

Biosorption of Nickel (II) from Aqueous Solution Using Waste Tea (*Camella cinencis*) Materials

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Abstract: Biosorption is potentially an attractive technology for treatment of waste water for retaining heavy metals from dilute solutions. Several research in environmental biotechnology have shown that many biosorbents present in our environment have the capacity to remove heavy metals from solutions. This paper presents the result of studies carried out on sorption of nickel ions from aqueous solutions by waste tea (*Camellia cinencis*) powder as a low cost sorbent. The biosorption experiment were performed under various conditions such as different initial metal concentrations, pH and reaction time. It was found that, different concentration of nickel solution reached equilibrium at different times. About 0.2g of waste tea powder was found to be enough to remove 98% of 10g/L nickel ion concentration from 30ml metal solution. The optimum pH was found to be 5. The pseudo first order, pseudo second order, Elovich, intraparticle diffusion and parabolic diffusion models were used to describe the kinetic data. The data were best fitted with pseudo second order kinetic model for nickel. The experimental adsorption also reasonably fitted well the Langmuir and Freundlich isotherm.

Key words:

INTRODUCTION

The discharge of heavy metal 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, beside the fact that these metals kill micro organisms during biological treatment of waste water with a consequent delay of the process of water purification. 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 [1]. 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. 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. [2]. Unfortunately, the cost of these processes are expensive hence, the use of agricultural residues or industrial bi-products having biological activities have been received with considerable attention [3].

In recent years, a number of agricultural materials such as coconut husk [4], rice husk [5], almond husk [3] 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 functional groups associated with protein, polysaccharides, lignin and cellulose as major constituents. Metal uptake is believed to occur through sorption process involving the functional groups.

Tea waste is readily available in great abundance in Mambilla Plateau in Taraba State where it is grown extensively. During the production of highland tea, greater quantity of by-product is discarded as waste. The cell wall of waste tea consist of cellulose, lignin, carbohydrates which have hydroxyl groups in their structures. This paper report the effect of pH, contact time and initial concentration on Ni ²⁺ sorption by using waste tea powder.

Biosorbent Material: Tea waste was collected from the highland tea factory located on the Mambilla-Plateau in Taraba State. The bi-product was oven dried at 80°C for 8 hours. The dried material was then pulverised and sieved with 200 micron sieve.

Preparation of Stock Solution: All reagents were of analytical reagent grade. A stock solution of 1000mg/L of Ni (II) was prepared by dissolving 4.4790g of ultra pure nickel sulphate (NiSO₄. 6H₂O) in double distilled water.

Biosorption Experiments: Biosorption experiments were performed in a rotary shaker at 180 rpm using 250ml Erlenmeyer flask containing 0.2g of waste tea powder and 30ml of 10g/L, 20g/L, 30g/L and 50g/L 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.

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

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).

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

RESULTS AND DISCUSSION

Kinetic Modeling of Ni (II) Adsorption: 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 [6].

To investigate the mechanism of adsorption of Ni²⁺ into 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.

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 [7].

Linear regressions are frequently used to determine the best fitting kinetic models. The most common method used in the coefficient of determination R², since a kinetic model is concerned with the effect of observable parameters on the overall rate [8]. 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 R² values closest to unity is taken as the most appropriate mechanism of sorption.

Effect of PH: It is well known that the pH of the medium affects the solubility of metal ion 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, calcium carbonate solubility and metal speciation in the solution [9].

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 Ni²⁺ 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 between hydrogen and nickel ions in the sorption site, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as a consequence of the repulsive force.. Biosorption of Ni²⁺ 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, [10] who had maximum Ni(II) sorption at pH 5 using activated charcoal. It is also observed from the result Fig. (), that the initial metal concentration of solution

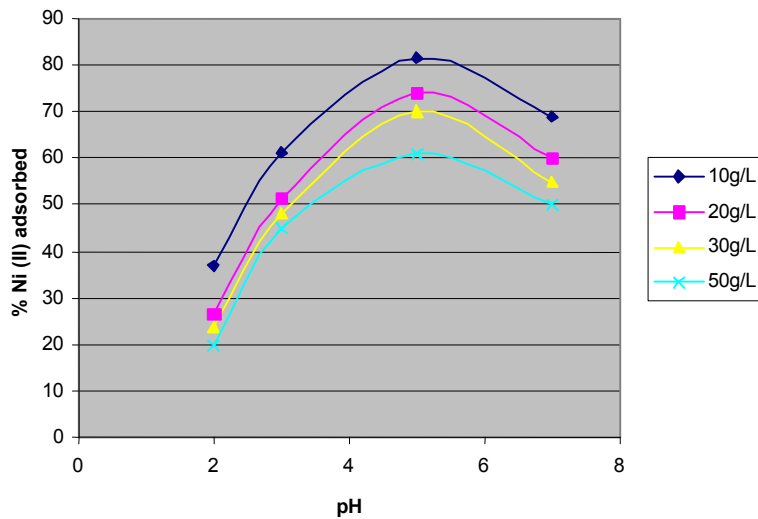


Fig. 1: Effect of solution pH on percent Ni (II) adsorption

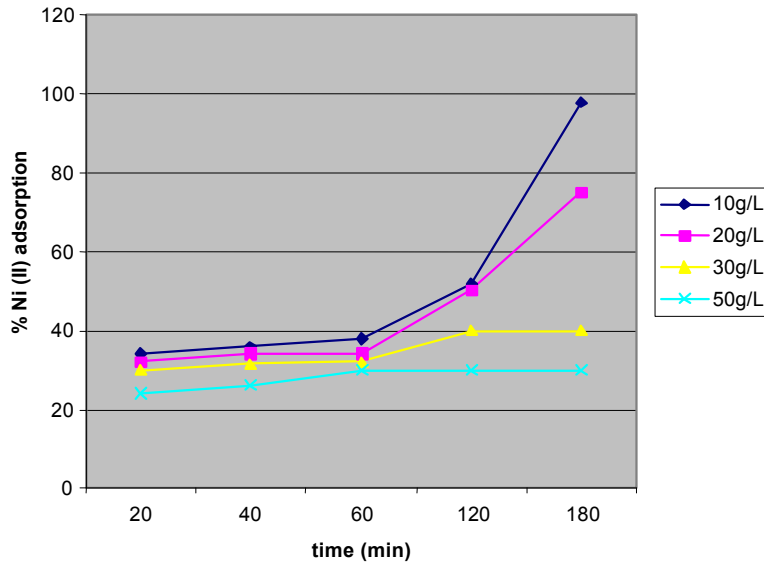


Fig. 2: Effect of Initial metal concentration of percent Ni(II) adsorption

could be an additional factor in amount of metal sorbed at various pH levels. Within the same pH, the amount of Ni(II) adsorbed decreased with increased initial metal concentration.

Effect of Initial Metal Concentration on Percentage Metal Uptake: Figure (2) shows the effect of metal ion concentration on the adsorption of Nickel by waste tea powder. The data shows that the metal uptake increases and the percentage adsorption of Ni (II) decreases with increase in metal ion concentration. This increase is a result of increase in the driving force i.e. concentration gradient. However, the percentage adsorption of Ni(II) ions on the biomass decreased from 98% to 30%. Though

an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of metal displays an opposite trend. 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 Ni(II) ionic concentrations. 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 [11].

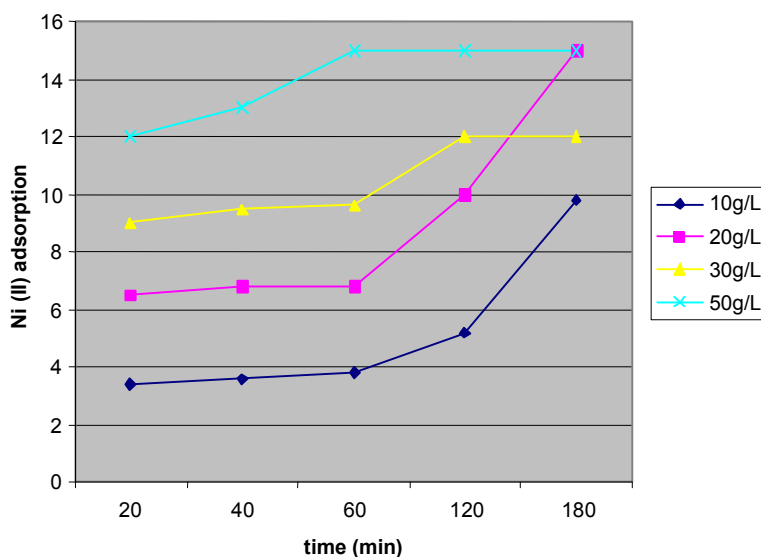


Fig. 3: Effect of reaction time on Ni(II) sorption

Effect of Reaction Time on Nickel Adsorption:

Performance of waste tea on the biosorption of Ni²⁺ at varying concentration was carried out with initial Ni²⁺ concentration of 10g/L, 20g/L, 30g/L and 50g/L and the biosorbant dose was 14g/L. Result (Figure 3) shows 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 Ni²⁺ absorbed 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 esteemed the binding of Ni²⁺ into functional groups present in the biomass. Result also shows that, the highest biosorption capacity of waste is within the experimental condition is at 10g/L ni²⁺. Result also shows that, biosorption reaction for the solution with initial Ni²⁺ concentration of 30g/L got to saturation at 120min of reactions while solution with initial concentration of 50g/L got to saturation at 60mins of the reaction.

Langmuir Isotherm: The equilibrium adsorption isotherm is of importance in the design of adsorption system [12]. 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.

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

$$\frac{1}{q_e} = \frac{1}{b q_e C_e} + \frac{1}{q_m}$$

Where:

q_e is the adsorbent amount (mg/g) of the Ni (II), C_e is the equilibrium concentration of the Ni(ii) in solution (mg/L), q_m is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (mg/L). 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) 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 [13].

$$R_L = \frac{1}{(1 + b C_0)}$$

Where:

C₀ 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.

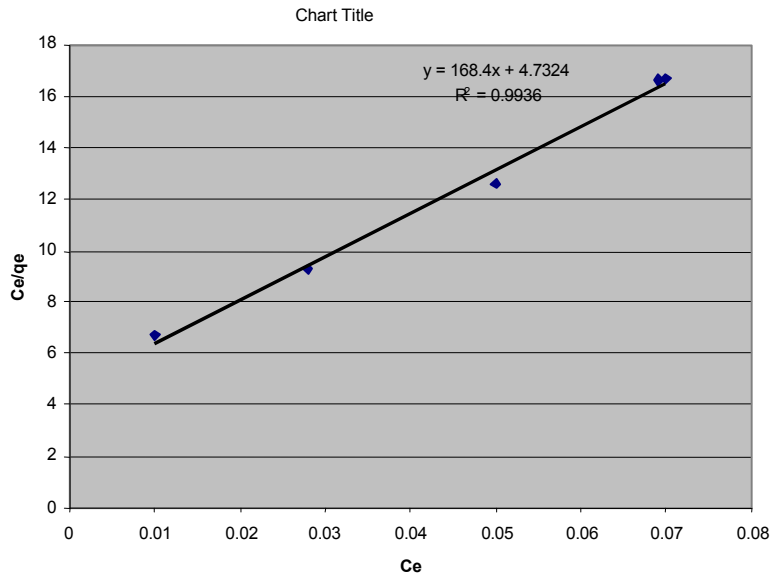


Fig. 4: Langmuir isotherm of Ni (II) adsorption on waste tea powder

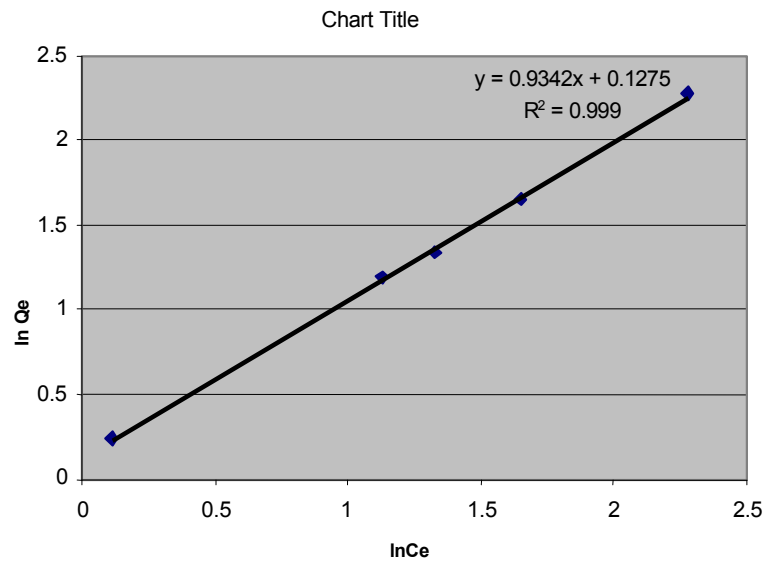


Fig. 5: Freundlich Isotherm of Ni(II) adsorption on waste tea powder

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 and Daifulla, [13].

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 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 obeys 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 $\frac{1}{n}$ ($0 < \frac{1}{n} < 1$) [14].

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:

$$\frac{dq_t}{dt} = k(q_e - q_t)$$

$$\frac{dq_t}{dt} = K(q_e - q_t)^2$$

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

$$\frac{t}{(q_e - q_t)} = \frac{1}{q_e} + Kt$$

Equation above can be rearranged to obtain a linear form:

$$\frac{t}{q_e} = \frac{1}{kq_e^2} + \frac{1}{q_e} t$$

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 t/q_t 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 0.9989 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 [15]. 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 [16]. 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 [17]. 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.

Pseudo-First Order Equation: The pseudo-first order equation of Lagergren [18] 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:

$$\text{Log}(q_e - q_t) = \text{log}(q_e) - \frac{K_1}{2.303} t$$

The equation is applicable to experimental results and generally differs from a true first order equation in two ways [19].

- The parameter K_1 ($q_e - q_t$) does not represent the number of available sites; and
- The parameter $\text{log}(q_e)$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\text{log}(q_e - q_t)$ against t , whereas in a true first order sorption reaction $\text{log}(q_e)$ should be equal to the intercept of a plot of $\text{log}(q_e - q_t)$ 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 [20]. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well

Table 1: Elovich equation parameters of the adsorption of Ni (II) on waste tea

Ni (II) Concentration	1/α	Ln (a α)	R ₂
10g/L	2.5269	-5.3356	0.67
20g/L	1.9873	-3.6292	0.6558
30g/L	0.6964	0.8825	0.8289
50g/L	0.0814	2.8550	0.7933

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

Ni (II) Concentration	1/q _e	1/qe ²	R ²
10g/L	0.0791	8.2095	0.6091
20g/L	0.0978	8.3186	0.6773
30g/L	0.2008	3.7035	0.9889
50g/L	0.3053	0.3533	0.9999

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

Ni (II) Concentration	a	K _d	R ²
10g/L	0.8863	-3.0116	0.9067
20g/L	0.7562	-2.45	0.906
30g/L	0.4056	-0.2906	0.7229
50g/L	0.2433	0.5402	0.4326

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

Ni (II) Concentration	K ₁	q _e	R ²
10g/L	-0.0047	1.003	0.8105
20g/L	-0.0015	0.7479	0.8961
30g/L	-0.0013	0.13	0.8929
50g/L	-0.0055	-0.6867	0.8501

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

Ni (II) Concentration	a	K _{id}	R ₂
10g/L	0.4471	0.8715	0.7687
20g/L	0.3817	0.6454	0.7183
30g/L	0.1884	0.7542	0.8264
50g/L	0.0209	0.7663	0.7910

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) onto 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 0.81-0.8961 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.

Elovich Equation: The Elovich equation [21] 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 ‘ a ’ values of 0.39, 0.5, 1.44 and 11.88 respectively. In Elovich equation, a decrease in ‘ a ’ indicates a reduction in the adsorption reaction rate [22]. Therefore, the rate of Ni(II) adsorbed by waste tea powder follows the order of $50 > 30 > 20 > 10\text{mg/L Ni(II)}$. 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 Elovich model.

The Intra-particle Diffusion Model: The intra-particle diffusion model is expressed as $R = K_{id} (t)^a$ [23]. A linearized form of the equation is followed by:

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

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 [24]. 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

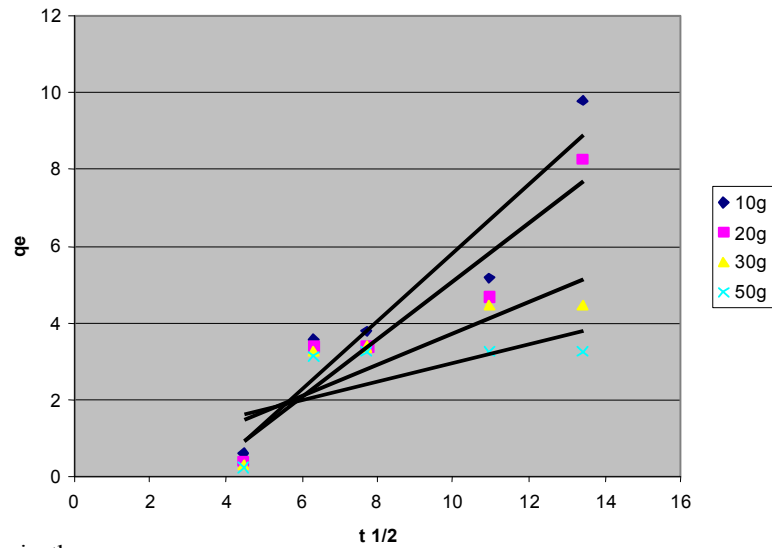


Fig. 6: Parabolic diffusion isotherm

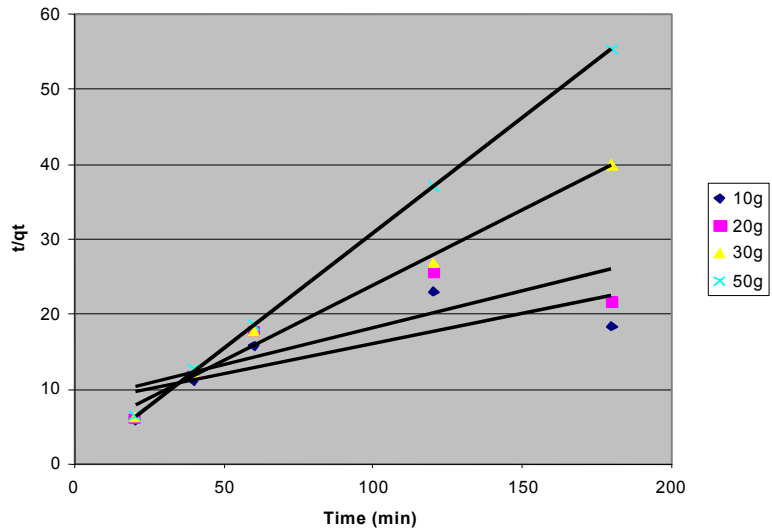


Fig. 7: Pseudo-second order kinetic isotherm

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

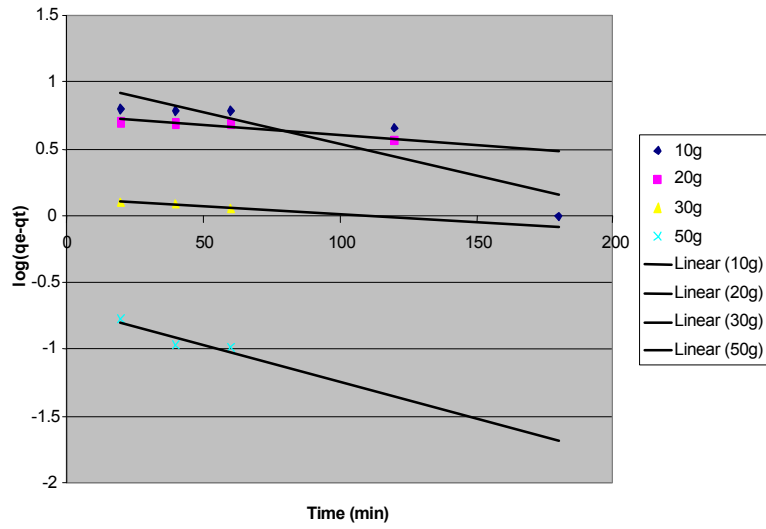


Fig. 8: Pseudo-first order kinetic isotherm

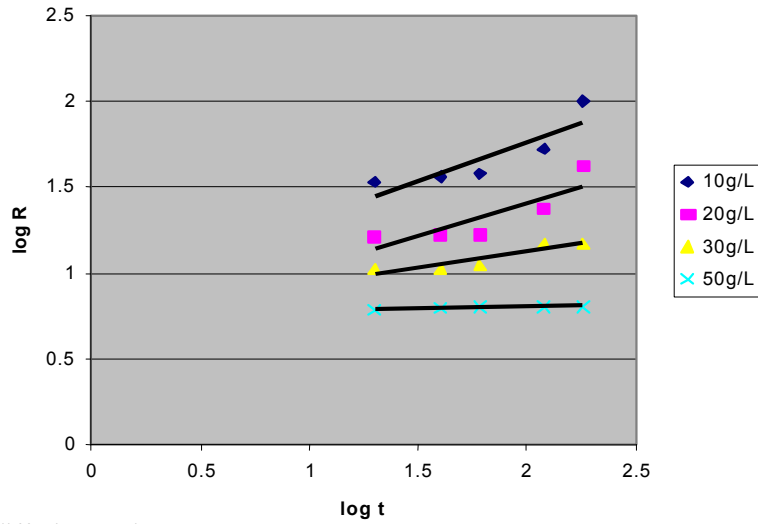


Fig. 9: Intra-particle diffusion Isotherm

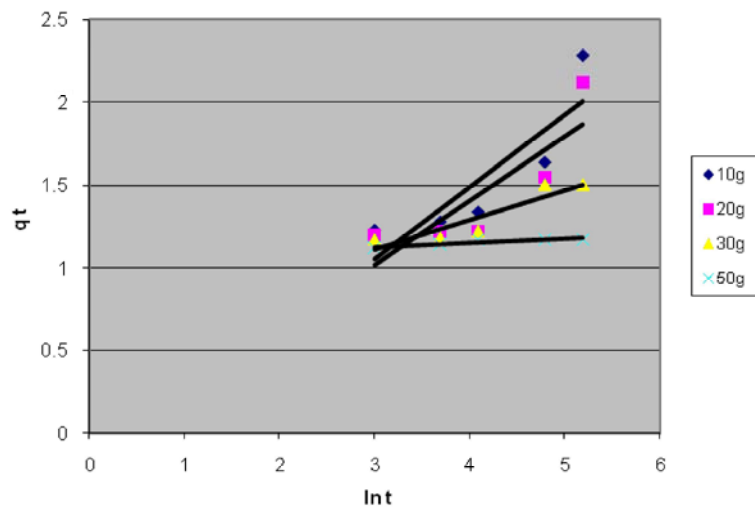


Fig. 10: Elovich model isotherm

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.

CONCLUSION

The present study shows that waste tea powder was an effective biosorbent for the adsorption of Nickel(II) ions from aqueous solutions. The effect of process parameters like pH, metal ion concentration and reaction time were studied. 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 optimally for waste water treatment, nickel contaminated industrial effluent should be diluted to 102/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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