

Kinetics and Equilibrium Modeling of Nickel Adsorption by Cassava Peel

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Abstract: The use of cassava peel activated carbon for the removal of Nickel from aqueous solution at different contact times, pH, adsorbent doses and initial nickel concentration was investigated. The percentage of Ni (ii) removal decreased with increasing adsorbent dosage. The equilibrium sorption isotherms have been analyzed by Freundlich, Langmuir and Temkin models. The equilibrium data fitted well to the 3 models. Temkin model had the highest correlation coefficient followed by Freundlich model. In order to investigate the mechanisms of adsorption, the pseudo 1st-order, pseudo 2nd-order, 2nd-order and simple Elovich kinetic models were used. The results indicated that Ni (ii) uptake process followed pseudo 2nd-order rate expression.

Key words: Cassava peel, activated carbon, nickel, isotherm, adsorption, equilibrium, kinetic

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 (Al-Omar and El-Sharkawy, 2001). The presence of heavy metals in the aquatic environment has been of great concern to scientists and engineers because of their increased discharge, toxic nature and other adverse effects on receiving water (Sekar *et al.*, 2004). 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 (Ong *et al.*, 2007; Ceribas and Yetis, 2001). Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity (Volesky and Holan, 1995).

Nickel salts are commonly used in metal plating and its concentration in industrial wastewater varies between 6 and 12 mg L⁻¹, which is above the safe limit (Bansal and Goyal, 2005). 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 (Erdogan *et al.*, 2005).

Several methods such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption have been proposed for treatment of wastewater contaminated with heavy metals (Gupta *et al.*, 2003). 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 (Ahmad *et al.*, 2006). However, commercially available activated carbons are still considered expensive (Chakraborty *et al.*, 2005). 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 (Mohan *et al.*, 2002), fly ash (Nollet *et al.*, 2003; Gupta *et al.*, 2003; Gupta and Ali, 2004; Ricou *et al.*, 2003), activated clay (Wu *et al.*, 2001), palm fruit bunch (Nassar, 1997), rice husk (Low and Lee, 1997), hazelnut shell (Koby, 2004), coconut shell (Sekar *et al.*, 2004; Lee *et al.*, 2006), peat (Brown *et al.*, 2000; Ho and McKay, 2000), etc.

The objective of this study, was to evaluate the feasibility of using this activated carbon produced from cassava for the removal of nickel from aqueous solution. The influence of experimental parameter such as pH, adsorbent dosage and initial Ni (ii) concentrations were studied. Pseudo-first order, Pseudo-second order, second-order and simple Elovich reaction kinetic models were used to analyze the experimental kinetic data.

MATERIALS AND METHODS

Preparation of activated carbon: Cassava tubers were harvested from a local farm in Ogidi, Anambra State, Nigeria. The tubers were peeled. The peels were washed with water, dried and pulverized. The sample was mixed

with zinc chloride (1:1 w v⁻¹) and kept at atmospheric temperature for about 24h with occasional stirring. The mixture was dried at 150°C and then carbonized at 500°C for 2 h in a muffle furnace. The carbonized sample was repeatedly washed with double distilled water until a pH of 5.4 was obtained. The washed sample was dried at 120°C. The activated carbon was crushed and sieved with 325 µm sieve and stored in a desiccators until use.

Characterization of Cassava Peel Activated Carbon (CPAC)

pH determination: The pH value of the carbon was determined by soaking 1 g sample in 100 mL distilled water and stirring for 1 h.

Bulk density determination: The bulk density of the activated carbon was determined by the tamping procedure by Ahmedna *et al.* (1997).

Iodine number: The iodine number was determined based on ASTM D4607-86 (1986) by using the sodium thiosulphate volumetric method. The standard iodine solution was added over activated carbon (0.5 g) and after equilibration time of 30 sec, the residual iodine concentration was determined by titration with standard sodium thiosulphate with starch as an indicator. The iodine number was defined as the quantity of iodine adsorbed (in mg g⁻¹ carbon) at a residual iodine concentration.

Batch adsorption experiments: The experimental nickel solution of desired concentrations were prepared from the stock solution with the appropriate dilution and the pH was adjusted to 5.0 with nitric acid and sodium hydroxide

Effect of initial nickel concentration was studied by using 0.25 g of activated carbon with 50 mL of nickel solution for batch experiments. Nickel solution concentrations of 10, 20, 30, 40 and 50 mg L⁻¹ were used. The experiments were performed using pH of 5.4 for 2 h. The sorbent was separated by centrifuging and the Ni (ii) remaining in solution was analyzed spectrophotometrically at a wavelength of 232 nm. The effect of adsorbent dose on Ni (ii) removal was studied by using initial Ni (ii) concentration of 50 mg L⁻¹ in conjunction with 0.25, 0.5, 1.0, 1.5 and 2.0 g L⁻¹.

The effect of pH on Ni (ii) removal was studied using 50 mL of 50 mg L⁻¹ solution of Nickel adjusted to initial pH 2-10 and agitated with 0.25g L⁻¹ of adsorbent for 2 h. The thermodynamic effect was studied by agitating 50 mg L⁻¹ of Ni (ii) solution with 0.25 g L⁻¹ of adsorbent at temperature of 10, 20, 30, 40 and 50°C for 2 h.

The amount of Ni (ii) adsorbed in mg g⁻¹ at time t was computed by using the following equation:

$$q_t = \frac{(C_o - C_t) V}{m} \quad (1)$$

where:

C_o and C_t = The Ni (ii) concentrations in mg L⁻¹ initially and at a given t, respectively
 V = The volume of the Ni (ii) solution in mL
 m = The weight of activated carbon in g

The percentage of removed Ni (ii) ions in solution was calculated using equation:

$$\text{Ni (ii) removed (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Characteristics of activated carbon prepared from cassava peel is shown in Table 1.

Effect of initial adsorbate concentration on adsorption

process: Removal of Ni (ii) at different initial concentration but constant pH and temperature is shown in Fig. 1. 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 Ni (ii) was dependent on the concentration of Ni (ii) as decrease in the initial concentration increased the amount of Ni (ii) removed.

Effect of adsorbent dosage on adsorption process: The percentage of Ni (ii) removal increased with increasing amount of CPAC (Fig. 2). The highest percentage of Ni (ii) removal of 75.9% was recorded at carbon dosage of 2 g.

The effect of pH: The results of Ni (ii) adsorption with increasing pH from 2-10 are shown in Fig. 1. It was found

Table 1: Characteristics of cassava peel based activated carbon

Characteristics	Value
Surface area (iodine number in m ² g ⁻¹)	306.400
Bulk density (g cm ⁻³)	0.404
pH	5.300

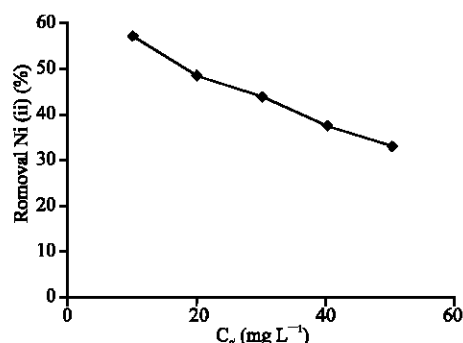


Fig. 1: Effect of initial concentration on sorption of Ni (ii)

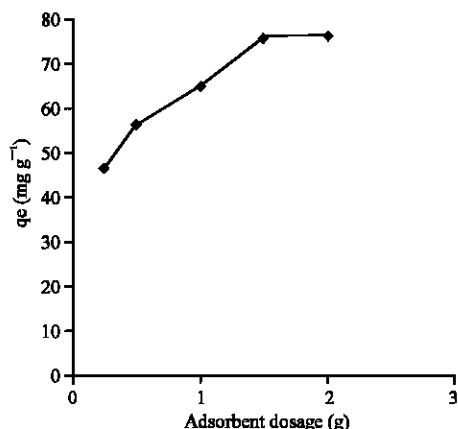


Fig. 2: Effect adsorbent dosage on the sorption of Ni (ii) at 30°C

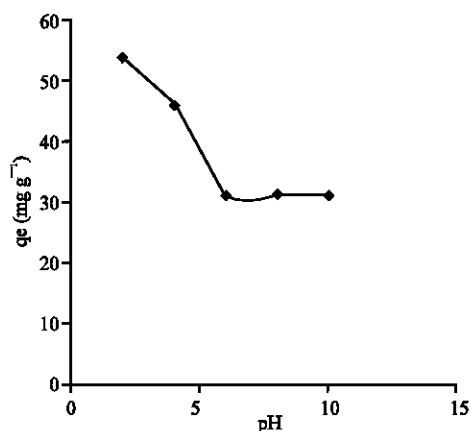


Fig. 3: Effect of pH on the sorption of Ni (ii)

that Ni (ii) adsorption capacity (in percentage) on CPAC decreased with increasing pH. The optimum pH was obtained at 2. Above this pH, adsorption of Ni (ii) on CPAC tends to decrease slightly (Fig. 3).

Adsorption isotherms: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Hameed *et al.*, 2006). The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (El-Guendi, 1991). The adsorption capacity of this system was investigated by the three adsorption isotherms as Langmuir, Freundlich and Temkin isotherm.

Langmuir isotherm: The Langmuir adsorption model is given by:

$$q_e = Q \frac{b C_e}{1 + b C_e} \quad (3)$$

Table 2: Langmuir, freundlich and temkin constant for Ni (ii) onto CPAC

Constant	Value
Langmuir isotherm	
Q (mg g ⁻¹)	4.740
b (L mg ⁻¹)	0.063
R ²	0.967
R _L	0.241
Freundlich	
1/n	0.534
K _F (mg g ⁻¹) ^{1/n}	1.850
R ²	0.982
Temkin	
b	1.050
a (l/g)	0.420
R ²	0.994

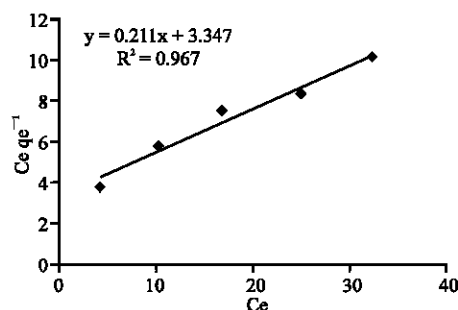


Fig. 4: Langmuir isotherm for the sorption of Ni (ii)

The linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_b} + \left[\frac{1}{Q} \right] C_e \quad (4)$$

where:

Ce = The equilibrium concentration of the adsorbate (mg L⁻¹)

qe = The amount of the adsorbate adsorbed per unit mass of adsorbate (mg g⁻¹)

Q and b = Langmuir constants related to adsorption capacity and rate of adsorption, respectively

When C_e/q_e was plotted against C_e, straight line with slope 1/Q was obtained (Fig. 4), indicating that the adsorption of Nickel on CPAC followed the Langmuir isotherm. The Langmuir constants 'b' and 'Q' were calculated from the isotherm and their values are given in Table 2. Correlation coefficient of 0.967 was obtained, also indicating that sorption followed Langmuir model.

The essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless separation parameter R_L, which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable. R_L is defined as:

$$R_L = 1/(1 + bC_0) \quad (5)$$

where:

b = Langmuir constant

C₀ = Initial concentration of the adsorbate (mg L⁻¹)

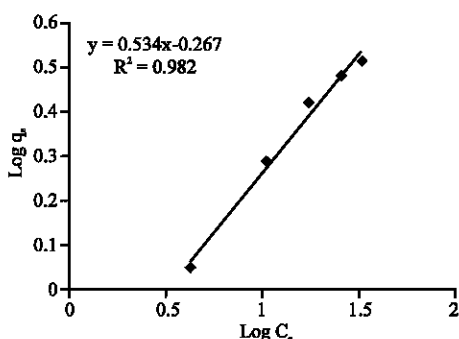


Fig. 5: Freundlich isotherm for the sorption of Ni (ii)

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.241 and confirmed that the adsorbent is favourable for adsorption of Ni (ii) under the condition used in this study.

Freundlich isotherm: The empirical Freundlich equation based on sorption on a heterogeneous surface is given by Eq. 6:

$$q_e = K_F C_e^{1/n} \quad (6)$$

The equation can be linearized by taking logarithms to find the parameters K_F and n

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ Log } C_e \quad (7)$$

where:

- q_e = The amount adsorbed at equilibrium (mg g⁻¹)
- C_e = The equilibrium concentration of the adsorbate
- K_F and n = Freundlich constants

The value of $1/n < 1$, indicates favourable adsorption of Ni (ii) on CPAC. That is, K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model (El-Guendi, 1991; Lakshmi *et al.*, 1994; McKay *et al.*, 1999; Aksu and Tezer, 2000). From the plot of $\log q_e$ versus $\log C_e$, K_F and $1/n$ were determined from intercept and slope, respectively. The values of K_F and $1/n$ are shown in Table 2. Freundlich isotherm fitted well with the correlation coefficient of 0.982 (Fig. 5).

Temkin isotherm: Temkin isotherm is given in linearized form as follows:

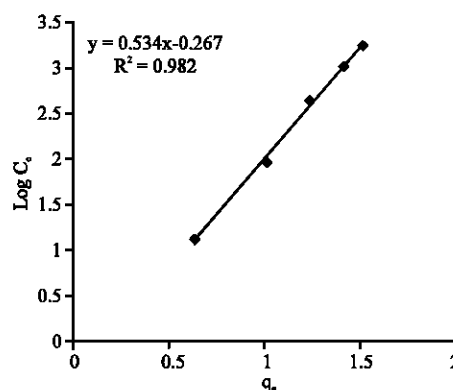


Fig. 6: Temkin isotherm for the sorption of Ni (ii)

$$q_e = a + 2.3036 \log C_e \quad (8)$$

where, a and b are Temkin constants.

The correlation coefficient of 0.994 obtained showed that adsorption of Ni (ii) also followed Temkin model. The values of a and b are given in Table 2 and Fig. 6.

Kinetic modeling: In order to analyze the adsorption kinetics of Ni (ii), the Pseudo 1st-order, pseudo 2nd-order, 2nd-order and Simple Elovich kinetic models were applied to data.

The pseudo 1st-order equation is generally expressed as follows:

$$\frac{dq_t}{q_t} = K_1 (q_e - q_t) \quad (9)$$

where:

- q_e and q_t = The adsorption capacity at equilibrium and at time t , respectively (mg g⁻¹)
- K_1 = The rate constant of Pseudo first-order adsorption (L min⁻¹)

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_e = 0$ to $q_t = q_e$, the integrated form of Eq. (9) becomes:

$$\text{Log } (q_e - q_t) = \text{log } (q_e) - \frac{k_1}{2.303} t \quad (10)$$

K_1 and q_e were determined from the slope and intercept of the plot of $\log (q_e - q_t)$ versus t (Fig. 7). The values of K_1 and q_e are given in Table 3. With the coefficient of 0.676, it seen that adsorption of Ni (ii) on CPAC did not follow Pseudo 1st-order kinetics.

Pseudo 2nd order Kinetic model (Ho and McKay, 2000) is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

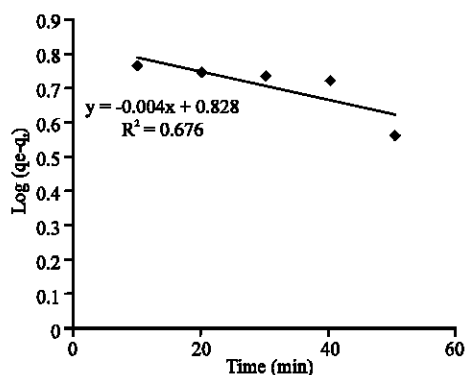


Fig. 7: Pseudo 1st-order kinetic for the sorption of Ni (ii)

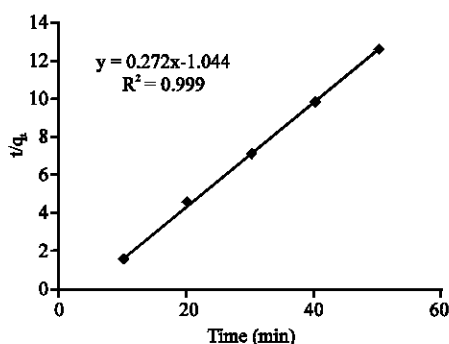


Fig. 8: Pseudo 2nd-order kinetics for the sorption of Ni (ii)

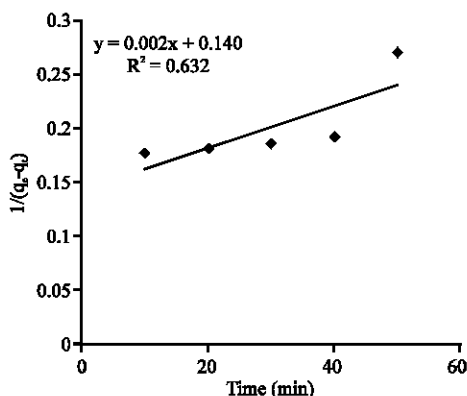


Fig. 9: 2nd-order kinetics for the sorption of Ni (ii)

where, K_2 is the rate constant of pseudo-second order kinetics. From the plot of t/q_t versus t (Fig. 8), the K_2 and q_e were calculated and recorded in Table 3. It is seen from Fig. 8 that adsorption of Ni (ii) on CPAC followed pseudo second-order kinetic model.

The Lagergren second order kinetic model is given as follows:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - K_2 t \quad (12)$$

Table 3: Adsorption kinetic parameters of Ni (ii) onto CPAC

Parameters	Value
Pseudo-first order	
K_1 (min^{-1})	0.0092
q_e (mg g^{-1})	6.7300
R^2	0.6760
Pseudo-second order	
K_2 ($\text{g mg}^{-1} \text{min}$)	0.0710
q_e (mg g^{-1})	3.6800
R^2	0.9990
Second-order	
K_2 ($\text{g mg}^{-1} \text{min}$)	0.0020
q_e	7.1400
R^2	0.6320
Simple elovich equation	
b	0.0190
a	5.8400
R^2	0.6900

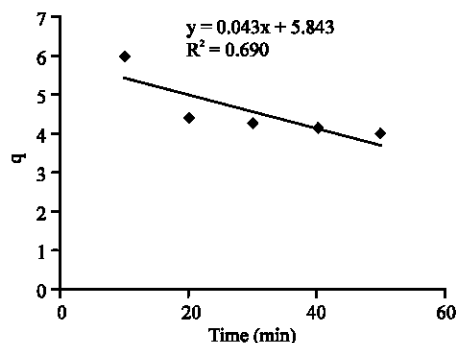


Fig. 10: Simple Elovich eqn for the sorption of Ni (ii)

where, K_2 is Lagergren 2nd-order rate constant

K_2 and q_e were calculated from the plot of $1/(q_e - q_t)$ versus t (Fig. 9). K_2 and q_e values are shown in Table 3.

Simple elovich equation: The Kinetic data was tested with simple Elovich equation (Goswami and Ghosh, 2005).

$$q = a + 2.303 b \log t \quad (13)$$

The constants, a and b were obtained from the slope and intercept of the plot of q versus $\log t$ (Fig. 10). The values of a and b are given in Table 3.

CONCLUSION

The capability of the use of cassava peel for removing Ni (ii) from aqueous solution was examined. The present investigation showed that cassava peel can be effectively used as a raw material for the preparation of activated carbon for the removal of Ni (ii) from aqueous solution. Adsorption behaviour is described by Freundlich, Langmuir and Temkin isotherm models. Kinetic data follows the pseudo second-order kinetic model.

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