

## Efficiency of Seed oil (Pentaclethramacrophylla) Shell in Removal of Nickel (II) ion Aqueous solution

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**Abstract:** An Abundance agricultural waste Pentaclethramacrophylla shells in rural areas of Eastern, Southern and Northern part of Nigeria; studied for the removal of nickel (II) ion in aqueous solution in a batch system by Atomic Absorption spectrophotometer (mechanic Perkin Elmer analyst 2000). The influence of pH, initial ion concentration, adsorbent dosage and contact time was studied at 30<sup>o</sup> C. sorption increased with increasing dosage, initial ion concentration and optimum plateau sorption of 97.83% reached at pH 7.5 within 60min. Mathematical models describing kinetic and equilibrium of sorption were proposed; kinetic sorption data fitted well to the Ho pseudo-second-order model with correlation coefficient of  $R^2 = 1$  and was found that adsorption of Ni (II) ion onto PMS correlated well ( $R^2 = 0.9797$ ) with the Freundlich isotherm model compared to Langmuir isotherm model under the same varied initial Ni (II) ion concentration studied. Furthermore, practical implication of this research work is the development of efficient, economical and sustainable environment technology for Ni<sup>2+</sup> removal from contaminated water, which is especially useful when Pentaclethramacrophylla shells is locally available "waste to health to wealth".

**Key words:** Adsorption, efficiency, isotherm, Pentaclethramacrophylla shell (PMS).

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### I. Introduction

Nature treats water in its own way through the hydrologic cycle, though we still need to treat the water before use due to all the pollution in the environment, likewise water bodies are major sites of heavy metal deposits due to the fact that streams and rivers flows through agricultural areas where pesticides and fungicides may have been used, through industrial districts where there may have been many metal deposits and direct discharges of effluents into these water bodies [1].

Metal find many useful applications in our daily life, increased industrialization and various domestic activities have contributed largely toward introduction of heavy metals into the aquatic medium, as well as into the terrestrial environment.

Heavy metals are considered to be particularly dangerous pollutants. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low concentrations [2,3,4].

Moreover, the presence of nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis [5].

Live and dead biomaterials have been proved possible solution in remediating heavy metal contaminated aquatic environment, mainly caused through the industrial discharges, metal smelting, agricultural and other anthropogenic activities that involves heavy metals.

Heavy metal pollution of aquatic medium has been a major concern in recent years due to their non-biodegradability and toxicity. Most of the heavy metal salt are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical separation methods [6].

The remediation and removal of heavy metals from aqueous media has received considerable attention in recent years, however convectional (electrochemical treatment, chemical precipitation, ion exchange, electro dialysis, reverse osmosis etc.) methods have been found to be sometimes restricted, because of expensive investment, operational costs, potential generation of secondary pollution, and its disposal is not eco-friendly [7].

Furthermore, available low cost and high efficiency of some waste agricultural materials in removal of heavy metals have been reported; such as: sawdust of spruce [8], maize and husk [9], fluted pumpkin seed shell [10], maize leaf [11], coconut husk [12], melon seed husk [13], black gram husk [14] and so on.

Available in abundance of Pentaclethramacrophylla shells as agricultural waste material in rural areas of Eastern, Southern and Northern part of Nigeria made it easy in this research as biosorbent for the removal of Ni(II) ion solution. This study investigated the effect P<sup>H</sup> of solution, contact time, adsorbent dosage and initial metal concentration; meanwhile the metal sorption was assessed based on the Langmuir and Freundlich adsorption isotherm model at 30<sup>o</sup>C.

**Symbols and abbreviations:**

PMS	Pentaclethramacrophylla shell			
SOS	seed oil shell			
C <sub>o</sub>	initial metal ion concentration			
C <sub>a</sub>	concentration of metals ions adsorbed (mg/L)			
q <sub>e</sub>	metal uptake in mg/g equilibrium			
q <sub>t</sub>	metal uptake in mg/g at time t			
C <sub>e</sub>	metal ion concentration in solution at equilibrium			
q <sub>max</sub>	maximum adsorption capacity (mg/g)			
R <sup>2</sup>	regression correlation coefficient			
t	time (min)			
V	volume of the solution in ml			
K <sub>L</sub>	separation factor			
b	Langmuir constant (L/mg)			
n	Freundlich constants, intensity of adsorption (mg/g)/(mg/L) <sup>1/n</sup>			
K <sub>f</sub>	empirical constant that provides an indication of the adsorption capacity biosorbent,			
K <sub>1</sub>	pseudo-first order rate constant (min <sup>-1</sup> )			
K <sub>2</sub>	pseudo-second	order	rate	constant (mg/g/min)

**II. Materials And Methods**

**2.1 Biomass**

Samples of Pentaclethramacrophylla shells were collected from local seed oil food spice production site, in Oke-Odan, Yewa South local government area of Ogun State, Nigeria. Where hugely generated as primary agricultural waste, Seed Oil shells were extensively washed with distilled water to removed dirt and other extraneous matter that might interact with sorbed metal ion and grounded into powdery form, using pre-cleaned local mortar and pestle and sieved with a mesh to maximum particle size of 2mm the unformed material produced was stored in air-tight moisture free plastic containers and subsequently used for biosorption studies.

**2.2 Chemical reagents and adsorbate**

Analytical grade Nickel nitrate salt was used for the stock solutions (1000mg/l), 1.4285g of Ni(NO<sub>3</sub>)<sub>2</sub> was accurately weighed and dissolved in little distilled water inside a beaker. The solution was quantitatively transferred into 1litre volumetric flask and made up to the mark with distilled water and the solutions for all experiments were prepared through dilution of stock solution.

**2.3 Sorption Studies**

The batch adsorption experiments were conducted with powered Pentaclethramacrophylla shell at 30<sup>o</sup>C. The effect of pH on the adsorption capacity was investigated at pH values of 3,4,5,7,8 and 9 using known volume of 100mg/L Ni(II) solutions, the P<sup>H</sup> of solution was adjusted to a set of value by adding 0.1M HNO<sub>3</sub> and 0.1M NaOH. 1g sorbent was added to 25ml of desired pH and gently agitated on mechanical shaker for 1 hour. The effect contact time was of studied in the time range 60-180min at the optimum pH value 7.5. Effects of dosages (ranges 0.4g -2.0g) were also determined.

Similarly above, metal concentrations were also investigated in the range of 100mg/l-500mg/l. At the end of adsorption process, the suspensions were filtered and metal ion concentration of filtrate was determined using Atomic Absorption spectrophotometer, mechanic Perkin Elmer analyst (2000) and adsorption capacity was determined by mass balance calculation

$$Q = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where, Q is adsorption capacity (mg/g), C<sub>o</sub> and C<sub>e</sub> initial equilibrated concentration of metal ions (mg/l) respectively, V is volume of added solution(l) and W is the weight of dry powered Pentaclethramacrophylla shell

The Ni(II) ions removed percentage can be calculated as:

$$\text{Removal \%} = \left( \frac{C_o - C_t}{C_o} \right) \times 100 \tag{2}$$

Where C<sub>t</sub> (mg/l) is liquid- phase concentration of Ni(II) ion at time t.

**III. Results And Discussion**

**3.1 Effect of pH on adsorption**

The pH of aqueous solutions is an important controlling parameter in the adsorption process because it affects the solubility of the metals ions, the concentration of counter ions on the surface of the adsorbent and the degree of ionization of the adsorbate during the reaction [15]. Fig.1. showed the effect of the initial pH solution

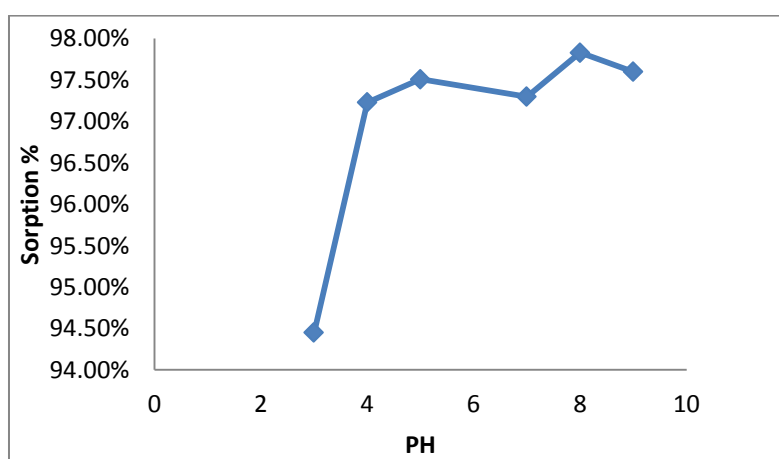
on Ni<sup>2+</sup> removal by Pentaclethramacrophylla shells. At pH 7.5-8.0, plateau adsorption rate was observed on Ni(II) metal ion, sorption % rate increased from pH 3-5 and discontinued to 97.30% at pH 6 and sharply increased at pH 7.5 - 8 while slightly drop occurred at pH 9 to 97.60%.

The effect of initial pH on biosorption provides an insight on the nature of physicochemical interaction between solute in solution and adsorptive sites of the adsorbent and could be attributed to the change in the degree of ionization of the biosorbent and sorbate.

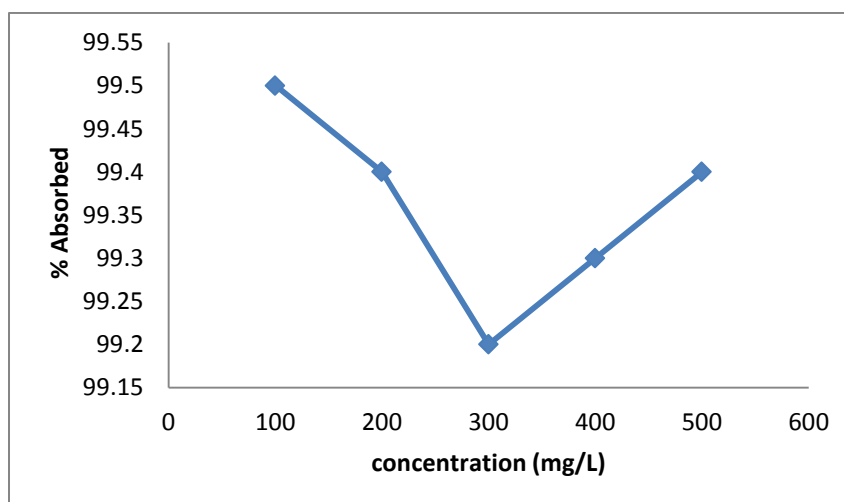
### 3.2 Effect of initial concentration of Ni (II) ion

Initial concentration studied range from 100mg/L to 500 mg/L under pre-determined optimized conditions of 1hour contact time and pH 8 gives adsorption percentage of 99.5 for 100mg/l and 99.4% for 200mg/l while removal efficiency increases with increases in concentration from 300mg/L to 500mg/L recorded and shown in fig. 3. This is attributed to the increase in number of metal ions competing for available sites on the adsorbent at higher concentration levels [16].

According to the values of R<sup>2</sup>, K<sub>f</sub>, and K<sub>L</sub> shown in tab. 2, it was observed that the Langmuir isotherm show good fit to the experimental equilibrium adsorption data than the Freundlich isotherm equation. K<sub>L</sub> value which less than one and greater than zero indicating favorable sorption of Ni(II) ion onto PMS.



**Fig.1: showing the effect of pH on the biosorption of Ni(II) ions from aqueous solution using PMS.**



**Fig. 2: Effect of initial Ni (II) ion concentration on the sorption by SOS powder at 1g/25mL of sorbent concentration at 30°C and contact time of 1hour.**

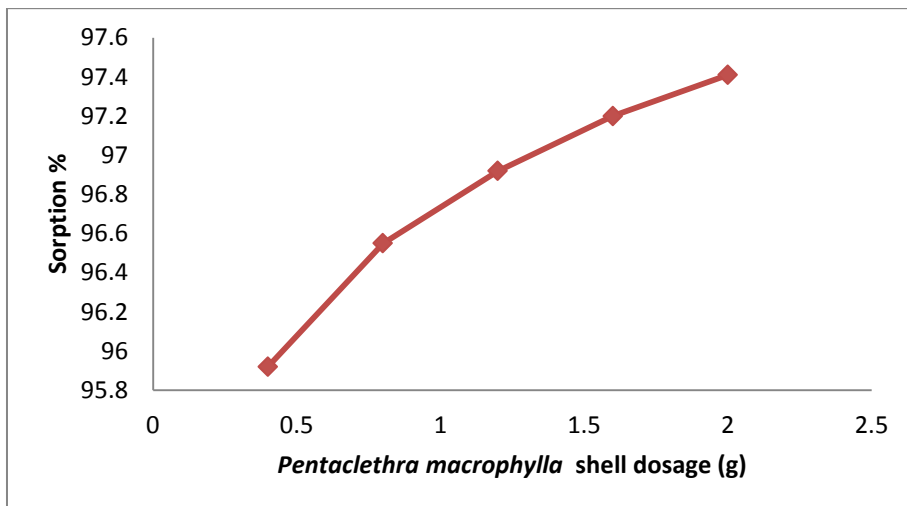


Fig 3: Effect of biosorbent dosage on metal ions sorption by *Pentaclethramacrophylla* shell for 100mg/L Nickel metal ion on pH 8 at 30°C

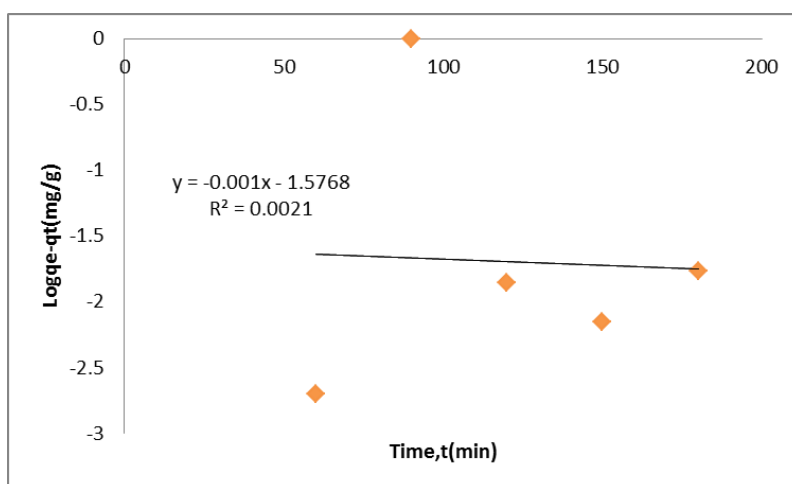


Fig 4: Pseudo-first order for the biosorption of Ni (II) by *Pentaclethramacrophylla* shell for 100mg/L of metal and 1g of 25ml on sorbent.

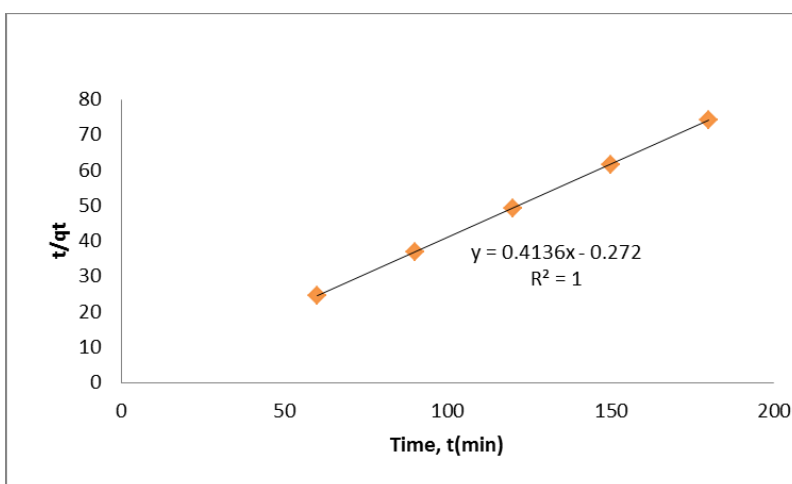


Fig 5: Pseudo second order for the biosorption of heavy metals on Ni(II) by seed oil shell for 100mg/L of metal and 1g of 25ml of the sorbent.

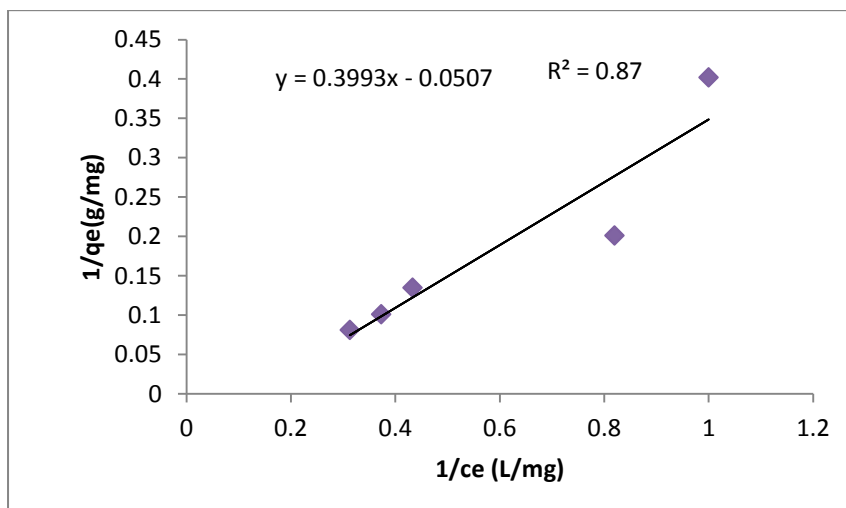


Fig.6: Langmuir isotherm for the adsorption of Ni<sup>2+</sup> with Seed oil shell at 30°C.

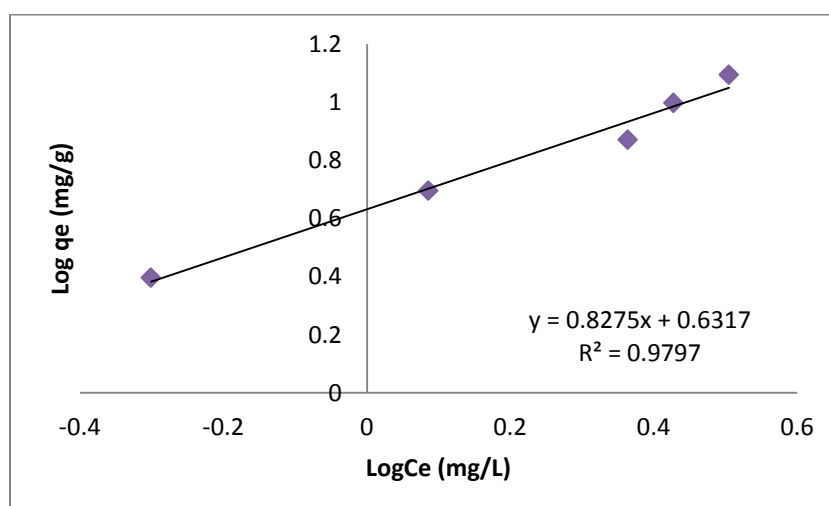


Fig.7: Freundlich isotherm for the adsorption of Ni<sup>2+</sup> with Seed oil shell at 30°C.

### 3.3 Effect of contact time

The results obtained for the variation of contact time 60, 90, 120, 150, 180 min of nickel ions on PMS are shown in table 6. More than 97% ions sorbed onto PMS within first 60 minutes.

### 3.4 Effect of adsorbent dosage

As gram of *Pentaclethramacrophylla* shell dose increases, it was discovered that the sorption percentage of Ni (II) ions removal also increased in order of 95.92% > 96.55% > 96.92% > 97.20% > 97.41% and such is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the biosorbent.

The results are presented in table 5 and the effect of varying the PMS dosage on the sorption of Nickel metal ions is shown in fig.3, respectively.

### 3.5 Kinetic studies of Ni (II) ion biosorption

Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism of the biosorption process. The mechanisms used for the kinetic biosorption of Ni (II) ions are the Pseudo first-order and Pseudo- second order. Both models are test for fitness by their correlation. R<sup>2</sup> is approximately one (R<sup>2</sup> ≈ 1) [17].

3.5.1 Lagergren Pseudo-first order equation; linear given as:

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

The plot of  $\log(q_e - q_t)$  versus time  $t$  for Ni (II) ion of the sorbent used and the pseudo-first order parameter  $K_1$ ,  $q_e$  calculated and the regression coefficient (R<sup>2</sup>) are shown in fig.4 and table 3, respectively. Where  $q_t$  and  $q_e$  are the amount of Ni (II) ion adsorb (mg/g) at time  $t$  (min) and at equilibrium respectively. The

constant  $K_1$  obtained from the slope,  $q_e$  calculated result differ from experimental  $q_e$  value, which indicate that, pseudo first-order is not appropriate to explain the biosorption process, meanwhile,  $R^2$  also proved that first-order model not appropriately discussed the sorption process.

The Ho Pseudo second-order model for sorption kinetics is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \quad (4)$$

Where,  $K_2$  (g/mg.min) is the second order rate constant. The second order constants are used to calculate the initial biosorption rate, given by:

$$h = K_2 q_e^2 \quad (5)$$

Plot of pseudo second order for Ni (II) ions for this study shown in figure 4, which gives  $\frac{1}{q_e}$  as slope and  $\frac{1}{K_2 q_e^2}$  as intercept from which  $K_2$  expressed. The plots identify distinct fits between the precise curves and the experimental data points. Its analyzed excellent linearization of the experimental data, therefore showing the proposal that chemisorption is the rate limiting step and that the mechanism follows a pseudo second order reaction model. The equilibrium sorption capacity  $q_e$  calculated, the initial sorption capacity  $h$ , the rate constant  $K_2$  and the regression coefficient  $R^2$  are formed from the plot are shown in table 5.

There is no significant different between equilibrium capacity  $q_e$  calculated and the  $q_e$  experimental, also a unit value of  $R^2$  support pseudo second order reaction model.

In comparison;  $R^2$ ,  $q_e(\text{cal})$  and  $q_e(\text{exp})$  parameters of both pseudo order kinetic model; Regression coefficient of first order kinetic value so small to a unit value of second order kinetic model, meanwhile closeness of  $q_e(\text{cal})$  to  $q_e(\text{exp})$  value in second order kinetic model shows that kinetic of nickel ion by Pentaclethramacrophylla shell is better described pseudo-second kinetic model rather than 0.0265 value of pseudo first order calculate.

Several authors reported that most metal sorption follow pseudo second order mechanism, thus, the sorption of Ni (II) ions onto seed oil shell follows the pseudo second order kinetic model.

### 3.5.2 Langmuir and Freundlich Isotherm Model

Both Langmuir's and Freundlich's adsorption isotherm equilibrium models were used for the analysis of the metal-adsorbent system. Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between adsorbed molecules. Fig. 6 and fig.7 shows the plots of  $1/q_e$  (g/mg) versus  $1/C_e$  (L/mg) and  $\log q_e$  (mg/g) versus  $\log C_e$  (mg/L), respectively.

The Langmuir linear equation below was used to calculate the maximum adsorption capacity of the adsorbent [18].

$$\frac{1}{q_e} = \frac{1}{b q_{\max} C_e} + \frac{1}{q_{\max}} \quad (6)$$

The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor ( $K_L$ ) that can be defined by the following relationship [19].

$$K_L = \frac{1}{1 + b C_0} \quad (7)$$

Where  $C_0$  is the initial concentration (mg/L), while  $b$  is the Langmuir equilibrium constant (L/mg). The value of separation parameter  $K_L$  provides important information about the nature of adsorption. The value of  $K_L$  indicated the type of Langmuir isotherm to be irreversible ( $K_L=0$ ), favorable ( $0 < K_L < 1$ ), linear ( $K_L=1$ ) or unfavorable ( $K_L > 1$ ). It can be explained apparently that when  $b > 0$ , sorption system is favorable [20].

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as [21]: the isotherm model proposes a monolayer sorption with a heterogeneous distribution of active sites, accompanied by interactions between adsorbed molecules.

$$\log q_e = \log K_f + \frac{1}{n} (\log C_e) \quad (8)$$

The adsorption constants ( $K_f$  and  $1/n$ ) were obtained by plotting  $\log q$  against  $\log C_e$ , the Freundlich isotherm parameter  $1/n$ .

**Table 1: pH dependent study of the sorption of Nickel (II) onto Pentaclethramacrophylla shell.**

pH	$C_a$ (mg/L)	$C_0 - C_e$ (mg/L)	Sorption %	$q$ (mg/g)
3	5.51	94.49	94.49	2.36
4	2.77	97.23	97.23	2.43
5	2.49	97.51	97.51	2.44
7	2.70	97.30	97.30	2.43
8	2.17	97.83	97.83	2.45
9	2.40	97.60	97.60	2.44

**Table 2: Langmuir and Freundlich isotherms parameters for the adsorption of metal ions by Seed oil shell**

Langmuir isotherm parameters					Freundlich isotherm parameters				
	b	q <sub>max</sub>	K <sub>L</sub>	R <sup>2</sup>	1/n	n	K <sub>f</sub>	R <sup>2</sup>	
Ni	0.127	19.724	0.7	0.87	0.83	1.208	4.282	0.9797	

**Table 3: Pseudo first-order parameters for the sorption of Nickel (II) metal ion by PM shell**

Pseudo first	Order	Parameters
Metal	q <sub>e</sub> (cal)mg/g	K <sub>1</sub> (g/mg.min) R <sup>2</sup> q <sub>e</sub> (exp)mg/g
Ni	0.0265	0.0023 0.0021 2.441

**Table 4: Pseudo second- order parameters for the sorption of Nickel (II) metal ion by PM shell**

Pseudo	Second	Order	Parameters
Metal	q <sub>e</sub> (mg/g.min)	h(mg/g.min)	K <sub>2</sub> (g/mg.min) R <sup>2</sup> q <sub>e</sub> (exp)mg/g
Ni	2.4177	-3.6761	-0.6289 1 2.441

**Table 5: Effect of dosage on sorption of Ni (II) onto seed oil shell**

Dosage (mg/g)	C <sub>o</sub> (mg/l)	C <sub>e</sub> (mg/l)	Sorption %
0.4	100	4.08	95.92
0.8	100	3.45	96.55
1.2	100	3.08	96.92
1.6	100	2.59	97.41
2.0	100	2.80	97.20

**Table 6: Table showing the data obtained for the time variation study of the biosorption of Ni metal ion using Pentaclethramacrophylla shell**

Time(min)	C <sub>e</sub> (mg/g)	C <sub>a</sub> (mg/g)	q <sub>t</sub> (mg/g)	q <sub>e</sub> -q <sub>t</sub> mg/g	Log mg/g	t/q <sub>t</sub> (gmin/mg)
60	2.36	97.64	2.439	0.002	-2.699	24.60
90	2.43	97.57	2.442	0.000	0.000	36.87
120	2.94	97.06	2.427	0.014	-1.854	49.44
150	2.65	97.35	2.434	0.007	-2.155	61.63
180	3.03	96.97	2.424	0.017	-1.770	74.26

#### IV. Conclusion

Results obtained for the four critical examined conditions and from the mathematical kinetic models expression of the Ni<sup>2+</sup> ion onto seed oil shells, confirmed the good chemical reaction mechanism for the Pseudo second-order and also equilibrium sorption Langmuir and Freundlich isotherm model fitted well. Meanwhile, this research work showed the excellent efficiency of powdered Pentaclethramacrophylla shells in removal of Ni(II) ion from its aqueous solution. This also confirmed the importance, possibility and usefulness of known agricultural waste Pentaclethramacrophylla shell for the clean-up of heavy metals in industrial waste water.

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