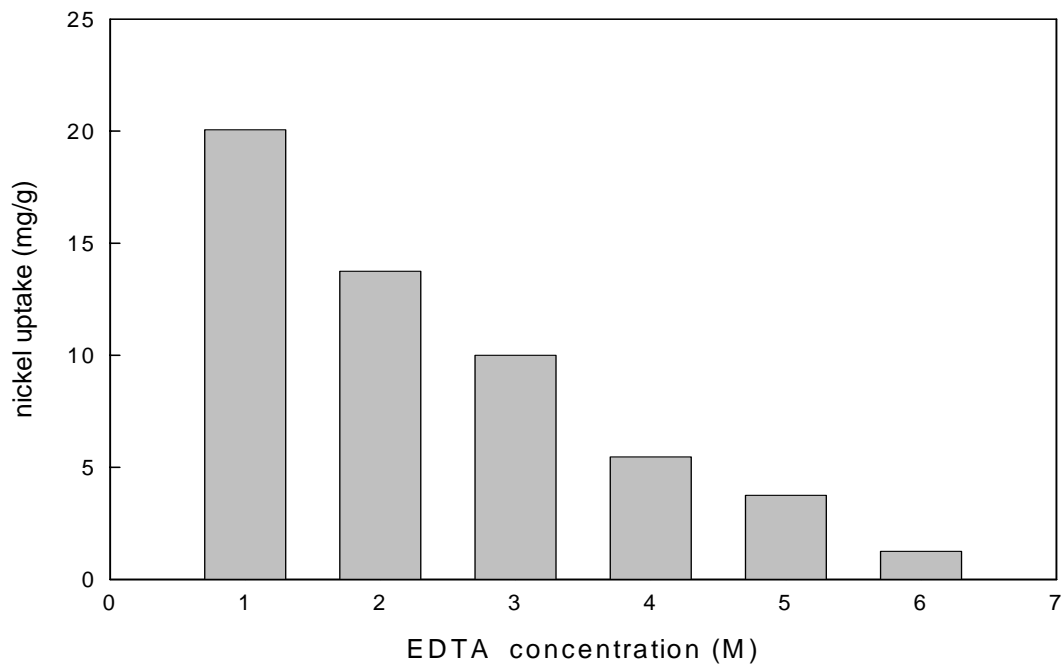
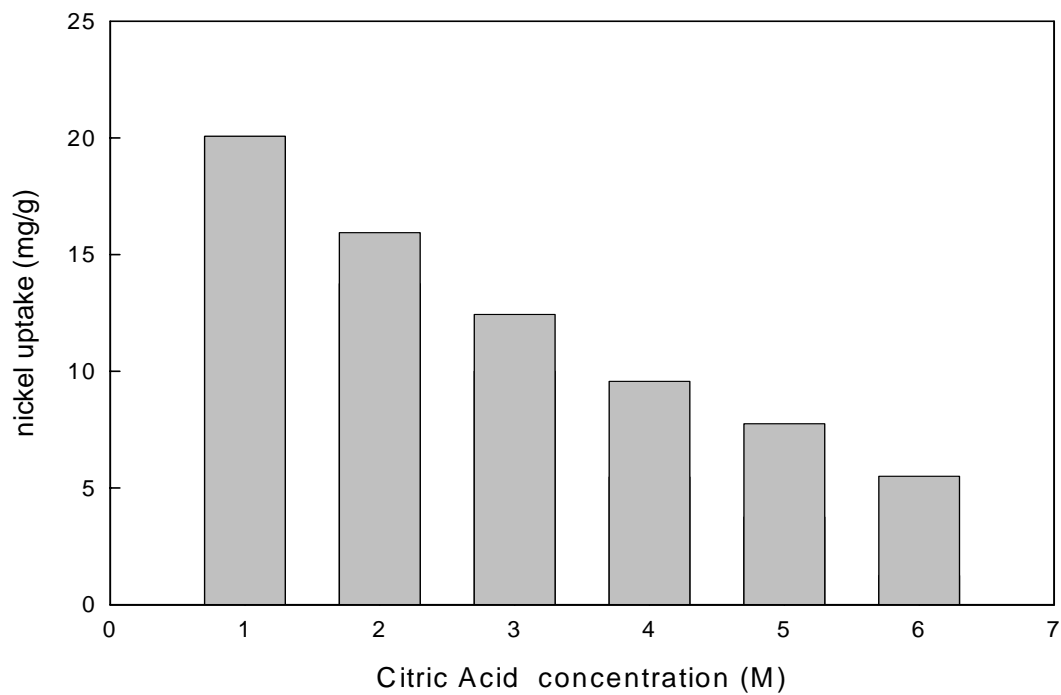


Fig. (8): Effect of blocking the carboxyl groups on the biosorption of nickel on palm tree leaves (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).



**Fig. (9):** Effect of EDTA on the biosorption of nickel on palm tree leaves (initial nickel ions concentration = 100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).



**Fig. 10.** Effect of citric acid on the biosorption of nickel on palm tree leaves (initial nickel ions concentration=100 ppm, pH = 6.0 and mass of palm tree leaves = 0.08 g).

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \quad (15)$$

The applicability of the above equation can be examined by plotting  $t/q_t$  vs.  $t$ . Figure 6 shows a plot of  $t/q_t$  vs.  $t$  for the biosorption of nickel on palm tree leaves.

The linearity of the plot indicates the applicability of the model. The values of  $q_e$  and  $k$  calculated from the slopes and the intercept of the straight line shown in Fig. 6, were 20.4 mg/g and 0.043 g/mg.s, respectively, with the value of  $R^2 = 0.999$ . The analysis of the correlation coefficients ( $R^2$ ) showed that the experimental data fit the pseudo-second-order model.

### Mass Transfer Models

#### Intraparticle Diffusion

Weber and Morris (1963) proposed a model to examine the contribution of intraparticle diffusion in the sorption process. According to this model, the initial rate of intraparticle diffusion can be calculated by linearization of the curve  $q=f(t^{0.5})$ .

$$q_t = k_d t^{0.5} ; \quad (16)$$

where  $q_t$  is the amount of adsorbed metal ions on the biomass at time  $t$  (mg/g);  $t$  is the time (s);  $k_d$  is the diffusion coefficient in the solid (mg/g.s<sup>1/2</sup>). Figure 7 is a plot of  $q_t$  versus  $t^{0.5}$  that confirms the validity of the linear relationship. The results can be represented by such a linear relationship, but they do not pass through the origin. This indicates that intraparticle diffusion is involved in the sorption process, but it is not the only rate-limiting mechanism and that some other mechanisms are involved. The contribution of this mechanism to the biosorption process can be further investigated by calculation of the diffusion coefficient in the solid;  $D_w$  (m<sup>2</sup>/s), which is related to  $k_d$  by the relation (Gardea-Torresdey et al., 1996):

$$k_d = \left( \frac{12q_e}{d_p} \right) \left( \frac{D_w}{\pi} \right)^{0.5} ; \quad (17)$$

where  $d_p$  is the particle size diameter (m). The diffusion coefficient in the solid;  $D_w$  was calculated and found to be  $1.95 \times 10^{-11}$  (m<sup>2</sup> /s). A comparison of the value of  $D_w$  coefficient with that of molecules in water ( $10^{-9}$  m<sup>2</sup> /s) indicates a poor intraparticle diffusion (Selatnia et al., 2004).

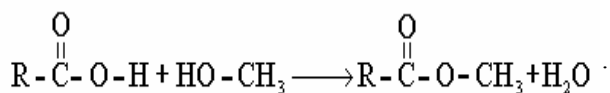
#### Ionic Exchange Mechanism

The contribution of ion-exchange mechanism to the biosorption of nickel ions on palm tree leaves was investigated in this work by following the release of Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> from palm tree leaves after the biosorption process. The amounts of the released cations were compared with those in a control sample, which consists of palm tree leaves and distilled water. The difference is due to the binding of Ni<sup>2+</sup> to palm tree leaves. The equivalent ratio ( $R_{b/r}$ ), defined as the ratio of metal bound to cations released, is next calculated. If this ratio is greater than unity, then the ion exchange mechanism is not the only mechanism in the adsorption process. Table 3 shows the amount of metal ions bound and the amount of cations released due to Ni<sup>2+</sup> binding along with the calculated  $R_{b/r}$ . As can be seen from this table, the amount of bound Ni<sup>2+</sup> is greater than the amount of cations released, which resulted in  $R_{b/r}$  values greater than one. This implies that ion exchange mechanism is not the only mechanism in the sorption process. Ion exchange mechanism can also be investigated using the DR model. According to this model, the range for  $E$  values in ion-exchange mechanisms is 8-16 kJ/mol. The value of  $E$  for the biosorption of nickel ions on palm tree leaves was found to be 14.1 kJ/mol. Thus, ion- exchange may contribute significantly in the biosorption of Ni<sup>2+</sup> on palm tree leaves.

#### Effect of Fisher Esterification

Table 1 shows that among the functional groups the surface of palm tree leaves, which may be responsible for the ion exchange and complexation, is the carboxyl group. The contribution of carboxyl groups to the

biosorption process was studied by blocking the carboxyl groups on the palm tree leaves. This was done using the method proposed by Gardea-Torresdey *et al.* (1996). According to this method, the carboxyl groups are chemically blocked by methanol esterification according to the following reaction:



If the interaction with carboxyl groups contributes to the binding of nickel ions on palm tree leaves, blocking of the carboxyl groups would cause a reduction in the nickel ions binding. Figure 8 shows the effect of esterification on the biosorption of  $\text{Ni}^{2+}$  on palm tree leaves. As can be noticed from this figure, blocking of carboxyl results in about 30% reduction in  $\text{Ni}^{2+}$  uptake. These results show that carboxylic groups palm tree leaves biomass plays an important role in the binding of nickel ions.

The previous results show that there is no single mechanism responsible for the biosorption of nickel ions on palm tree leaves, whereas ion-exchange, adsorption-complexation and intraparticle diffusion are involved in the biosorption process.

#### Effect of Ions Interference

The effects of the presence of other pollutants, such as ethylenediamine tetraacetic acid (EDTA) and citric acid, on the biosorption of nickel ions on palm tree leaves are

shown in Figures 9 and 10, respectively. These figures show that the presence of either EDTA or citric acid resulted in suppression in nickel uptake. Furthermore, the extent of suppression was also enhanced by increasing either the EDTA or citric acid concentration. The suppression of nickel ions uptake in competitive conditions is thought to be a response to increased competition between like charged species for binding sites of the palm tree leaves. This progressive suppression in biosorption by EDTA or citric acid indicates a degree of overlap in the biosorption site function at a higher equilibrium concentration.

### CONCLUSIONS

The biosorption of nickel ions on palm tree leaves was studied. It has been proved that this biosorbent has technologically acceptable sorption capacity towards the investigated metal ions. The biosorption of nickel ions by palm tree leaves was strongly affected by solution pH and nickel ions concentration. The biosorption of nickel on palm tree leaves has been found to follow the Langmuir, Freundlich, DR, Sips and Redlich-Peterson isotherm models. The effect of pH was analyzed using a Langmuir-type isotherm model. Dynamics studies revealed that the biosorption of nickel on palm tree leaves was found to follow pseudo-second order. Mechanistic studies have shown that ion-exchange, adsorption-complexation and intraparticle diffusion are involved in the biosorption process. The presence of either EDTA or citric acid was found to reduce nickel removal.

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