Equilibrium, Kinetic and Thermodynamic Assessment of the Adsorption of Cadmium Using Water Lily (Nymphaea Ampla) Leaf Biomass

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Abstract: The adsorption of cadmium (II) ions from aqueous solution by Nymphaea ampla leaf biomass was carried out with effects of initial cadmium concentration, solution pH, contact time, adsorbent dose and temperature of the process investigated. An adsorbent dosage of 120 mg showed maximum metal uptake capacity (q_e) of 2.75 mg/g (82.6%) for an initial metal ion concentration of 2.0 mg/L and pH 7. Sorption equilibrium time was observed in 30 minutes. The equilibrium adsorption data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherm models. Freundlich isotherm yielded the best fit to the experimental equilibrium adsorption data with a correlation coefficient (R^2) of 0.990. The kinetics of cadmium (II) ions adsorption was discussed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. It was discovered that the adsorption of cadmium (II) ions could be described by the pseudo-second-order kinetic model. Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy change of the sorption (ΔS°) evaluated showed that the process was spontaneous, feasible and exothermic in nature. The results indicated that Nymphaea ampla leaf biomass can be used as an effective and low-cost adsorbent to remove cadmium (II) ions from aqueous solutions.

To cite this article

Keywords: Adsorption, Biomass, Cadmium (II) ion, Equilibrium, Kinetics, Thermodynamics

1. Introduction:

Heavy metals are present in the environment through natural and artificial sources. Industrialization has led to the generation of large quantities of liquid effluents, most of which contain heavy metals such as cadmium, lead, nickel, mercury, arsenic, chromium, zinc… etc. (Andres et al., 1992; Varma et al., 2010). Heavy metals are threats to both flora and fauna due to their bioaccumulation tendency and toxicity in biological systems (Friis and Myers - Keith, 1986; Singh et al., 2012). Cadmium is one of the heavy metals whose toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer, and diabetes (Hussein & Mohey, 2011). Cadmium concentrates in the kidney, liver, and other organs and is considered more toxic than both lead and mercury. The removal of these metals from both municipal and industrial wastes/effluents before being discharged into the ambient environment. Therefore, paramount in order to reduce the negative effects (Asiagwu, 2012).

Conventional treatment methods such as ion-exchange, reverse osmosis, precipitation, flocculation, electro thermal treatment, solvent extraction… etc. have disadvantages like incomplete metal removal, high reagent and energy requirements, high cost and generation of toxic sludge’s to mention but few. The search for suitable environmental – friendly alternative techniques that are affordable, efficient and can complement or replace the existing methods has been in place for some time now and attention is been directed to biosorption based on metal binding capacities of various biological materials (Tien, 2002; Hanif et al., 2007; Tuzen et al., 2008). In this study, the potential of Nymphaea ampla leaf to adsorb cadmium from aqueous solutions is being studied.

2. Materials and Methods:
2.1. Preparation of Biosorbent:

Matured Nymphaea ampla leaves were harvested from a farm behind the Abuja Hostel of the University of Jos, Plateau State, Nigeria. The leaves were thoroughly washed with deionized water and air-dried. The dried leaves were then grinded and sieved...
with a 250µm mesh and stored in an air-tight container.

2.2. Batch Adsorption Experiments:

All glassware’s were washed with 1M HNO₃ and subsequently rinsed severally with deionized water to remove all possible interferences. Batch adsorption studies were carried out in 250 mL Erlenmeyer flasks to study the influence of initial cadmium ion concentration (0.5 mg/L to 5.0 mg/L), pH (4.5 to 7.0), contact time (5 to 120 min), adsorbent dose (10 mg to 120 mg) and temperature (150°C to 55°C). The experimental flasks were agitated at 200rpm in a rotating shaker for a specified time period. The pH of the solution was adjusted with 0.1M NaOH and HNO₃ as the case may be. At the end of the experiments, the flasks were removed from the shaker and the solutions separated from the biomass by filtration using filter paper (Whatman no.1) and the filtrate analyzed for residual cadmium (II) ion concentration using atomic adsorption spectrophotometer (AAS), model DK420. The metal uptake capacity (qₑ) and the adsorption efficiency (E) were calculated using the following equations:

\[
q_e = \frac{(C_i - C_e)V}{M}
\]

(1)

\[
E = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

(2)

where \( C_i \) = Initial cadmium concentration in mg/L, \( C_f \) = Final cadmium concentration in mg/L, \( V \) = Volume of the reaction mixture (L) and \( M \) = mass of the adsorbent in the reaction mixture (g).

3. Results and Discussion:

3.1. Effect of initial Cadmium (II) ion concentration:

The rate of adsorption is a function of the initial concentration of the adsorbate which makes it an important factor to be considered for effective adsorption. As shown in Figure 1, the adsorption capacity at equilibrium increased with increase in initial cadmium (II) ion concentration. This is considered possible due to the fact that the initial concentration of the metal ions provided the necessary driving force to overcome the mass transfer resistance of the cadmium (II) ions in the aqueous phase (Chowdhury and Saha, 2010). The increase in initial concentration also enhances the interaction between the cadmium ions in the aqueous phase and the biomass. Similar results were obtained in the adsorption of chromium (VI) ions onto natural plant materials by Devaprasath et al. (2007).

3.2. Effect of pH

The effect of pH on the removal efficiency of cadmium (II) ion by Nymphaea ampla leaf biomass is shown in Figure 2 for a pH range of 4.5 to 7.0. Maximum adsorption was obtained at pH 7.0 which was subsequently used for other batch studies. The results showed that acidic conditions did not favour sorption of cadmium (II) ions onto Nymphaea ampla leaf. The reason could be that, under acidic conditions, the surface of the adsorbent may be closely associated with H⁺ and H₃O⁺ which may hinder the access of metal ions to the surface of the adsorbent thereby reducing the percentage metal ion adsorption (Sar and D'Souza, 2002).

3.3. Effect of Contact Time

The uptake of cadmium (II) ion as a function of contact time is shown in Figure 3. Adsorption of cadmium (II) ion increased with the rise in contact time up to 30 minutes. Further increase in contact time resulted in decreased adsorption. At 30min., 80.8% adsorption was achieved. The fast adsorption rate at the initial stage may be as a result of more availability of active adsorbing / binding sites in the adsorbent surface (DAS et al., 2012). The decrease in adsorption observed as time progresses beyond 30min. may be due to the fact that every adsorbent has limited a number of active sites which becomes occupied with
time and continuous agitation may result in desorption (Badmus et al., 2007). Similar results were obtained by Dawodu et al., (2012) who observed maximum adsorption of cadmium (II) ion onto Agbani clay from aqueous solutions at 50 min.

Figure 3. Effect of contact time (pH = 7.0, concentration = 2.0 mg/L, dose = 30 mg).

3.4. Effect of Biomass Dose

The adsorbent dose is a significant factor for sorbent – sorbate equilibrium of a system (Saleem and Bhatti, 2011). From Figure 4, the percent removal increased with increase in adsorbent dose. This was possible due to increased surface area of the adsorbent which in turn increased the number of active binding sites. Maximum cadmium uptake (83%) was observed with the 120 mg dose. Similar results were reported by Varma et al. (2010) for cadmium (II) ion adsorption using Psidium guajava leaves powder.

Figure 4. Effect of adsorbent dose (pH = 7.0, concentration = 2.0 mg/L, time = 30 min).

3.5. Effect of Temperature

The temperature effect is shown in Figure 5. From the results, the adsorption of cadmium (II) ion decreased with increasing temperature. This is probably due to the exothermic behaviour between the surface of the biomass and cadmium ions which resulted from the weakening of attractive forces between them and decreases in the thickness of the boundary layer (Cruz et al., 2004; Horsfall and Spiff, 2005; Bhatti et al., 2009). Similar results were obtained for the adsorption of cadmium (II) using Nymphaea ampla root biomass (Gongden et al., 2014).

Figure 5. Effect of temperature (pH = 7, concentration = 2.0 mg/L, time = 30 min, dose = 120 mg).

3.6. Adsorption Isotherm Models

The extent of adsorption was estimated using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherms. Adsorption isotherm is the basic requirement for designing any adsorption system. Isotherm expresses the relation between the amounts of adsorbate removed from the liquid phase by a unit mass of adsorbent at constant temperature (Shokoohi et al., 2009). The obtained experimental data here are expectedly well fitted with the Linearized form of these four two-parameter isotherm models.

Langmuir Isotherm:

\[ q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \]  

Linearised Langmuir Isotherm:

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L C_e} \]  

where \( q_{\text{max}} \) is the maximum adsorption capacity (mg/g) and \( K_L \) is the Langmuir equilibrium constant (L/mg) related to the energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. To further quantify the adsorption properties of the Langmuir isotherm, a dimensionless separation factor, \( R_L \) was used. This is given as:

\[ R_L = \frac{1}{1 + K_L C_e} \]  

The value of RL indicates the type of Langmuir isotherm to be irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)) or unfavorable.
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(R_L > 1). Apparently when K_L > 0, sorption is favorable (Langmuir, 1918; Ho et al., 2002).

The Freundlich isotherm, applicable to nonideal heterogeneous surfaces was chosen to estimate the adsorption intensity of the adsorbent and the linear form of the isotherm can be represented as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (6)

Where $K_F$ and $n$ are Freundlich constants which correlated to the maximum adsorption capacity and adsorption intensity respectively (Freundlich, 1906).

Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage (Liu and Liu, 2008).

Temkin isotherm:  
$$q_e = \frac{RT}{b_T} \ln(AC_e)$$  \hspace{1cm} (7)

Linearised Temkin isotherm:  
$$q_e = B \ln A + B \ln C_e$$  \hspace{1cm} (8)

where $T$ is the temperature (°K), $R$ is the ideal gas constant (8.314 Jmol⁻¹K⁻¹), $A$ and $B$ are constants. The constant $b_T$ is related to the heat of adsorption and $A$ is the equilibrium binding constant (L/g) corresponding to the maximum binding energy (Pearce et al., 2003; Akkyar and Özer, 2005).

The Dubinin-Radushkevich (D-R) model was chosen to estimate the heterogeneity of the surface energies. The linear form of D-R isotherm equation is represented as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2; \text{ where } \varepsilon = RT \ln(1+1/C_e)$$  \hspace{1cm} (9)

where $q_m$ is the theoretical saturation capacity (mg/g), $\beta$ is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol⁻²J²) and $\varepsilon$ is the Polanyi potential. $R$ (Jmol⁻¹K⁻¹) is the gas constant and $T$ (°K) is the absolute temperature. The constant $\beta$ gives an idea about the mean free energy $E$ (J/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship (Erdem et al., 2004; Kundu, and Gupta 2006):

$$E = \frac{1}{\sqrt{2\beta}}$$  \hspace{1cm} (10)

The isotherm plots for the sorption of the metal ions are shown in Figures 6 to 9 and the results are as shown in Table 1. Freundlich adsorption isotherm model yielded best fit to the experimental equilibrium adsorption data than the Langmuir, Temkin, and D-R isotherm models for cadmium (II) adsorption according to the values of $R^2$ obtained. It was also seen that the Langmuir maximum adsorption capacity ($q_{max}$) is 3 mg/g and the equilibrium constant ($K_L$) is 13 L/mg. From the values of $R_L$ (Table 2), it could be seen that the isotherm was favorable for the adsorption of cadmium (II) ion onto the biomass.

According to Abasi et al. (2011), n values between 1 and 10 shows easy separation beneficial adsorption and high affinity of the adsorbent to the metal ions. For D-R isotherm, it has been reported that physisorption processes usually have adsorption energies < 40 KJ/mol and above this value, sorption is of chemisorption mechanism (Horsfall et al., 2004). If the mean biosorption energy ($E$) value is between 8.0 and 16.0 KJ/mol, the biosorption process follows chemical ion exchange and if $E < 8.0$ KJ/mol, the biosorption process is of a physical nature (Lodeiro et al., 2006; Sari et al., 2007). Therefore, $E$ value of 3.54 KJ/mol showed that the sorption process was of a physical nature for the adsorption of cadmium (II) ion onto Nymphaea ampla leaf biomass.

Figure 6. Langmuir isotherm model for cadmium adsorption.

Figure 7. Freundlich isotherm model for cadmium adsorption.
3.7. Adsorption Kinetic Modeling

In order to analyze the rate of adsorption and possible adsorption mechanism of Cd (II) onto the biomass, the Lagergren first-order, pseudo-second order and intra-particle diffusion kinetic models were applied to adsorption data.

The Lagergren first-order rate equation is represented as (Lagergren, 1891):

$$\log (q_e - q_t) = \log q_e - \frac{kt}{2.303}$$  (11)

The pseudo-second order equation is given as (Saleem and Bhatti, 2011):

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  (12)
3.8. Thermodynamic Treatment of the Sorption Process

The thermodynamic parameters such as free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were evaluated using the following expressions:

$$\Delta G = -RT \ln K_c$$  \hspace{0.5cm} (14)

$$K_c = \frac{C_{Ac}}{C_e}$$  \hspace{0.5cm} (15)

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H}{2.303RT}$$  \hspace{0.5cm} (16)

where $C_e$ is the equilibrium concentration in solution in mg/L, $C_{Ac}$ is the equilibrium concentration on the sorbent in mg/L and $K_C$ is the thermodynamic equilibrium constant.

$T$ is the absolute temperature in Kelvin and $R$ is the universal gas constant (8.314 JK$^{-1}$mol$^{-1}$). The Gibbs free energy ($\Delta G^0$) for the adsorption of cadmium (II) onto biomass at all temperatures was obtained from Eq. 14 and is presented in Table 4.

The values of $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept of the plot log$K_c$ against $1/T$ (Figure 13) and are also listed in Table 5. In order to support that physical adsorption is the predominant mechanism, the values of activation energy (Ea) and sticking probability ($S^*$) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage ($\theta$) as follows (Horsfall and spiff, 2005):

$$\theta = \left(1 - \frac{\theta^*}{\theta^*}ight) \text{ and } S^* = (1 - \theta) \exp \left(\frac{E_a}{R \theta^*} \right)$$  \hspace{0.5cm} (17)

The guidelines for the potential sticking probability are; $S^* > 1$ indicates no sorption, $S^* = 1$ indicates linear sticking relationship between adsorbent and adsorbate and mixture of physisorption and chemisorption, $S^* = 0$ indicates indefinite sticking of adsorbate to adsorbent with chemisorption being the predominant mechanism and $0 < S^* < 1$ indicates favorable sticking of the adsorbate with physisorption being the predominant mechanism.

From Table 4 it is clear that the reaction is spontaneous in nature as $\Delta G^0$ values are negative at all the temperatures studied. Again negative $\Delta H^0$ value confirms that the sorption is exothermic in nature. The negative value of $\Delta S^0$ reflects decreased randomness at the solid-solution interface during the adsorption of cadmium (II) ions. The value of $E_a$ was found to be -1.88 kJ/mol for the adsorption of cadmium (II) onto biomass. The negative value of $E_a$ indicates the exothermic nature of the adsorption process which is in accordance with the negative value of $\Delta H^0$. The result as shown in Table 5 indicate that the probability of the cadmium (II) ions to stick on the surface of biomass is high as $S^* < 1$, these values confirm that the sorption process is physisorption.

![Figure 12. Intra-particle diffusion model for cadmium (II) adsorption.](image)

![Table 3: Comparison between kinetic models for Cadmium (II) ions sorption unto Nymphaea ampla leaf biomass.](table)

<table>
<thead>
<tr>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e$, exp = 2.694mg/g</td>
<td>$q_e$, cal = 0.05mg/g</td>
<td>$q_e$, cal = 2.5mg/g</td>
</tr>
<tr>
<td>$K_i$ = 0.213g/mg.min</td>
<td>$K_i$ = 0.033mg/mg.min$^{-2}$</td>
<td>$K_i$ = 2.363</td>
</tr>
<tr>
<td>$K_i$ = 1.38x10$^{-3}$min$^{-1}$</td>
<td>$R^2$ = 0.997</td>
<td>$R^2$ = 0.104</td>
</tr>
<tr>
<td>$R^2$ = 0.966</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 13. The plot of log$K_c$ against $1/T$ for Cd (II) ion adsorption.](image)

![Table 4: Values for Gibb’s Free Energy at Various Temperatures.](table)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>288</th>
<th>298</th>
<th>310</th>
<th>318</th>
<th>328</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^0$(KJ/mol)</td>
<td>-1.860</td>
<td>-1.860</td>
<td>-1.798</td>
<td>-0.482</td>
<td>-1.447</td>
</tr>
</tbody>
</table>

![Table 5: Thermodynamic Parameters for adsorption of Cd (II) ions unto Nymphaea ampla Biomass.](table)

<table>
<thead>
<tr>
<th>$\Delta S^0$(KJ/mol)</th>
<th>$\Delta H^0$(KJ/mol)</th>
<th>Ea(KJ/mol)</th>
<th>$S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0078</td>
<td>-4.10</td>
<td>-1.88</td>
<td>0.752</td>
</tr>
</tbody>
</table>
4. Conclusion

The biomass of Nymphaea ampla leaf proves to be highly efficient adsorbent for the removal of cadmium (II) ions from aqueous solution. The adsorption process is also dependent on numerous factors such as initial metal ion concentration, the solution pH, contact time, adsorbent dosage and temperature. The maximum adsorption of cadmium (II) ions was found to be at pH 7 for a 3.2 mg/g biomass and initial cadmium concentration of 2.0 mg/L. The study on equilibrium sorption revealed that Freundlich isotherm model gave the best fit to experimental data. In the study of the kinetics of sorption, the pseudo-second-order kinetic model provides better correlation of the sorption data. Intra-particle diffusion was not the sole rate-limiting step. The calculated thermodynamic parameters showed the exothermic and spontaneous nature of the adsorption of cadmium onto Nymphaea ampla leaf biomass. Furthermore, calculated sticking probability indicates excellent sticking of metal ions onto Nymphaea ampla leaf biomass. The present findings suggest that Nymphaea ampla leaf biomass may be used as an inexpensive and effective adsorbent for the removal of cadmium (II) ions from aqueous solution.

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