

## EMPIRICAL MODELS DEVELOPMENT FOR THE SORPTION OF Ni(II) ONTO CLAY

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### *Abstract*

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*This paper examined the kinetics of nickel removal from aqueous solution by a kaolinitic clay and also developed a predictive kinetic model for it. The adsorbent used was first characterized before it was used for the adsorption of Ni(II) from aqueous solution using the batch mode. After a preliminary equilibrium studies, the kinetic studies were carried out by varying the adsorbent doses from 0.2g to 1g at fixed adsorbate concentration while varying the time from 5min to 120 min. The kinetic studies were also carried out by varying by varying the metal ion concentration from 2mg/l to 8mg/l at a constant adsorbent dose while varying the time from 5 min to 120 min. The kinetic profile was modeled using pseudo-first-order model, pseudo-second-order model and Elovich model. The kinetic sorption profiles offered excellent fit with pseudo-second-order model with high coefficient of determination,  $R^2$  values of 0.9970 to 0.9990 and 0.9989 to 0.9999 when varying adsorbent dose and when varying heavy metal ion concentration respectively. Empirical models were developed to predict metal ion uptake at any time in terms of varying initial metal ion concentration and contact time, as well as for varying adsorbent dose at any contact time. The developed models were validated using root mean square error (RMSE). The low RMSE values of 0.0701 and 0.00620 respectively for varying adsorbent dose and contact time and for varying initial metal ion concentration and contact time show that the empirical models derived from the experimental data were able to predict the metal ion uptake at any time quite well. The empirical models developed indicate that the metal ion uptake at any contact time is higher as initial metal ion concentration but decreased with a increased adsorbent dose.*

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**Keywords:** Clay, kinetic modelling, adsorbent, adsorption kinetics

### **1.0 Introduction**

Heavy metals generally have toxic effects on the environment even in small concentrations, hence the need for their removal from aqueous solutions before discharging into the environment. Heavy metals have been found in wastewaters from many industries, including metallurgical, chemical manufacturing, mining and battery manufacturing industries. Many physicochemical methods have been developed for heavy metal removal from aqueous solution, including, chemical coagulation, adsorption, extraction, ion exchange and membrane separation process. Among these methods, adsorption has attracted much interest because it requires less investment in terms of both initial cost and land, simple design and easy operation [1].

Commercial activated carbon (CAC) has been the dominant adsorbent for decades yet despite its prolific use, it remains an expensive and wasteful process [2]. Recent research of low-cost alternatives to CAC for waste and wastewater treatment is of interest. The reasons for the interest in clay are the increasing demand for low-cost adsorbent materials in fields such as pollution control, their wide availability on the earth and their effective removal of heavy metals [3-6].

Most of the studies on heavy metals adsorption with different adsorbents did not address the fundamental questions needed to implement this technology on a practical basis. However, for an optimal design of an industrial adsorption process, it is important to have accurate modelling of kinetic behaviour. The hitherto developed mathematical models have used different degrees of complexity to describe adsorption processes. The objective of this work was to develop a predictive kinetic model, which could be easily used for the evaluation the kinetics of adsorption of nickel onto clay.

### **2.0 Materials and Methods**

#### **2.1 Preparation and Characterization of Adsorbent**

The adsorbent used in the present study was clay obtained from the clay deposits at Ikpoba in Ikpoba-Okha local government area, Edo state, Nigeria. The clay was washed thoroughly with deionised water in order to remove any dissolved impurities and then dried at 120°C and sorted for further use. The specific surface area was determined by the adsorption-desorption isotherms of nitrogen (BET - Surface Area Analyzer Tristar 3000). The total pore volume was determined by pycnometry. The mineralogical composition of the clay was obtained by XRD ( PAN analytical X'Pert PRO MPD, PW 3040/60 ) studies. X-ray Fluorescence Spectrometer (model PW 4030) was used to determine the chemical composition of the clay samples.

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2.2 Adsorbate preparation

Stock solution (1000mg/l) of Ni(II) was prepared by dissolving appropriate amounts of analytical grade nickel(II) sulphate with deionized water. Working solutions were got by diluting stock solution with appropriate amounts of deionized water.

2.3 Kinetic studies

A preliminary equilibrium studies was carried out with adsorbate and adsorbent doses used in this study. Kinetic studies were carried out by adding 0.2g to 1g of the clay sample (adsorbent) to 50ml of the aqueous solutions of Ni(II) ions with the desired initial concentrations in separate conical flasks. The suspensions were maintained at 303 K and shaken at a constant speed of 100rpm on a rotary orbital shaker and the samples withdrawn at time intervals of 5, 10,15, 20, 40, 60, 80 100 and 120 min and filtered. The concentrations of the metal ions in the filtrates were determined by atomic absorption spectrophotometry, AAS (Buck Scientific 205). A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results [7], and the average values were used for further calculations. The procedure was repeated with varying metal ion concentrations of 2mg/l to 8mg/l with the desired adsorbent dose.

The adsorbate uptake  $q_t$  (mg/g) at time,  $t$  was calculated as:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{1}$$

Where  $q_t$  is the amount of sorbate on the surface of the sorbent at any time  $t$ (mg g<sup>-1</sup>) ;  $C_0$  and  $C_t$  are respectively the initial metal ion concentration and metal ion concentration at time,  $t$  (mg l<sup>-1</sup>) ;  $V$  the volume of aqueous solution in litres and  $m$  is the adsorbent dose in grams.

Based on kinetic data, the models applied to examine the dynamics of the sorption process in this study include Lagergren’s pseudo-first order, pseudo-second order and the Elovich models.

The pseudo-first-order kinetic model based on the capacity for sorption analysis by Lagergren is generally expressed in the linearised form as [8,9]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

Where  $q_e$  is the amount of sorbate on the surface of the sorbent at equilibrium (mg g<sup>-1</sup>) and  $k_1$  is the pseudo-first-order rate constant (min<sup>-1</sup>).

If the rate of sorption is a second order mechanism, the pseudo- second -order chemisorptive kinetic rate is expressed as[10] :

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{3}$$

where  $k$  is the pseudo- second -order rate constant (g mg<sup>-1</sup>min<sup>-1</sup>)

The Elovich equation has also been successfully applied in aqueous systems to describe adsorption and desorption reactions [11,12] as:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \tag{4}$$

Where  $\alpha$  and  $\beta$  are constants,  $t$  the time. The Elovich equation can be derived from either a diffusion-controlled process or a reaction-controlled process.

When the term  $\alpha\beta t$  is much greater than 1, Elovich equation has been simplified to:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta t) = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{5}$$

3 Results and Discussion

3.1. Adsorbents characterization

The chemical and mineralogical composition of the adsorbent as obtained from X-Ray Fluorescence (XRF) analysis and XRD are presented in Tables 1 and 2 respectively.

Table 1: Chemical Composition of Clay

Chemical Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	K <sub>2</sub> O	Cr <sub>2</sub> O <sub>3</sub>	CaO	TiO <sub>2</sub>	ZnO
Percentage	78.65	15.17	3.49	0.62	0.02	0.27	0.01	0.14	1.57	0.06

The major constituent of the adsorbent used in this study was SiO<sub>2</sub> which accounted for 78.65 % of the weight of the clay characterized. This was followed by Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> which accounted for about 15.17, 3.49 and 1.57% respectively as shown in Table 1. Some other oxides such as K<sub>2</sub>O, Na<sub>2</sub>O, TiO<sub>2</sub> and MnO<sub>2</sub> were also found to be present in small amounts (< 1% each).

Table 2: Mineralogical composition of clay

Mineral	Treated Ikpoba clay Composition (%)
Kaolinite	32.56
Quartz	31.45
Anatase	14.11
Goethite	13.42
Violarite	8.46

From XRD analysis presented in Table 2, the results show that kaolinite has the highest percentage of 32.56 in the adsorbent while the lowest mineral is Violarite with 8.46%. The results presented in Tables are similar to those reported in the literature for a kaolinitic clay [13].

The physical properties of the adsorbent are presented in Tables 3.

**Table 3: Physical properties of clay**

Parmeter	Value
Specific surface area - BET (m <sup>2</sup> /g)	8.6932
Average Pore Diameter (nm )	26.22612
Pore Volume (cm <sup>3</sup> /g)	0.101267

The specific surface area, average pore diameter and pore volume of adsorbent used in this study are presented in Table 3. The results presented in Table 3 are similar to those reported in the literature for a kaolinitic clay [14,15].

**3.2 Sorption kinetics**

The goodness of fit of kinetic data to selected kinetic models was assessed based on evaluation of coefficient of determination, R<sup>2</sup> for the linear regression; that is, the isotherm giving an R<sup>2</sup> value closest to unity was deemed to provide the best fit. Tables 4 and 5 give the values of kinetic parameters at different adsorbent doses and adsorbate concentrations, and their corresponding R<sup>2</sup> values.

**Table 4: Kinetic parameters determined with varying adsorbent dose**

m(g)	0.2	0.4	0.6	0.8	1
Pseudo-first order					
q <sub>e</sub> (mg/g)	0.882	0.457	0.312	0.241	0.194
k <sub>f</sub> (min <sup>-1</sup> )	0.109	0.121	0.150	0.151	0.161
R <sup>2</sup>	0.9010	0.9140	0.9060	0.9002	0.8912
Pseudo-Second order					
q <sub>e</sub> (mg/g)	0.954	0.491	0.328	0.256	0.204
k(g/mg/min)	0.182	0.391	0.833	1.080	1.430
R <sup>2</sup>	0.9990	0.9980	0.9970	0.9970	0.9970
Elovich					
α(mg/g/min)	0.429	0.300	0.447	0.350	0.384
β(g/mg)	5.29	10.87	18.87	24.40	32.58
R <sup>2</sup>	0.8780	0.8590	0.8520	0.8400	0.8580

**Table 5: Kinetic parameters determined with varying initial metal ion concentration**

Co(mg/l)	2	4	6	8
Pseudo-first order				
q <sub>e</sub> (mg/g)	0.4724	0.9262	1.3868	1.8489
k <sub>f</sub> (min <sup>-1</sup> )	0.1949	0.3151	0.4091	0.4901
R <sup>2</sup>	0.7652	0.8614	0.8399	0.8279
Pseudo-Second order				
q <sub>e</sub> (mg/g)	0.4904	0.9500	1.4099	1.8700
k(g/mg/min)	0.7987	0.9600	1.1000	1.2800
R <sup>2</sup>	0.9999	0.9998	0.9989	0.9999
Elovich				
α(mg/g/min)	226.15	57164	1.7x10 <sup>9</sup>	3.2x10 <sup>18</sup>
β(g/mg)	27.575	19.316	20.332	26.982
R <sup>2</sup>	0.9004	0.8842	0.8734	0.8445

From Tables 4 and 5 it is seen that the R<sup>2</sup> values range from 0.8912 to 0.9140 and 0.7652 to 0.8614 for pseudo-first order model when varying the adsorbent dose from 0.2g to 1g and when varying the adsorbate concentrations from 2mg/l to 8mg/l respectively; the R<sup>2</sup> values range from 0.9970 to 0.9990 and 0.9989 to 0.9999 for pseudo-second order model when varying the adsorbent dose from 0.2g to 1g and when varying the adsorbate concentrations from 2mg/l to 8mg/l respectively; the R<sup>2</sup> values range from 0.8400 to 0.8780 and 0.8445 to 0.9004 for Elovich model when varying the adsorbent dose from 0.2g to 1g and when varying the adsorbate concentrations from 2mg/l to 8mg/l respectively. These results indicate that the sorption of Ni(II) ion onto the adsorbent best fit pseudo-second order kinetic model as it has the coefficient of determination value closest to unity for both initial metal ion concentration variation and adsorbent dose variation.

**3.3 Kinetic modelling**

The pseudo-second-order kinetic model based on the solid capacity for sorption analysis given by another researcher [10] is generally expressed as Equation (3) . .

Rearranging and integrating within the boundary t= 0 to t = t and q<sub>t</sub>= 0 to q<sub>t</sub> = q<sub>e</sub>, gives the linearized form as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{6}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (6) can be rearranged to obtain:

$$q_t = \frac{t}{1/kq_e^2 + t/q_e} \tag{7}$$

Rearranging Eq. (7) reduces to:

$$t/q_t = 1/h + t/q_e \tag{8}$$

where  $k$  is the pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $h$  is the initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ), given by  $h = kq_e^2$

Based on the linearized form of pseudo-second-order model (Eq. (8)), a plot of  $t/q_t$  versus contact time ( $t$ ) when the adsorbent dose and initial concentrations of Ni(II) ions were respectively varied are shown in Figures 1 and 2.

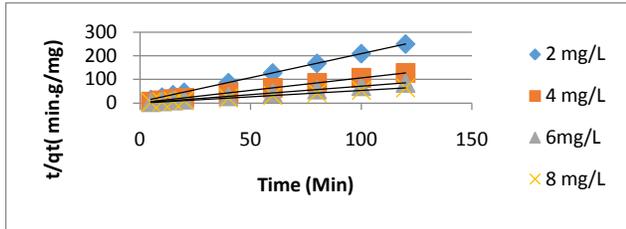


Figure 1: Time per sorbed capacity versus time at varying initial metal ion concentration

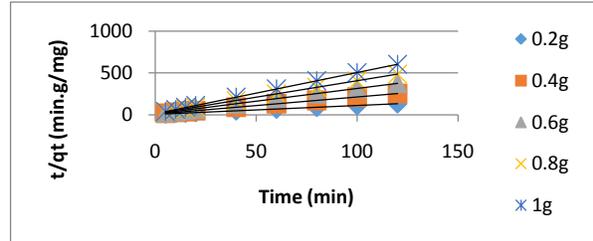


Figure 2: Time per sorbed capacity against time at varying adsorbent doses

The data showed excellent agreement with the proposed pseudo-second-order model as demonstrated by the high correlation of the plots (Fig 1 and 2) as shown in Tables 6 and 7. The values of the initial sorption rates,  $h$ , and the equilibrium sorption capacity were determined by using the respective values of the reciprocal of the intercept and the reciprocal of the slope of the plots in Figures 1 and 2.

Tables 6 and 7 give values of the initial sorption rates, the equilibrium capacity and the corresponding  $R^2$  values obtained from Figures 1 and 2.

**Table 6: Effect of adsorbent dose on metal ion adsorption data**

m (g)	$R^2$	$q_e$ (mg/g)	$h$ (mg/gmin)
0.2	1.0000	0.954	0.1638
0.4	1.0000	0.49	0.0985
0.6	1.0000	0.33	0.09083
0.8	1.0000	0.254	0.07097
1	0.9990	0.204	0.0625

**Table 7: Effect of initial metal ion concentration on metal ion adsorption data.**

$C_o$ (mg/l)	$R^2$	$q_e$ (mg/g)	$h$ (mg/gmin)
2	1.0000	0.49	0.192
4	1.0000	0.951	0.867
6	1.0000	1.41	2.188
8	1.0000	1.873	4.484

As shown in Table 6, the initial sorption rate decreases with an increase in the adsorbent dose. The initial sorption rate was however found to increase with an increase in the initial metal ion concentration (Table 7). It was shown in the data that the initial metal ion concentrations influenced the contact time necessary to reach equilibrium and that the sorption capacity increased for the higher initial metal ion concentrations. The  $h$  values vary from 0.192 to 4.484  $\text{mg/g min}$  as initial metal ion varied from 2 to 8mg/l, but varied from 0.0985 to 0.0625 as adsorbent dose varied from 0.2 to 1g.

The corresponding linear plots of the values of  $q_e$  and  $h$  against initial metal ion concentration,  $C_o$  were regressed to obtain expressions for these values in terms of the initial metal ion concentration with high correlation coefficients (Table 8). Similarly, the corresponding plots of the values of  $q_e$  and  $h$  against adsorbent dose,  $m$  were regressed to obtain expressions for these values in terms of the adsorbent dose with high correlation coefficients (Table 9). Therefore it is further considered that  $q_e$  and  $h$  can be expressed as a function of  $C_o$  and  $m$  as follows:

$$q_e = A_q C_o + B_q \tag{9}$$

$$h = A_h C_o + B_h \tag{10}$$

$$q_e = a_q m^{b_q} \tag{11}$$

$$h = a_h m^{b_h} \tag{12}$$

From the linear plot of  $q_e$  vs  $C_o$ ,  $A_q$  and  $B_q$  were obtained as slope and intercept respectively. Also, from the plot of  $h$  against  $C_o$ ,  $A_h$  and  $B_h$  were obtained as slope and intercept respectively. Similarly, from the plot of  $q_e$  vs  $m$ ,  $a_q$  and  $b_q$  were obtained as the coefficient and index of  $m$  respectively. Similarly, from the plot of  $h$  vs  $m$ ,  $a_h$  and  $b_h$  were obtained as the coefficient and index of  $m$  respectively. Values of empirical parameters determined from plots are given in Tables 8 and 9.

**Table 8: Empirical parameters determined for  $q_e$  and  $h$  from  $C_o$**

$A_q$	$B_q$	$R^2$	$A_h$	$B_h$	$R^2$
0.23	0.029	0.9999	0.709	-1.616	0.938

**Table 9:** Empirical parameters determined for  $q_e$  and  $h$  from  $m$ 

$a_q$	$b_q$	$R^2$	$a_h$	$b_h$	$R^2$
0.203	-0.95	0.999	0.062	-0.57	0.977

Substituting the Eqs (9) and (10) into Eq. (7) and Eqs (11) and (12) into Eq. (7) the rate law for a pseudo-second order and the relationship of  $q_t$ ,  $C_0$  and  $t$  and  $q_t$ ,  $m$  and  $t$  can respectively be represented as follows:

$$q_t = \frac{t}{\left(\frac{1}{A_h C_0 + B_h}\right) + \left(\frac{t}{A_q C_0 + B_q}\right)} \quad (13)$$

$$q_t = \frac{t}{\left(\frac{1}{a_h m + b_h}\right) + \left(\frac{t}{a_q m + b_q}\right)} \quad (14)$$

Substituting the values of the empirical parameters  $A_h$ ,  $B_h$ ,  $A_q$  and  $B_q$  from Table 6 and Table 7 into Eq. (13) and Eq. (14) respectively, the rate law for a pseudo-second order and the relationship of  $q_t$ ,  $C_0$  and  $t$  and  $q_t$ ,  $m$  and  $t$  can be represented as follows:

$$q_t = \frac{t}{\left(\frac{1}{0.709 \times C_0 - 1.616}\right) + \left(\frac{t}{0.23 C_0 + 0.029}\right)} \quad (15)$$

$$q_t = \frac{t}{\left(\frac{1}{0.062 m - 0.57}\right) + \left(\frac{t}{0.203 m - 0.95}\right)} \quad (16)$$

These equations (15) and (16) are the empirical predictive models for the adsorption of Ni(II) onto the adsorbent with varying metal ion concentrations and adsorbent dose respectively; and can then be used to obtain the sorption amount of Ni(II) at any given dosage or initial metal ion concentration and the reaction time. Equations (14) and (15) respectively indicate that the metal ion uptake at any contact time is higher as initial metal ion concentration but higher with a decreased adsorbent dose.

### 3.5 Validation of model

The root mean square error (RMSE) is chosen as indicator of performance of the predictive empirical models and is calculated by:

$$RMSE = \sqrt{\frac{\sum(\text{Observed} - \text{Predicted})^2}{\text{Number of data}}} \quad (17)$$

**Table 10:** RMSE values of the empirical models for the adsorption of Ni(II) on adsorbent

Model	RMSE Value
varying initial metal ion concentration	0.0701
varying adsorbent dosage	0.00620

In this study, Microsoft Excel was used to program equations 15 and 16 for the general predictive empirical models developed for nickel. The simulated data when compared to the experimental data gave RMSE values for the predictive empirical models as shown in Table 10. The values of RMSE calculated (Table 10) show that the empirical models derived from the experimental data were able to predict the sorption capacity of adsorbent for the divalent metal ion studied quite well.

### 4.0 Conclusion

The kinetics of the adsorption of Ni(II) onto clay was investigated in this study. The following conclusions can be drawn from this study:

- I. The sorption could be better described by pseudo-second-order model indicating a chemisorptive adsorption.
- II. XRD reveals that the dominant mineral present in the clay is kaolinite
- III. From the XRF analysis the chemical component in the highest amount is  $\text{SiO}_2$ , while CaO is the component present in the least amount
- IV. The initial sorption rate decreases with an increase in the adsorbent dose, and also increases with an increase in initial metal ion concentration.
- V. It was shown that the sorption capacity increased as the initial metal ion concentrations increased
- VI. The developed empirical predictive models for the adsorption of Ni(II) show that at any time, as adsorbent dose is increased the metal ion uptake is decreased. The model developed also show that at any time the initial metal ion is increased the metal ion uptake is increased also.

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