



## NICKEL IONS REMOVAL FROM AQUEOUS SOLUTIONS USING SAWDUST AS ADSORBENT: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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**Abstract:** This work is concentrate on removal of some environmentally relevant contaminants, such as nickel ions from simulated wastewater by sawdust low- cost natural sorbents. Sorption batch tests were investigated in the removal process at initial concentration of nickel ions (100 mg/l). Equilibrium, kinetics and thermodynamic studies were investigated for the removal process. Parameters affect as pH, amount of sawdust, contact time and temperature were studied. The uptake capacity was 12.5 mg/g; also FTIR demonstrated that carboxyl and hydroxyl groups were involved in the adsorption of the metal ions. The results indicated that adsorption is an endothermic process and rate of removal increased with increase temperature.

**Keywords:** Ni (II) ions; sawdust; Equilibrium; kinetics; thermodynamic.

### إزالة أيونات النيكل من المحاليل المائية باستخدام نشارة الخشب كوسط ماز: دراسة الأتزان، الديناميكية الحركية والثرموداينمك

**الخلاصة:** ان الهدف من هذا العمل هو التركيز على ازالة بعض الملوثات البيئية (أيونات النيكل) من مياه ملوثة مُصنعة باستخدام ممتازات واطئة الكلفة وطبيعية (نشارة الخشب). أجريت تجارب الباج (الدفعة) لازالة تركيز 100 ملغم/لتر من ايونات النيكل. تمت دراسة العوامل المختلفة على عملية الأمتزاز مثل قيمة الدالة الحامضية ، كمية القشور المستعملة، زمن التماس و درجة الحرارة. نتائج فحص التحليل الكيفي اظهر المجموعات الفعالة للمركبات العضوية مثل المجموعات الكربوكسيلية والهيدروكسيل. و كانت سعة الامتزاز 12.5 ملغم/غم، وكانت نسبة الأزالة تزداد بزيادة الحرارة و ذات طابع ماص للحرارة وفقا لنتائج الحرارية.

## 1. Introduction

Environmental contaminated is now one of the fundamental issues going up against humankind. Water contamination considered as the main all inclusive reason for 80 % of illnesses [1]. As per the United Nations association reports there are 1.1 billion individuals still don't have entry to safe supply of drinking water; the larger part of them are among the world's poorest and creating nations [2, 3].

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Heavy metals are without uncertainty well thoroughly considered as the most unsafe and destructive metals regardless of the possibility that they present as follows, since they aggregate in the tissue of living beings [4]. Nickel is a shiny white, hard, flexible and malleable metal. It is a far reaching appropriation in the earth, it has a nuclear number of 28 and the maximum contaminant limit (MCL) is 0.2 mg/L. Drinking water by and large contains nickel at concentration under 10 mg/l. Accepting a day by day admission of 1.5 liter of water and a level of 5 to 10 mg nickel/liter, the mean day by day admission of the nickel from water for grown-ups would be between 7.5 to 15 mg. Nickel is utilized as a part of different structures for nickel plating, as an impetus, as a stringent and in fired coatings and so on [5, 6].

Nickel and Nickel compounds back to exemplary harmful specialists experienced in industry additionally known not non-occupationally uncovered people. Inward breath introduction in word related zone is an essential course for nickel incited danger and may bring about lethal impacts in the respiratory tract and safe framework [6].

Many techniques have been examined to remove heavy metal ions from industrial effluents involve ion-exchange, chemical-precipitation, electrode-dialysis, membrane-filtration, reverse-osmosis, ultra-filtration, coagulation, floatation and adsorption. All these methods have some advantages and disadvantages; biosorption has been utilization due to its ease. It is a property of both living and dead organisms (and their components) which can be characterized as the removal of substances from solution by organic materials [7]. Biosorption depicts any system incorporates a sorbate (an atom, molecule, a molecular ion) cooperate with a biosorbent (a solid surface of a biological matrix) causing in a gathering at the sorbate–biosorbent interface, and led to a decrease of sorbent concentration in the solution [8].

Activated carbon is known as an adsorbent utilized to remove the metals yet the high cost of activated carbon hinders its widely use as an adsorbent. For this problem, Many researchers have been carried out for using the low cost adsorbent that are resulted from various wastes and by-products such as rice-husk-ash, coconut-husk, Neem-bark, pellets of peanut-hull, tea-wastes, sugarcane-Bagasse, cow-bone charcoal, tamarind fruit-shell, sawdust, etc.[3]. This study shows the possibility of utilizing sawdust as a low-cost adsorbent to remove nickel form wastewater.

## 2. Materials and method

Sawdust has been broadly studied to remove metal ions from waste water. A research group has investigated an expensive study on treated and untreated saw dust and the initial adsorption was seen to be quick [7].

The sawdust was gathered from the nearby Carpentry market; washed with refined water to remove surface impurities and dried at 105 C<sup>o</sup> for 24 hr, powdered to pass through a sieve of size 0.6mm size.

Simulated wastewater of nickel (100 mg/l) was prepared by dissolved  $N_2NiO_6.6H_2O$  in distilled water; the required concentration of metal was calculated by Eq. (1) [9].

$$W = V \times C_i \times \frac{M.wt}{At.wt} \quad (1)$$

Where:

W: Weight of heavy metal salt (mg)

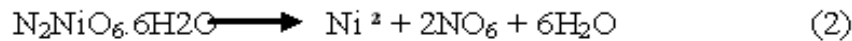
V: Volume of solution (1L)

C<sub>i</sub>: Initial concentration of metal ions in solution (mg/L)

M.wt: Molecular weight of metal salt (g/mole)

At.wt: Atomic weight of metal ion (g/mole)

Nickel nitrate has a molecular weight (M.wt) = 290.81 g/mole. The molecular weight of Ni is 58.81 g/mole. To achieve a concentration in distilled water of 100 mg/L of Nickel cations (Ni<sup>2+</sup>) the following equations were used [9]:



$$W = 1(L) \times 100 (mg) \times \frac{290.81 (g/mole)}{58.81 (g/mole)} = 4.9449 \text{ mg } N_2NiO_6 \cdot 6H_2O$$

pH of solution was adjusted by adding 0.1 M HNO<sub>3</sub> or 0.1 M NaOH. The concentration of nickel was measured by Atomic Absorption spectrophotometer (AAS) (GBC 933 plus, Australia).

### 2.1. Batch adsorption study

Batch experiments were carried out at various pH (2-8), adsorbent amount range (0.2-2.5g/L) and mixing speed (200 rpm) for a contact time of 60 min. for each experiment, 100 ml of 100 mg/l metal ions solution was used.

After adjust pH and adding desired amount of adsorbent the mixture was mixed on mechanical shaker for 60 min.; after the mixture was filtered to separate the adsorbent from supernatant. The residual concentration of ions was measured by AAS. The removal percentage (R %) of nickel was calculated by the following expression [9]:

$$R\% = \frac{C_i - C_f}{C_i} \times 100 \quad (3)$$

Where:

C<sub>i</sub> = initial concentration of the metal (mg/L).

C<sub>f</sub> = final concentration of the metal (mg/L).

### 3. Results and discussion

#### 3.1. Fourier Transform Infrared Spectroscopy (FT-IR)

Fig. 1 shows the changes in the functional groups of the sawdust after adsorption by FTIR spectra. The spectra of unloaded and nickel loaded adsorbent were measured in the range of  $4000\text{-}400\text{cm}^{-1}$  wave number. The FTIR spectrum reveals complex nature of the adsorbents as evidenced by the presence of a large number of peaks. Table 1 presents infrared adsorption wavelength of each peak and corresponding functional groups of the adsorbent before and after use.

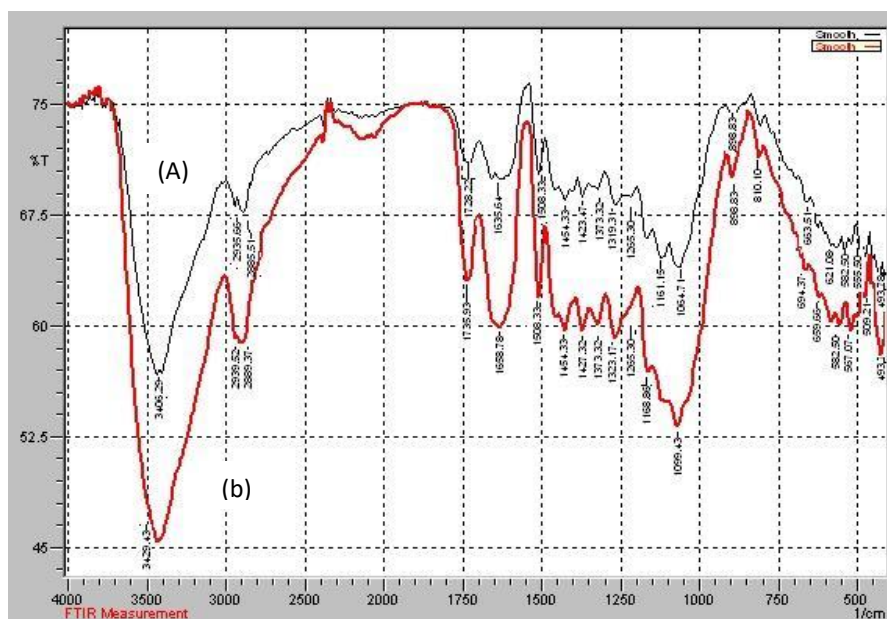


Figure 1: FTIR spectrum of sawdust (a), sawdust- $\text{Ni}^{+2}$  (b)

Table 1. Functional groups in control of control of nickel sorption by sawdust

Wave number ( $\text{cm}^{-1}$ )	Functional groups	After adsorption of nickel ( $\text{cm}^{-1}$ )
3406.29	Carboxylic acid, Amides, Alcohols, Amines	3429.43
2935.66	Alkanes, Carboxylic acid	2939.52
2885.51	Alkanes, Carboxylic acid	2889.37
1728.22	Alkanes, Carboxylic acid	1735.93
1635.64	Alkanes	1658.78
1423.47	Carboxylic acid	1427.32
1319.31	Carboxylic acid	1323.17
1161.15	Carboxylic acid	1168.86
1064.71	Alcohols, Carboxylic acid	1099.43
663.51	Alkyl halides	694.37
621.08	Alkyl halides	659.66
555.50	Alkyl halides	567.07

### 3.2 Effect of pH

In order to evaluate the effect of pH on the adsorption process, the batch studies at pH range of 2.0-8.0. From results (Fig.2) it is found that the optimum pH was at 6.0, pH of the solution play a very important role in the metal uptake.

Both adsorbent surface metal binding sites as well as metal chemistry in solution are influenced by solution pH. At low pH values, metal cations and protons compete for binding sites on adsorbent surface which results in lower uptake of metal.

It has been suggested that at highly acidic condition, adsorbent surface ligands would be closely associated with  $H_3O^+$  that restricts access to ligands by metal ions as a result of repulsive forces. It is to be expected that with increase in pH values, more and more ligands having negative charge would be exposed which result in increase in attraction of positively charged metal ions. In addition at higher pH the lower binding is attributed to reduced solubility of the metal and its precipitation [10].

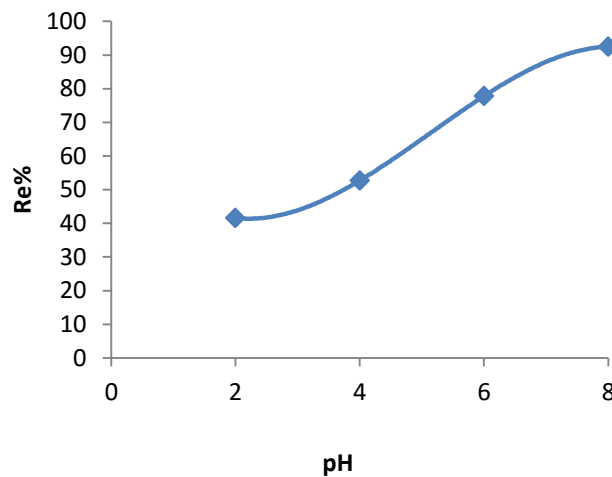


Figure 2. Effect of pH on removal of Ni (II) ions (conc. = 100 mg/L; adsorbent dose = 0.5 g/100 ml; contact time = 60 min; stirring speed =200 rpm; temp = 25°C)

### 3.3 Effect of sawdust amount

The amount of sawdust (adsorbent) was studied in the range of 0.2-2.5 g/ 100 ml. Fig. 3 appears the effect of different amount of adsorbent on removal efficiency. The maximum removal of Ni (II) was 94.6% at 1.75 g/100 ml of adsorbents amount.

The phenomenon of increase in percentage removal of Ni (II) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface becomes available for metal ion to adsorb and this increase the rate of adsorption [10].

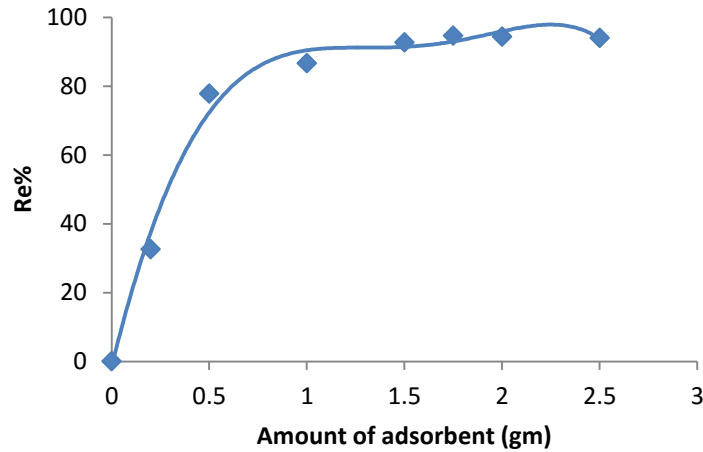


Figure 3. Effect of sawdust amount on removal of Ni (II) ions (conc. = 100 mg/L; pH= 6.0; contact time = 60 min; stirring speed =200 rpm; temp = 25°C).

### 3.4 Effect of contact time

It has been observed from Fig.4 that rate of removal efficiency of Ni (II) ions was increased from 42.52% to 94.6% with increased time from 30 to 180 min. Maximum removal was occurred at 120 min (equilibrium). It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later because of exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [11].

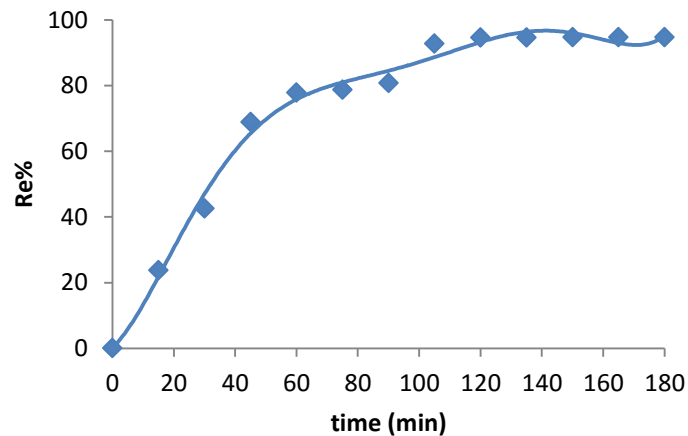


Figure 4. Effect of contact time on removal of Ni (II) ions (conc. = 100 mg/L; pH= 6.0; amount of sawdust = 1.75g/100ml; stirring speed =200 rpm; temp = 25°C)

### 3.5 Effect of temperature

The effect of vary temperature (15, 25, 35, and 45 °C) and the thermodynamic parameters such as ( $\Delta H^{\circ}$ ), ( $\Delta S^{\circ}$ ), ( $\Delta G^{\circ}$ ) are necessary to estimate whether the reaction

of adsorption is endothermic or exothermic. The thermodynamic parameters were calculated from Eqs. (4) and (5) [12]:

$$\ln K_d = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right) \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \quad (5)$$

Where  $K_d$  is the distribution coefficient;  $\Delta H$  (J/mol),  $\Delta S$  (J/mol K), and  $T$  the enthalpy, entropy, and temperature in Kelvin, respectively;  $R$  is the gas constant (8.314 J/mol K) and Gibbs free energy change  $\Delta G^\circ$ . From the results in Fig.5 and Tables (2, 3); it is showed that the adsorption is normally endothermic, thus capacity of adsorption for Ni (II) ions increase at increase in temperature. The maximum rate of removal was reached at 45°C which was 97.5%.

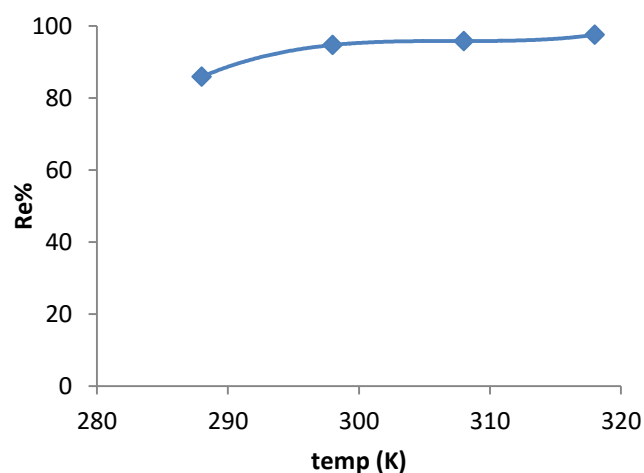


Figure 5. Effect of temperature on removal of Ni (II) ions (conc. = 100 mg/L; pH= 6.0; amount of sawdust = 1.75g/100ml; stirring speed =200 rpm)

Table 2, The distribution coefficients at different temperature

Metal	$k_d$				$R^2$
	288 k	298 k	308 k	318 k	
Nickel (II)	6.0771	17.8680	22.80952	39.000	0.936

Table.3, The thermodynamic parameters for the adsorption of Ni(II) ions on sawdust adsorbent.

Metal	$\Delta H(J/mol)$	$\Delta S(J/mol K)$	$\Delta G (kJ/mol)$			
			288 k	298 k	308 k	318 k
Nickel (II)	1.44664	-31.6350	9.1123	9.4286	9.7450	10.0613

The results indicated that the  $\Delta G^\circ$  values are positive and increased in their absolute values with temperature. This result suggested that a high temperature is favored for the adsorption of nickel ions on sawdust, displayed a spontaneous adsorption process.

The values of heat of adsorption,  $\Delta H$  is positive for metals ion, showed that the adsorption process of heavy metals on banana peel was endothermic; negative  $\Delta S$  suggested that the adsorption was enthalpy driven and spontaneous in nature [13].

### 3.6 Adsorption isotherms

Two models have been used in this study; namely Langmuir and Freundlich models. These isotherms represented the amount of solute adsorbed at equilibrium per unit weight of adsorbent,  $x/m$  (mg/g), to the adsorbate concentration at equilibrium,  $C_e$  (mg/L).

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented in Eq. (6) [10]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (6)$$

Where:  $q_e$  is the sorbed metal ions on the biomass (mg/g),  $q_m$  is the maximum sorption capacity for monolayer coverage (mg/g),  $b$  is the constant related to the affinity of the binding site (L/mg), and  $C_e$  is metal ions concentration in the solution at equilibrium (mg/L). Constant for the adsorbate-adsorbent equilibrium and the capacity of monolayer  $b$  and  $q_e$  were identified from the slope and intercept of the Langmuir plot (Figure 6).

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linear Freundlich model isotherm was applied for the adsorption of nickel and is expressed as [10]:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (7)$$

Where:  $K$  is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g).  $1/n$  is the constant indicative of the intensity of the adsorption. Both  $K$  and  $n$  being an indication of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively.

The linear Freundlich plots are obtained by plotting  $\log q_e$  versus  $\log C_e$  from which the adsorption coefficients could be estimated (Figure7). All constants identified from Langmuir and Freundlich isotherms are given in Table 4.



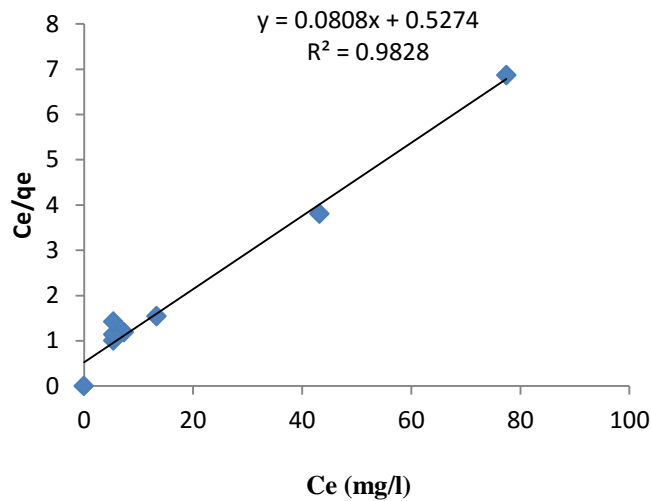


Figure 6. Langmuir plot of Ni (II) adsorption on sawdust (pH 6; rpm 200)

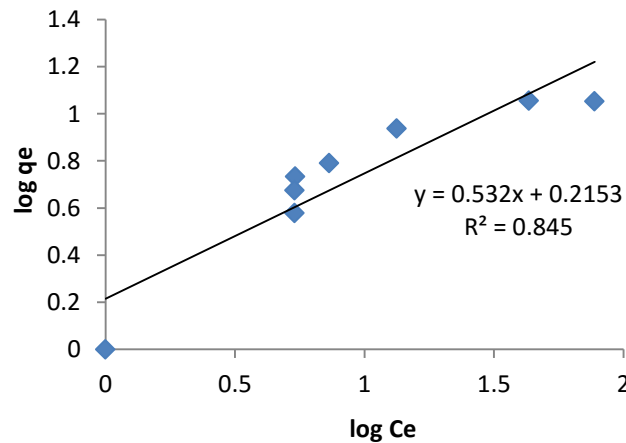


Figure 7. Freundlich plot of Ni (II) adsorption on sawdust (pH 6; rpm 200)

Table.4, Parameters of the Langmuir, Freundlich isotherms for the adsorption of Ni (II) onto sawdust.

Langmuir model	Ni (II)	Freundlich model	Ni (II)
$R^2$	0.982	$R^2$	0.845
$q_m$ (mg/g)	12.5	$1/n$	0.532
$b$ (1/mg)	0.152	$K$ (mg/g)(1/mg) $^{1/n}$	1.6410

From above Table 4, it is clear that the best model used to estimate the removal process was Langmuir model according to the correlation coefficient ( $R^2$ ).

### 3.7 Kinetic adsorption models

The investigation of adsorption kinetics estimate the uptake rate of heavy metal ions, and obviously this rate controls the occupant time of these ions at the solid liquid interface. Hence it is imperative to evaluate the time dependency of such systems for different pollutant removal processes. Thus, the required contact time for the adsorption

to be completed is essential to give knowledge into a sorption process. This also gives data on the base time required for impressive adsorption to happen and the possible diffusion control mechanism between the adsorbed ion as it moves from the bulk solution towards the adsorbent surface [6]. At the starting stage of the process of adsorption, the removal rate of ions is higher. The faster starting rate might be because of the accessibility of the uncovered surface area of the adsorbent at first. The adsorption kinetics relies upon; (i) the surface area of the adsorbent, (ii) the nature and concentration of the surface groups (active sites), which are in charge of interacting with targeted ions. The kinetics models include: the pseudo-first order and pseudo-second order [6]; Eq. (8) and (9); respectively.

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \right) \quad (9)$$

Where  $q_{eq}$  is the amount of metal sorbed at equilibrium (mg/g);  $q_t$  is the amount of metal sorbed at time  $t$  (mg/g); and  $k_1$  is the rate constant of the first-order adsorption (1/min) and  $k_2$  is the pseudo-second order rate constant (g/mg h). The slopes and intercept of  $\ln(q_e - q_t)$  versus  $t$  plot (Fig.8a) were used to describe the pseudo first order rate constants ( $k_1$ ) and  $q_e$ . A plot of  $t/q_t$  versus  $t$  (Fig.8b) was used to describe the pseudo-second-order rate.

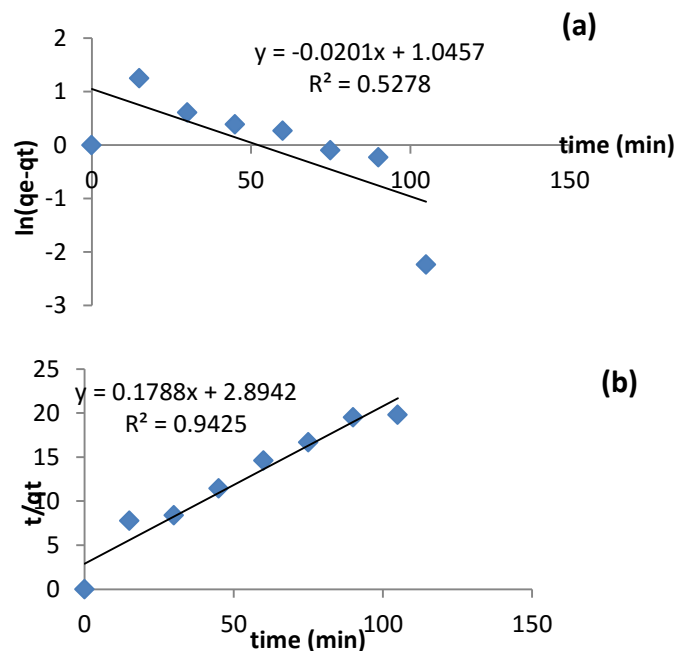


Figure 8. kinetic models plot of Ni (II) adsorption on sawdust: (a) pseudo- first- order model; (b) pseudo-second- order model

The values of correlation coefficient ( $R^2$ ) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of

$q_e$  calculated from the second order kinetic model compatibility well with the experimental values. Results showed in Table 5.

Table.5, Comparison of adsorption rate constants, experimental and calculated  $q_e$  values for the pseudo-first- and –second-order reaction kinetics for component systems.

Metal	$q_e$ experimental (mg/g)	pseudo first order			pseudo second order		
		$K_1$ 1/min	$q_e$ calculated (mg/g)	$R^2$	$K_2$ g/mg.min	$q_e$ calculated (mg/g)	$R^2$
Ni (II)	5.41	-0.02	2.8434	0.527	10.910	5.62	0.942

#### 4. Conclusions

Overview of this search clarifies that possibility of replacement of expensive adsorbents by low cost, and available waste by-products as adsorbents such as sawdust. Results evidently appear that the sawdust is effective for the removal of Ni (II) ions (Re% =94.6%). Optimum pH was found to be pH 6.0. Equilibrium adsorption data suitable fit with Langmuir isotherm. Equilibrium was at 120 min and adsorption process followed pseudo- second- order kinetic model.

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