EVALUATION OF TEA BIOMASS FOR NICKEL CONTAMINATED WASTE WATER TREATMENT

P.E. AIKPOKPODION1, R.R. IPINMOROTI1 AND S.M. OMOTOSO2

1Cocoa Research Institute of Nigeria, P.M.B. 5244, Ibadan, Nigeria, 2Rotas soilab, Ibadan, Nigeria.

Corresponding author & E-mail address: P.E. Aikpokpodion, E-mail: paulaikpokpodion2@yahoo.com
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ABSTRACT


Industrial effluents loaded with heavy metals are a cause of health hazard to human and other forms of life as a result of their discharge into water bodies. Conventional methods for the removal of heavy metals from waste water are however, often expensive having inadequate efficiencies at low metal concentrations. These constraints have caused the search for alternative technologies for sequestering metals to cost effective and environmentally acceptable level. Waste tea biomass which contain active sites for metal adsorption was evaluated for the treatment of nickel contaminated waste water. Biosorption experiment was performed in a rotary shaker at 180rpm at different reaction time of 20, 30, 40, 120 and 180 minutes. Five levels of nickel solutions were also prepared (10g L\(^{-1}\), 20g L\(^{-1}\), 30g L\(^{-1}\) and 50g L\(^{-1}\)) at different pH (2,3,5, and 7) in order to determine the best pH for optimum nickel adsorption. The generated data were fitted into Elovic, parabolic diffusion, intra-particle diffusion, pseudo-first order and pseudo-second order kinetic models. Langmuir and Freundlich equations were also used to determine which of the models best describe the adsorption process. Result showed that, Langmuir and Freundlich equations gave good fit into the adsorption of nickel on the biomass with correlation coefficients of determination \(R^2\) 0.999 and 0.998 respectively. The biomass adsorbed 98% of 10gL\(^{-1}\) nickel (II) solution while 30% of 50g L\(^{-1}\) nickel solution was adsorbed. Adsorption was found to increase as pH of solution increased up to 5 after which adsorption decreased. Pseudo second order best described the adsorption reaction rate with \(R^2\) value of 0.99. It can then be concluded that, the best solution pH for optimal removal of nickel from waste water is pH 5 and the appropriate metal concentration for nickel contaminated waste water treatment is 10gL\(^{-1}\). Hence, it is recommended that, industrial effluent contaminated with nickel should be diluted to 10g L\(^{-1}\) nickel.

Key words: biosorption, waste tea, nickel, adsorption

INTRODUCTION

Discharge of heavy metals into aquatic ecosystem has become a matter of concern over the last few decades. The pollutants of serious concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel etc. The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life (Mohammadi et al. 2005), besides the fact that these metals kill micro organisms during biological treatment of waste water with a consequent delay of the process of water purification (Wallace 2003) Most of the heavy metals salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical means of separation.

Nickel is a toxic heavy metal that is widely used in refineries (Kadirvelu et al. 2001). The chronic toxicity of nickel to humans and the environment has been documented. For example, high concentration of Ni\(^{2+}\) causes cancer of the lungs, nose and bone. It is essential to remove nickel from industrial wastewater before being discharged into the environment. So many advanced treatment processes such as chemical reduction, ion exchange, reverse osmosis, electro-dialysis and activated carbon adsorption are used for the treatment of wastewater before they are finally discharged into water bodies (Muhammadi et al. 2004). Unfortunately, the cost of these processes is high. Hence, the use of agricultural residues or industrial bi-products having biological activities have been received with considerable attention (Hasar et al. 2000).

In recent years, a number of agricultural materials such as coconut husk (Tan et al. 1993), rice husk (Munah & Zein, 1997), almond husk (Hasar & Cuci, 2000) and a host of other agricultural bi-products have been reported for the removal of toxic metals from aqueous solutions. Most of these materials contain certain functional groups associated with protein, polysaccharides, lignin and cellulose as major constituents. Metal uptake is believed to occur through sorption process involving these functional groups (Khalid et al. 2000).

Camellia sinensis (Tea) is extensively grown on the Mambilla Plateau and readily available in abundance as by-product of highland tea. The by-product is discarded after separating the useful part through sieving. Little or no information is available in Nigeria on the use of waste tea biomass in treating industrial effluent before discharge in the environment. It was therefore necessary to evaluate the potential of this material in adsorbing nickel from contaminated water.

MATERIALS AND METHODS

Biosorbent, stock solution and treatment factors

Waste tea used as clean-up material was collected from the highland tea factory located on the Mambilla-Plateau in Taraba State, Nigeria. Mambilla plateau (6.713837°N 11.25002°E) has the highest altitude and the coldest part of
country where the temperature hardly exceed 25 degrees centigrade. The rainfall pattern and the unique climatic condition favor the cultivation of highland tea (*Camellia sinensis*) in this part of the country. The bi-product was oven dried at 50°C for 8 hours. The dried material was then pulverized and sieved with 200 micron sieve.

Stock solution of 1000mg/L of Ni (II) was prepared by dissolving 4.4790g of ultra pure nickel sulphate (NiSO$_4$.6H$_2$O) in double distilled water. All reagents were of analytical reagent grade. Biosorption experiments were performed in a rotary shaker at 180 rpm using 250ml Erlenmeyer flask containing 0.4g of waste tea powder and 60ml of 10g L$^{-1}$, 20g L$^{-1}$, 30g L$^{-1}$ and 50g L$^{-1}$ Ni(II) solution. The experimental set was repeated for various time intervals of 20, 40, 60, 120 and 180 min. At the end of each contact time, the content of each flask was filtered using Whatman filter paper No 41. The metal content in the supernatant was determined using Buck Scientific Atomic absorption spectrophotometer. The amount of Ni(II) adsorbed by the biomass was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation.

$$q_e = \frac{(C_o - C_e) \times V}{M}$$

Where $q_e$ is the metal uptake (mg/g), $C_o$ and $C_e$ are the initial and equilibrium metal concentrations in the solution (mg/L), respectively, $V$ is the solution volume (ml) and $M$ is the mass of biosorbent (g).

**Sorption efficiency (%) =** $\frac{(C_o - C_e) \times 100}{C_o}$

**Methods used for determining nickel Contamination**

**Kinetic modeling of Ni (II) adsorption mechanisms:** Kinetics describe the solute uptake rate which in turn controls the resident time of sorbate uptake at the solid-solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. Adsorption kinetics of metal transport onto an adsorbent can be controlled by several independent processes. These are (i) Bulk diffusion (ii) External mass transfer (film diffusion) (iii) Chemical reaction (Chemisorptions) and (iv) Inter-particle diffusion. These processes can act in series or parallel to account for the surface transport of a metal into an adsorbent (Ho et al. 2000).

To investigate the mechanism of adsorption of nickel unto waste tea powder, some kinetics models were used to analyze the mechanism of Nickel(II) ion sorption. These kinetic models include: Pseudo-first order, Pseudo-second order, Elovich equation, parabolic diffusion and intra-particle diffusion model (Halil 2003).

To determine which of these mechanisms could account for Ni(II) ion transport unto the waste tea powder, it is necessary to assume that each one of the concurrent processes dominates over the others at specific time regimes of the sorption process (that is the rate determining step) and thereby study them independently (Loukidou et al. 2004). Linear regressions are frequently used to determine the best fitting kinetic models. The most commonly used method is the coefficient of determination $R^2$, since a kinetic model is concerned with the effect of observable parameters on the overall rate (Ho 2006). The best fitting kinetic model for the adsorption of Ni(II) ions by waste tea powder is the one with the highest coefficient of determination i.e. the kinetic model with $R^2$ values closest to unity is taken as the most appropriate mechanism of sorption.

**RESULTS AND DISCUSSION**

**Effect of pH**

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls. Thus, pH is an important process parameter on biosorption of metal ions from aqueous solution since it is responsible for protonation of metal binding sites. (Katarzyna 2005).

The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by functional groups that have cation-exchange properties. Result of effect of pH on Ni$^{2+}$ percent adsorption is presented in figure1. The solution pH ranged from 2 to 7. At lower pH values, nickel removal was inhibited possibly as a result of the competition for binding sites.

![Figure 1: Effect of solution pH on percent Ni(II) adsorption](image)
between hydrogen and nickel ions on the sorption site, with an apparent preponderance of hydrogen ions, which restricts the approach of metal ions as a consequence of the repulsive force. Biosorption of Ni\(^{2+}\) was at maximum at pH 5. As the pH exceeded 5, the biosorption began to decrease. This is possibly due to precipitation of Ni(II) ions as a result of hydroxide anions forming Nickel hydroxide precipitate.

This result is similar to the report of Halil (2003) who had maximum Ni(II) sorption at pH 5 using activated charcoal. It was also observed from the result fig(1), that the initial metal concentration of solution could be an additional factor that contributes to amount of metal adsorbed at various pH levels. Within the same pH, the amount of Ni(II) adsorbed decreased with increased initial metal concentration(fig. 1).

**Effect of initial metal concentration on percentage metal uptake**

Result (fig. 2) showed the effect of initial metal concentration on the adsorption of nickel on waste tea powder. Result showed that percent metal uptake decreased with increased initial metal concentration. The decrease in percent adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percent adsorption at higher concentration levels showed a decreasing trend whereas the equilibrium uptake of metal displays an opposite trend. The solution with the lowest initial metal concentration had the highest percent adsorption of nickel unto the biomass. At lower concentrations, almost all Ni(II) ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher nickel solutions. At higher concentration, lower adsorption yield is due to the saturation of adsorption sites which is a consequence of increase in the number of ions competing for available binding sites in the biomass (Puranik & Paknikar, 1999).

**Effect of reaction time on Nickel adsorption**

Performance of waste tea on the biosorption of Ni\(^{2+}\) at varying concentration was carried out with initial Ni\(^{2+}\) concentration of 10g L\(^{-1}\), 20g L\(^{-1}\), 30g L\(^{-1}\) and 50g L\(^{-1}\) and the biosorbant dose was 14g L\(^{-1}\). Result (fig. 3) showed that, capacity of biosorption increased with reaction time. The biosorption capacity increased slowly at the initial reaction time and steadily increased as the agitation time proceeds. The increase in amount of Ni\(^{2+}\) adsorbed as the chemical modification increase may be due to the increased number of binding sites due to the chemical modification. The agitation between the adsorbate and the adsorbent might have also increased the reactants energy which enhanced the binding of Ni\(^{2+}\) into functional groups present in the biomass. Result also showed that, the highest biosorption capacity of waste tea took place in initial10g L\(^{-1}\) nickel solution. Adsorption reaction in solution with initial Ni\(^{2+}\) concentration of 30g L\(^{-1}\) got to saturation at 120min of reactions while solution with initial concentration of 50g L\(^{-1}\) got to saturation at 60mins of the reaction.

**Langmuir Isotherm**

The equilibrium adsorption isotherm is of importance in the design of adsorption system (Wange et al. 2005). Several isotherm equations are available and the Langmuir is one of the selected isotherms in the study. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption processes of monolayer adsorption. The Langmuir adsorption isotherm can be written as:

\[
q_e = \frac{q_m b c_e}{1 + b c_e}
\]
The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from the above equation.

\[
\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}
\]

Where \(q_e\) is the adsorbent amount (mg g\(^{-1}\)) of the Ni (II), \(C_e\) is the equilibrium concentration of the Ni(II) in solution (mg L\(^{-1}\)), \(q_m\) is the monolayer adsorption capacity (mg g\(^{-1}\)) and \(b\) is the constant related to the free energy of adsorption (mg L\(^{-1}\)). The constants \(q_m\) and \(b\) are determined from the linear plots of \(C_e/q_e\) versus \(C_e\). The values of the \(q_m\) and \(b\) are determined from the slope and the intercept respectively in which \(q_m\) is the maximum adsorption while \(b\) (mg L\(^{-1}\)) represents the affinity between the sorbate and the sorbent. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter \(R_L\) was determined by using the following equation (Magdy and Daifullah, 1988).

\[
R_L = \frac{1}{1 + b C_0}
\]

Where \(C_0\) is the initial concentration and \(b\) is the Langmuir isotherm constant (intercept). The parameter \(R_L\) indicates the shape of isotherm. The process is irreversible if \(R_L = 0\), favorable if \(R_L < 1\), linear if \(R_L = 1\) and unfavorable if \(R_L > 1\).

The Langmuir equation was used to describe the data derived from the adsorption of Ni(II) from the solution by waste tea powder. The plot of \(C_e/q_e\) versus \(C_e\) presented in figure 4 shows that the experimental data fitted reasonably with the linearised equation of the Langmuir isotherm. The correlation coefficient of determination \(R^2\) value of 0.99 further confirm the fitness of Langmuir model in describing the adsorption of nickel by waste tea. \(q_{max}\) and \(b\) determined from the slope and intercept were found to be 1.07mg/g and 0.00016 L/mg respectively. The \(R_L\) value calculated to be 0.98 showed that the adsorption was favorable according to the rating of Magdy & Daifullah, 1998.

**Freundlich Equation**

The linear form of Freundlich isotherm model is given by the following relations:

\[
\ln q_e = \ln K + \frac{1}{n} \ln C_e
\]

Where \(q_e\) is the amount adsorbed of equilibrium (mg/g), \(C_e\) is the equilibrium concentration of the adsorbate (mg/L) and \(K\) and \(\frac{1}{n}\) is the Freundlich constants related to adsorption capacity and adsorption intensity respectively of the sorbent. The values of \(K\) and \(\frac{1}{n}\) can be obtained from the intercept and slope respectively of the linear plot of experimental data of \(\ln q_e\) versus \(\ln C_e\).

The data obtained from the adsorption isotherm were also fitted into the Freundlich model. The result revealed that the adsorption of Ni(II) on waste tea powder fits into the Freundlich adsorption isotherm with a correlation coefficient of determination \(R^2\) value of 0.99 which is close to unity. The high value of Freundlich constant \(K\) (0.9342), showed easy uptake of Ni(II) ions from aqueous solution. The \(n\) value calculated from the graph (7.84) reflects the intensity of sorption and also signifies that, the surface of the biosorbent is heterogeneous in nature i.e fractional value of \(\frac{1}{n}\) (0 < \(\frac{1}{n}\) <1) (Khalid et al. 2002).
Evaluation of tea biomass for nickel contaminated waste water treatment

**Figure 5: Freundlich Isotherm of Ni(II) adsorption on waste tea powder**

**Pseudo second order equation**

If the rate of the sorption is a second order mechanism, the pseudo-second order mechanism, the pseudo-second order chemisorptions kinetic rate equation is expressed as:

\[
\frac{dqt}{dt} = k (q_e - qt)
\]

\[
\frac{dqt}{dq_e} = K (qe-qt)^2
\]

Integrated pseudo-second order rate law can be obtained from equation (1) for the boundary conditions \( t = o – t \) and \( qt = 0 – qt \) gives:

\[\frac{1}{(q_e - qt)} = \frac{1}{qt} + Kt\]

Equation above can be rearranged to obtain a linear form:

\[\frac{t}{qt} = \frac{1}{kq2e} + \frac{1}{q2e} t\]

where “\( t \)” is the contact time (min), \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount of the solute adsorbed at equilibrium at any time \( t \). If pseudo-second order is applicable, the plot of \( \frac{1}{qt} \) against “\( t \)” should give a linear relationship, from which \( q_e \) and \( k \) can be determined from the slope and intercept of the plot respectively. Table 2 shows the parameters of pseudo-second order rate and the linear regression correlation coefficient value \( R^2 \). It was observed from the table that, 30g/L and 50g/L Ni(II) had lower \( q_e \) values of 4.98 and 3.28 respectively as compared with 10g/L and 20g/L with \( q_e \) values of 12.64 and 10.22 respectively. Table of result also showed that, 30g/L and 50g/L Ni(II) solution had the higher values of corresponding linear regression correlation coefficient \( R^2 \) of 0.99 and 0.9999 respectively compared with their counterpart solutions. The higher \( R^2 \) values of these two levels of Nickel solution confirm that the rate of adsorption is well described by pseudo-second order kinetic and hence, the adsorption of 30g/L and 50g/L Ni(II) ions unto adsorption sites is proportional to the square of the number of unoccupied sites (Aitunes et al. 2003). In addition, the pseudo-second order model is based on the assumption that the sorption of a metal by an adsorbent may involve a chemical sorption (chemisorptions) which can be the rate controlling step (Ho et al. 2002). The applicability of pseudo-second order rate also point to the fact that biosorption is the rate-limiting step; and that sorption of the metal ions involves two species, in this case, the metal ion and the biomass (Wallace et al. 2003). The slight deviation of \( R^2 \) values of 10mg/L and 20mg/L Ni(II) solutions suggest that, concentration of metal ions in solution could also influence the rate determining step.
Table 1: Elovich equation parameters of the adsorption of Ni(II) on waste tea

<table>
<thead>
<tr>
<th>Ni(II) Concentration</th>
<th>1/α</th>
<th>Ln (α α^1)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>2.6269</td>
<td>-5.3366</td>
<td>0.68</td>
</tr>
<tr>
<td>20g/L</td>
<td>1.8873</td>
<td>-3.6492</td>
<td>0.66</td>
</tr>
<tr>
<td>30g/L</td>
<td>0.7964</td>
<td>0.8725</td>
<td>0.83</td>
</tr>
<tr>
<td>50g/L</td>
<td>0.0714</td>
<td>2.8650</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 2: Pseudo second-order equation parameters of the adsorption of Ni(II) on waste tea

<table>
<thead>
<tr>
<th>Ni(II) Concentration</th>
<th>1/Qe</th>
<th>1/Qe^2</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>0.0891</td>
<td>8.2195</td>
<td>0.61</td>
</tr>
<tr>
<td>20g/L</td>
<td>0.0898</td>
<td>8.3286</td>
<td>0.68</td>
</tr>
<tr>
<td>30g/L</td>
<td>0.2508</td>
<td>3.7135</td>
<td>0.99</td>
</tr>
<tr>
<td>50g/L</td>
<td>0.3653</td>
<td>0.3433</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 3: Parabolic diffusion equation parameters of the adsorption of Ni(II) on waste tea

<table>
<thead>
<tr>
<th>Ni(II) Concentration</th>
<th>a</th>
<th>Kd</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>0.8763</td>
<td>-3.0216</td>
<td>0.91</td>
</tr>
<tr>
<td>20g/L</td>
<td>0.7662</td>
<td>-2.4500</td>
<td>0.91</td>
</tr>
<tr>
<td>30g/L</td>
<td>0.4456</td>
<td>-0.2806</td>
<td>0.72</td>
</tr>
<tr>
<td>50g/L</td>
<td>0.2533</td>
<td>0.5502</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 4: Pseudo first order model parameters of the adsorption of Ni(II) on waste tea

<table>
<thead>
<tr>
<th>Ni(II) Concentration</th>
<th>K1</th>
<th>qe</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>-0.0047</td>
<td>1.0030</td>
<td>0.81</td>
</tr>
<tr>
<td>20g/L</td>
<td>-0.0015</td>
<td>0.7579</td>
<td>0.90</td>
</tr>
<tr>
<td>30g/L</td>
<td>-0.0013</td>
<td>0.1400</td>
<td>0.89</td>
</tr>
<tr>
<td>50g/L</td>
<td>-0.0055</td>
<td>-0.6767</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 5: Intra-particle diffusion equation parameters of the adsorption of Ni(II) on waste tea

<table>
<thead>
<tr>
<th>Ni(II) Concentration</th>
<th>a</th>
<th>Kd</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>0.4371</td>
<td>0.8815</td>
<td>0.77</td>
</tr>
<tr>
<td>20g/L</td>
<td>0.3717</td>
<td>0.6554</td>
<td>0.72</td>
</tr>
<tr>
<td>30g/L</td>
<td>0.1984</td>
<td>0.7642</td>
<td>0.83</td>
</tr>
<tr>
<td>50g/L</td>
<td>0.0210</td>
<td>0.7563</td>
<td>0.79</td>
</tr>
</tbody>
</table>

**Pseudo-first order equation**

The pseudo-first order equation of Lagergren (Lagergren et al. 1898) is generally expressed as follows:

\[
\frac{dq_t}{dt} = K_1 (q_e - q_t)
\]

where \(q_e\) and \(q_t\) are the sorption capacities at equilibrium and at time \(t\), respectively (mg/g) and \(k\), is the rate constant of pseudo-first order sorption (L/min).

The integrated form becomes:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t
\]
The equation is applicable to experimental results and generally differs from a true first order equation in two ways (Aharoni & Sparks, 1991).

(i) The parameter $k_1 (q_e - q_t)$ does not represent the number of available sites; and 
(ii) The parameter log $(q_e)$ is an adjustable parameter which is often not found equal to the intercept of a plot of log $(q_e - q_t)$ against $t$, whereas in a true first order sorption reaction log $(q_e)$ should be equal to the intercept of a plot of log $(q_e - q_t)$ against $t$.

In order to fit the above equation to experimental data, the equilibrium sorption capacity $(q_e)$ must be known. In many cases $(q_e)$ is unknown and as chemisorption tends to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount (Ungarish & Aharoni, 1981). In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treating $(q_e)$ as an adjustable parameter to be determined by trial and error for this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity $(q_e)$, in order to analyse the pseudo-first order metal kinetics. In over 50% of literature references, based on analyzing sorption kinetics, the authors did not measure an equilibrium isotherm.

The pseudo-first order rate constant $k_1$ can be obtained from the slope of plot between log $(q_e - q_t)$ versus $t$. Figure 8 shows the Lagergren pseudo-first order kinetic plot for the adsorption of Ni(II) unto waste tea powder. The pseudo first order rate constant $k_1$ values were calculated from the slope. The calculated $k_1$ values and their corresponding linear regression correlation coefficient values are presented in table 4. The linear regression correlation coefficient value $R^2$ ranged from 0.81–0.90 for 10–50g/L Ni(II) solutions. The $R^2$ values show that this model can not be applied to predict the absorption kinetic model.

Elvich equation

The Elvich equation (Chem. & Dayton, 1980) was used to describe the adsorption rate of Ni(ii) by waste tea powder. The equation plots of Ni adsorbed $(q_e)$ versus ln of reaction time $(t)$ at 25°C for 0.2g of powder at 10, 20, 30 and 30g/L are shown in figure 10. A linear relationship exists between $q$ and ln $t$ for the four concentration levels. The result of the equation parameters is presented in Table 1. From the table, 10, 20, 30 and 50g/L Ni(II) had the ‘α’ values of 0.39, 0.5, 1.44, and 11.88 respectively. In Elvich equation, a decrease in ‘α’ indicates a reduction in the adsorption reaction rate (Chien and Clayton, 1980). Therefore, the rate of Ni(II) adsorbed by waste tea powder follows the order of 50>30>20>10mg/L Ni(II). This order of increase is a result of the concentration gradient (driving force) which is greatest in the 50g/L compared to the lower concentrated solutions of Ni (II) solution. Coefficients of correlation relating Ni(II) adsorption to ln of reaction time are presented in table 1. In all cases, $R^2$ values of 30g/L is the highest (0.82) followed by 50g/L (0.79). Solutions of 10g/L and 20g/L had lower $R^2$ values of 0.67 and 0.65 respectively compared with their counterpart solutions of higher Ni(II) concentrations. This then, suggest that, the higher the initial nickel concentration, the better the reaction rate is described by Elvich model.

The Intra-particle diffusion model

The intra-particle diffusion model is expressed as $R = K_{id} (t)^{1/2}$ (Srivastava et al. 1989)

A linearized form of the equation is followed by:

Log $R = \log K_{id} + a \log (t)$

Where R is the percent Ni$^{2+}$ adsorbed, $t$ is the contact time(min) “a” is the intraparticle diffusion rate constant(min$^{-1}$) $K_{id}$ may be taken as a rate factor i.e. percent Ni$^{2+}$ adsorbed per unit time (Demirbas et al. 2004). If the mechanism of adsorbed fits the intra-particle diffusion model, then a plot of log $R$ against log $t$ will yield a straight line with slope “a” and intercept of log $K_{id}$. The intra-particle diffusion model for the adsorption of Ni$^{2+}$ by waste tea powder is described in figure 9 while the model parameters are shown on table 5. Higher values of $K_{id}$ illustrate an enhancement in the rate of adsorption and better adsorption mechanism which is related to an improved bonding between the sorbate and adsorbent particles. The nickel solution with 10g/L Ni(II) had the highest $K_{id}$ value in the series of Nickel(II) concentrations while 20g/L Ni(II) solution had the least $K_{id}$ value of 0.645. On other hand, the coefficient of determination $R^2$ values (table 5) shows that, 30g/L and 50g/L solution of nickel solution had higher values which suggests that, initial concentration of Nickel (II) solution could be a factor that determines the pattern of intra-particle diffusion adsorption mechanism though all the data produced linear curve for the model.
Parabolic diffusion equation
Parabolic diffusion equation was used to describe the kinetic data of Ni(II) adsorption. The parabolic diffusion plots for Ni(II) ion adsorption on waste tea powder is presented in figure 6. Linear relationships exist between Nickel adsorbed (q) and $t^{1/2}$ for the four concentration levels of Ni(II) solutions. Parabolic diffusion law parameters were determined from the slope and intercept of the linear plots. Table 3 shows that 10g/L and 20g/L Ni(II) solution had the highest values of ‘a’ while the ‘a’ values of 30g/L and 50g/L Ni(II) solutions were much lower than their counterpart Nickel solution concentrations. The order of increase in the correlation coefficient of determination $R^2$ also follow the same order as that of ‘a’. This suggests that, there is much agreement between constant ‘a’ and $R^2$ in the parabolic diffusion equation. The $R^2$ values of 10g/L and 20g/L Ni(II) solution are much closer to unity while $R^2$ values of 30g/L and 50g/L Ni(II) solution are far from unity. This result suggests that, the concentration of metal solution seems to be a factor that determines the suitability of parabolic diffusion in describing the adsorption of metal (Nickel) by waste tea powder.

Figure 6: Parabolic diffusion isotherm

Figure 7: Pseudo-second order kinetics isotherm

Figure 8: Pseudo-first order kinetic isotherm

Figure 9: Intra-particle diffusion isotherm
CONCLUSION

The study revealed that, waste tea powder is an effective adsorbent for the adsorption of Nickel(II) ions from aqueous solutions. The effects of pH, metal ion concentration and reaction time on the adsorption process were distinct. The uptake of nickel ions by the biomass was increased by increasing metal ion concentration but decreased in percent adsorption of the total initial metal concentration. The metal uptake was also increased by increasing pH up to 5. Higher pH than 5 led to decrease in metal uptake. The highest percent adsorption of 98% was attained by metal initial concentration of 10g/L Ni(II). This then suggest that, for industrial application of waste tea powder to be effective in waste water treatment, nickel contaminated industrial effluent should be diluted to 10g/L Ni(II).

The adsorption isotherms of Ni(II) onto waste tea powder could be well fitted by the Langmuir and Freundlich equations. The biosorption could be best described by Pseudo-second order kinetics equation.

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