

## EQUILIBRIUM AND KINETIC STUDY OF ADSORPTION OF NICKEL FROM AQUEOUS SOLUTION ONTO BAEI TREE LEAF POWDER

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### Abstract

The ability of bael tree (BT) leaf powder to adsorb nickel,  $\text{Ni}^{2+}$ , from aqueous solutions has been investigated through batch experiments. The  $\text{Ni}^{2+}$  adsorption was found to be dependent on adsorbent dosage, initial concentration and contact time. All batch experiments were carried out at natural solution pH and at a constant temperature of  $30^\circ\text{C}$  using wrist-action shaker that operated at 120 rpm. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. The monolayer adsorption capacity is 1.527 mg Ni per g BT leaf powder. The experiments showed that highest removal rate was 60.21% for  $\text{Ni}^{2+}$  under optimal conditions. The kinetic processes of  $\text{Ni}^{2+}$  adsorption on BT leaf powder were described by applying pseudo-first-order and pseudo-second-order rate equations. The kinetic data for the adsorption process obeyed pseudo-second-order rate equations. The BT leaf powder investigated in this study exhibited a high potential for the removal of  $\text{Ni}^{2+}$  from aqueous solution.

Keywords: Nickel, Adsorbent, Adsorption isotherms, Batch adsorption, Removal.

### 1. Introduction

The progressive increase of industrial technology results in continuous increase of pollution, so that a great effort has been devoted for minimizing these hazardous pollutants and therefore, avoiding their dangerous effects on animals, plants and humans [1]. The presence of heavy metals in the aquatic environment has been of

**Nomenclatures**

$A$	Temkin constant, L/g
$B$	Temkin constant
$b$	Temkin constant
$C_e$	Equilibrium concentration of $\text{Ni}^{2+}$ solution, mg/L
$C_i$	Initial concentration of $\text{Ni}^{2+}$ solution, mg/L
$h$	Initial adsorption rate, $\text{mg g}^{-1}\text{min}^{-1}$
$K_f$	Freundlich constant, $(\text{mg/g})(\text{L/mg})^{(1/n)}$
$K_L$	Langmuir constant, L/mg
$k$	Rate constant of pseudo-second-order adsorption, $\text{g mg}^{-1}\text{min}^{-1}$
$k_{ad}$	Rate constant of the pseudo-first-order adsorption process, $\text{min}^{-1}$
$n$	Freundlich constant
$q_e$	Amount of nickel adsorbed per unit mass of adsorbent at equilibrium, mg/g
$q_m$	Langmuir constant, mg/g
$q_t$	Amount of nickel adsorbed per unit mass of adsorbent at time $t$ , mg/g
$R$	Gas constant, 8.314 J/mol/K
$T$	Temperature, K
$t$	Time, min
$V$	Volume of the adsorbent, L
$W$	Weight of the adsorbent, g
<i>Greek Symbols</i>	
$\Delta G^\circ$	Change in Gibbs free energy, kJ/mol
$\Delta H^\circ$	Change in Enthalpy, kJ/mol
$\Delta S^\circ$	Change in Entropy, kJ/mol/K

great concern to scientists and engineers because of their increased discharge, toxic nature and other adverse effects on receiving water [2]. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings [3, 4]. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [5].

Nickel salts are commonly used in metal plating and its concentration in industrial wastewater varies between 6 to 12 mg/L, which is above the safe limit (0.15 mg/L) [6]. The chronic toxicity of nickel to humans and the environment is well known and high nickel concentration causes gastrointestinal irritation and lung and bone cancers [7].

Several methods such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption have been proposed for treatment of wastewater contaminated with heavy metals [8]. Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques because of its capability of adsorbing a broad range of different

types of adsorbates efficiently and its simplicity of design [9]. However, commercially available activated carbons are still considered expensive [10]. As a result, many researchers have studied cheaper substitutes, which are relatively inexpensive and are at the same time endowed with reasonable adsorption capacity. These studies include the use of coal [11], fly ash [8, 12-14], activated clay [15], palm fruit bunch [16], rice husk [17], hazelnut shell [18], coconut shell [2, 19] and peat [20, 21].

The objective of this study was to evaluate the feasibility of using the bael tree (BT) leaf powder for the removal of nickel from aqueous solution. The influence of experimental parameter such as contact time, adsorbent dosage and initial Ni<sup>2+</sup> concentrations were studied. The adsorption process is studied from kinetic and isotherm standpoints.

## **2. Experimental**

### **2.1. Adsorbent**

The bael tree leaves were collected from Vaalmel Nandantha Amman Koil-Temple, Ilayangudi, Sivagangai District, Tamilnadu, India. It was gathered from twigs into clean plastic bags. Washed with triple distilled water and laid flat on clean table to dry. Dry leaves were grounded with grinder. After grounded, the leaf particles were sieved and stored into plastic bag by size, and ready to use.

### **2.2. Adsorbate**

Stock solution of nickel (100 mg/L) was prepared by dissolving NiSO<sub>4</sub>.6H<sub>2</sub>O (procured from Merck, India) in double distilled water. The concentration range of nickel prepared from stock solution varied between 10 to 50 mg/L. All the chemicals used were of analytical reagent grade.

### **2.3. Analysis**

The concentrations of nickel in the solutions before and after equilibrium were determined by Perkin-Elmer 3100 Atomic absorption spectrometer. The pH of solution was measured with a Hanna pH meter using a combined glass electrode. The shaking was carried out in a wrist action shaker.

### **2.4. Adsorption experiment**

Batch adsorption experiments were performed by contacting 2 g of the selected BT leaf powder with 100 ml of the aqueous solution of different initial concentrations (10 to 50 mg/L) at natural solution pH (6.2). The experiments were performed in wrist action shaker for a period of 1 hour at 120 rpm using 250 ml Erlenmeyer flasks containing 100 ml of different Ni<sup>2+</sup> concentrations at room temperature (30°C). Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm for better mass transfer with high interfacial area of contact. The remaining concentration of Ni<sup>2+</sup> in each

sample after adsorption at different time intervals was determined by atomic-absorption spectroscopy after filtering the adsorbent with Whatman filter paper No. 40 to make it adsorbent free. The  $\text{Ni}^{2+}$  concentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of  $\text{Ni}^{2+}$  solution respectively;  $V$  is the volume (L); and  $W$  is the mass (g) of the adsorbent.

The effect of adsorbent dosages (5-30 g/L) on the equilibrium adsorption of  $\text{Ni}^{2+}$  on the selected BT leaf powder was investigated by employing with initial concentration of 10 mg/L at room temperature (30°C). For these experiments, the flasks were shaken with natural solution pH (6.2) (natural solution means the actual solution in which it was prepared by dissolving the salts into the water) and agitation speed (120 rpm) for the minimum contact time required to attain equilibrium. The adsorption isotherm was found by agitating  $\text{Ni}^{2+}$  solution of different initial concentrations with the known amount of BT leaf powder till the equilibrium was achieved. The kinetics of adsorption was determined by analyzing adsorptive uptake of the  $\text{Ni}^{2+}$  from the aqueous solution at different time intervals.

### 3. Results and Discussion

#### 3.1. Effect of adsorbent dose

The effect of the adsorbent dose was studied at room temperature (30°C) by varying the sorbent amounts from 5 to 30 g/L. For all these runs, initial concentration of nickel was fixed as 10 mg/L. Figure 1 shows the adsorption of nickel increases rapidly with increase in the amount of BT leaf powder due to greater availability of the surface area at higher concentration of the adsorbent. The significant increase in uptake was observed when the dose was increased from 5 to 20 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [22]. From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on leaves is determined by the sorption capacity of the leaves. The maximum removal of nickel was obtained in the adsorbent dose of 20 g/L.

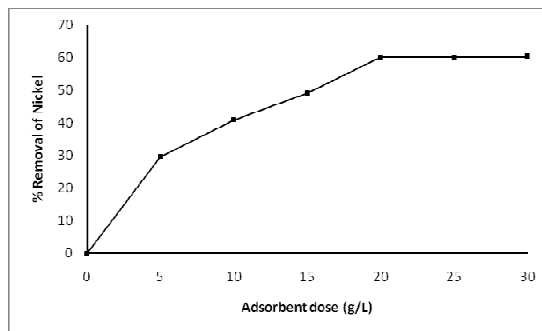


Fig. 1. Effect of Adsorbent Dose.

### 3.2. Effect of contact time

Adsorption of nickel was measured at given contact time for five different initial nickel concentrations from 10 to 50 mg/L. From Fig. 2, the plot reveals that the rate of percent nickel removal is higher at the beginning. This is probably due to larger surface area of the leaves being available at beginning for the adsorption of nickel ions. Most of the maximum percent nickel removal was attained after about 60 min of shaking time for different initial concentrations. The increasing contact time increased the nickel adsorption and it remains constant after equilibrium reached in 30 min for different initial concentrations.

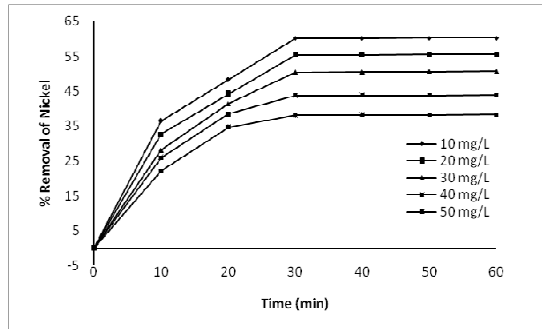


Fig. 2. Effect of Contact Time.

### 3.3. Effect of initial concentration

The effect of initial nickel concentration in the range of 10 to 50 mg/L on adsorption (investigated under the specified conditions; initial pH of 6.2; contact time of 30 min; adsorbent dosage of 20 g/L; and temperature of 30°C) is shown in Fig. 3. The amount of adsorbate in the solid phase with lower initial concentration of adsorbate was smaller than the amount when higher concentrations were used. It is seen that the removal of nickel was dependent on the concentration of nickel as the decrease in the initial concentration increased the amount of nickel removed. While the percentage nickel removal was found to be 60.21% for 10 mg/L of initial concentration, this value was 38.25% for that of 50 mg/L.

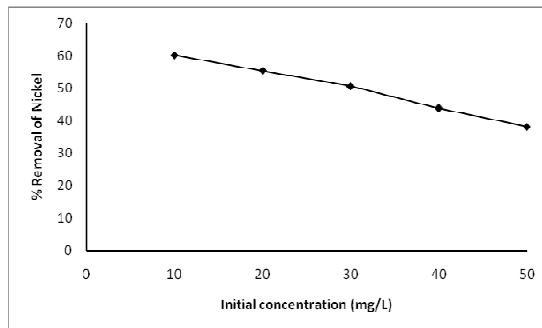


Fig. 3. Effect of Initial Concentration.  
(Initial pH of 6.2; Contact time of 30 min;  
Adsorbent dosage of 20 g/L; and Temperature of 30°C.)

### 3.4. Equilibrium study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate metal uptake per unit mass of adsorbent,  $q_e$ , to the equilibrium adsorbate concentration in the bulk fluid phase  $C_e$ .

#### 3.4.1. The Langmuir isotherm

The Langmuir model [23, 24] is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The constants in the Langmuir isotherm can be determined by plotting  $(1/q_e)$  versus  $(1/C_e)$  and making use of above equation rewritten as:

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

where  $q_m$  and  $K_L$  are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. It can be seen from Fig. 4 that the isotherm data fits the Langmuir equation well ( $R^2=0.998$ ). The values of  $q_m$  and  $K_L$  were determined from the figure and were found to be 1.527 mg/g and 0.0622 L/mg, respectively.

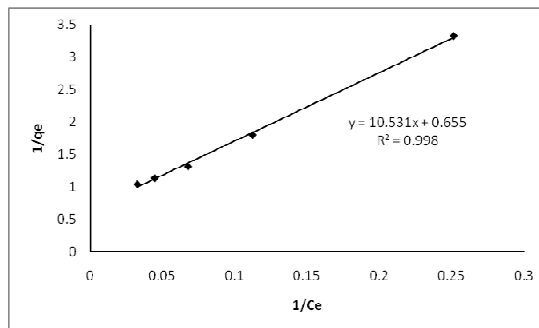


Fig. 4. Langmuir Adsorption Isotherm.

#### 3.4.2. The Freundlich isotherm

The Freundlich isotherm model [23, 25] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the

relationship between the amounts of nickel adsorbed per unit mass of adsorbent,  $q_e$ , and the concentration of the nickel at equilibrium,  $C_e$ .

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

The logarithmic form of the equation becomes,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where  $K_f$  and  $n$  are the Freundlich constants, the characteristics of the system.  $K_f$  and  $n$  are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of  $\log C_e$  vs.  $\log q_e$  was employed to generate the intercept value of  $K_f$  and the slope of  $n$ . From Fig. 5 the Freundlich constants  $K_f$  and  $n$  were found to be 0.1483 and 1.754 respectively. The magnitudes of  $K_f$  and  $n$  show easy separation of nickel ions from the aqueous solution and indicate favourable adsorption. The intercept  $K_f$  value is an indication of the adsorption capacity of the adsorbent; the slope  $1/n$  indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table 1,  $n$  value was found high enough for separation. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the correlation coefficient of 0.966.

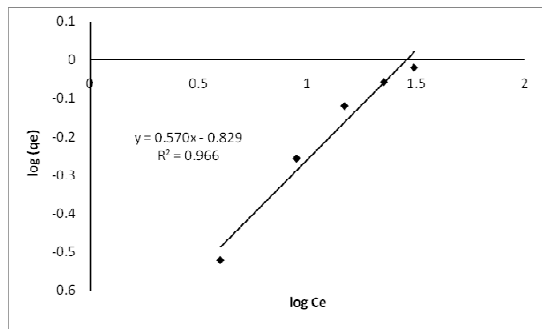


Fig. 5. Freundlich Adsorption Isotherm.

### 3.4.3. The Temkin isotherm

The Temkin isotherm [26] has been used in the following form:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (6)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (7)$$

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where  $B = \frac{RT}{b}$ ,  $R$  is gas constant (8.314 J/mol/K),  $T$  is Temperature (K)

The sorption data can be analyzed according to Eq. (8). Therefore a plot of  $q_e$  versus  $\ln C_e$  enables one to determine the constants  $A$  and  $B$ . The values of the Temkin constants  $A$  and  $B$  are listed in Table 1 and the plot of this isotherm is shown in Fig. 6. The correlation coefficient of 0.995 obtained showed that adsorption of  $\text{Ni}^{2+}$  also followed Temkin model.

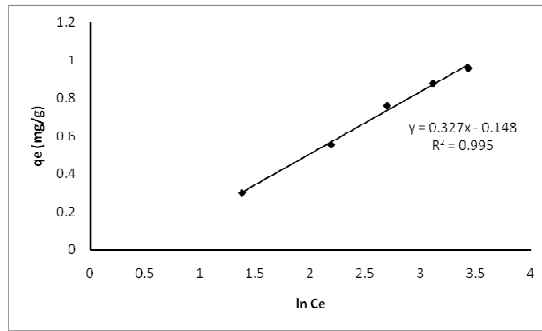


Fig. 6. Temkin Adsorption Isotherm.

The Langmuir, Freundlich and Temkin adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 1.

Table 1. Isotherm Models Constants and Correlation Coefficients for Adsorption of Nickel from Aqueous Solution.

Adsorbent	Langmuir isotherm		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$
BT leaf powder	1.527	0.0622	0.998

Adsorbent	Freundlich isotherm			Temkin		
	$K_f$	$n$	$R^2$	$A$ (L/g)	$B$	$R^2$
BT leaf powder	0.1483	1.754	0.966	0.636	0.327	0.995

It has been reported that  $\Delta G^\circ$  up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while  $\Delta G^\circ$  values more negative than -40 kJ/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) [27]. The  $\Delta G^\circ$  values obtained in this study for the  $\text{Ni}^{2+}$  ions are < -10 kJ/mol, which indicates that physical adsorption was the predominant mechanism



in the sorption process [28]. The other thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  could not be evaluated because the temperature does not vary in this work.

#### 4. Kinetic Study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of nickel adsorption onto BT leaf powder. The pseudo-first-order rate equation is given as [29]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (9)$$

where  $q_t$  and  $q_e$  are the amount adsorbed (mg/g) at time,  $t$ , and at equilibrium respectively and  $k_{ad}$  is the rate constant of the pseudo-first-order adsorption process ( $\text{min}^{-1}$ ). Straight line plots of  $\log(q_e - q_t)$  against were used to determine the rate constant,  $k_{ad}$ , and correlation coefficients,  $R^2$ , for different nickel concentrations, as shown in Fig. 7. With the coefficient of 0.930 (for 25 mg/L) and 0.909 (for 50 mg/L), it was seen that adsorption of  $\text{Ni}^{2+}$  on BT leaf powder did not follow pseudo first-order kinetics compare with the correlation coefficient of pseudo second-order kinetics.

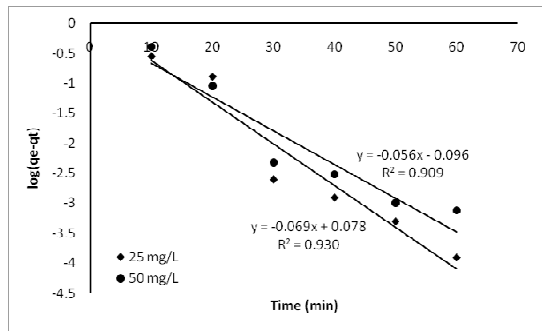


Fig. 7. Pseudo-first-order Reaction for  $\text{Ni}^{2+}$  Ions Adsorbed onto BT Leaf Powder at Different Concentrations.

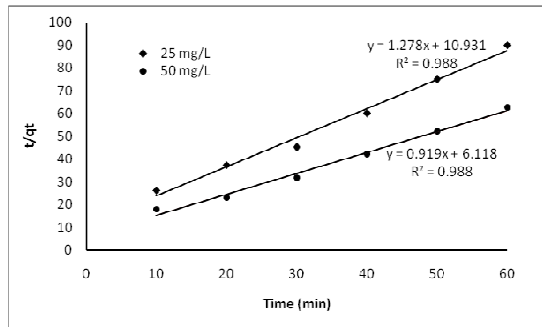
The pseudo-second-order equation is expressed as [30]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (10)$$

where  $h = kq_e^2$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) can be regarded as the initial adsorption rate as  $t \rightarrow 0$  and  $k$  is the rate constant of pseudo-second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The plot  $t/q_t$  versus  $t$  should give a straight line if pseudo-second-order kinetics is applicable and  $q_e$ ,  $k$  and  $h$  can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo-second-order reaction at different  $\text{Ni}^{2+}$  concentrations by BT leaf powder are

shown in Fig. 8. The pseudo-first-order and pseudo-second-order rate constants determined from Figs. 7 and 8 are presented in Table 2 along with the corresponding correlation coefficients.



**Fig. 8. Pseudo-second-order Reaction for Ni<sup>2+</sup> Ions Adsorbed onto BT Leaf Powder at Different Concentrations.**

**Table 2. Comparison between the Adsorption Rate Constants,  $q_e$ , Estimated and Correlation Coefficients Associated with Pseudo-first-order and to the Pseudo-second-order Rate Equations.**

Initial Ni <sup>2+</sup> Concn. (mg/L)	Pseudo-first-order rate equation		
	$k_{ad}$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$
25	0.1589	1.197	0.930
50	0.1290	0.8017	0.909

Initial Ni <sup>2+</sup> Concn. (mg/L)	Pseudo-second-order rate equation				
	$k$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$q_{e,exp}$ (mg/g)
25	0.1495	0.7824	0.988	0.0915	0.6665
50	0.1381	1.088	0.988	0.1635	0.9566

The plot of  $t/q_t$  versus  $t$  for pseudo-second-order model (Fig. 8) yields very good straight lines (correlation coefficient,  $R^2 > 0.98$ ) as compared to the plot of pseudo-first order. The pseudo-second-order rate constants were in the range of 0.1381 to 0.1495 g mg<sup>-1</sup> min<sup>-1</sup>. The theoretical values of  $q_e$  also agree very well with the experimental ones. Both facts suggest that the adsorption of Ni<sup>2+</sup> ions by BT leaf powder follows the pseudo-second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. In chemisorption (chemical adsorption), the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [31].

The pseudo-second-order kinetic analysis reveals that the values of the initial adsorption rates,  $h$ , increases with increase in the initial nickel concentration. The lower the concentration of metal ions in the solution, the lower the probability of collisions between these species is and hence the faster nickel ions could be bonded to the active sites on the surface of the adsorbent [32]. The equilibrium adsorption capacity,  $q_e$ , however increased with increase in initial nickel concentration due to large number of nickel ions are adsorbed at the available adsorption sites. Based on the values of  $R^2$  obtained from the plots of pseudo-first-order and pseudo-second-order rate equations, it is obvious that with increasing initial concentration of the adsorbate, the correlation of experimental data to the pseudo-second order kinetics model increases while that to the pseudo-first order model decreases. This finding from this study is in complete agreement with the kinetics model developed by Azizian [33].

## 5. Conclusions

The present investigation shows that BT leaf powder is an effective adsorbent for the removal of  $\text{Ni}^{2+}$  from aqueous solutions. From the kinetic studies, it is observed that adsorption of  $\text{Ni}^{2+}$  is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial  $\text{Ni}^{2+}$  concentration. The percentage removal of  $\text{Ni}^{2+}$  increases with the increase in adsorbent dosage and decreases with increase in initial  $\text{Ni}^{2+}$  concentration. Experimental results are in good agreement with Langmuir, Freundlich and Temkin adsorption isotherm models, and have shown a good fitting to the experimental data. Adsorption of  $\text{Ni}^{2+}$  obeys pseudo-second order equation with good correlation.

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