Kinetic and Isotherm Studies on Adsorption of Nickel (II) Ions by *Brassera Oleracea* as a Bioadsorbent

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Abstract: *An increase in population initiating rapid industrialization was found to consequently increase the effluents into the aquatic ecosystem. brassera oleracea - Cabbage, a vegetable wastes were used to produce bioadsorbent through environment friendly process. It were cut, washed, dried, grounded into powder and used for nickel(II) removal. Nickel(II) adsorption onto raw cabbage(RC) was depended upon the controlling parameters such as pH, contact time, initial concentration, adsorbent dosage, particle size and temperature. pH 5 was found to be suitable for nickel(II) removal. Equilibrium, thermodynamic and kinetic data were well fitted (R^2 = 0.991).   Various thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o have also been evaluated and it has been found that the adsorption process was spontaneous, endothermic and randomness in nature. The experimental data were analyzed using the Freundlich, Langmuir and Temkin adsorption isotherm equations. The equilibrium data were found to fit well in the Langmuir isotherm, which confirmed the monolayer coverage of Ni(II) ions onto RC. The monolayer adsorption capacity was 13.63mg/g. The R_L and 'n' values has proved the favorability of nickel(II) adsorption onto raw cabbage. The uptake of metal ions normally follows pseudo-first order kinetics and the adsorption capacity increase at elevated temperatures. The results indicate that the RC can be used to effectively adsorb nickel(II) ions from wastewater.*

Keywords: adsorbent, metal ion, adsorption, isotherms, kinetics, thermodynamic parameter

1. Introduction

The increase in usage of heavy metals in industrial activities has caused the existence of them in waste water. For example lead, cadmium and nickel which the waste water of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp contains them[1]. In the discharge of metal ions in industrial effluent using biosorption process has been an area of extensive research because of the presence and accumulation of toxic carcinogenic effect on living species[2]. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis and adsorption. Most of these methods suffer with high capital and regeneration costs of the material[3]. Therefore, there is currently a need for new and cost effective methods for the removal of toxic substances from wastewaters. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption[4]. In recent years, agricultural by-products have been widely studied from metal removal from water. These include peat, wood, bark, husk, dust, peel and leaves. The purpose of this present study was to assess the ability of brassera oleracea (Cabbage) to adsorb Ni(II) ions from aqueous solutions. The experiments were done in batch system and nickel adsorption was investigated with respect to pH, contact time, initial metal ion concentration, adsorbent dose, particle size and temperature. The main aim of this research was to determine the potentiality and adsorption capacity of raw cabbage(RC) as a bioadsorbent.

2. Materials and Methods

2.1 Materials

Nickel solution was prepared by diluting 1000ppm of nickel nitrate (Merck) stock solution with double distilled water. Different concentrations of metal solutions (5 to 25 mg/L) were prepared by dissolving required amount of stock solution.

Adsorbent: Cabbage was collected locally and washed under a tape water to remove any particulate and again washed with double distilled water. This bioadsorbent was cut into small pieces, oven dried, crushed and sieved without any further treatment. The adsorbent was called it as RC (Raw Cabbage) for further studies.

Characterization of adsorbents: The physical characteristics of the adsorbent samples were determined by known methods[5]. The pH values of the adsorbent slurry was determined by mixing 2 g of adsorbent in 100 mL of double distilled water and pH was recorded at every 3 h interval for a period of 24 h. The results showed that the pH of the slurry was nearly constant. The Electrical conductivity of the adsorbent sample was measured by mixing 2 g of adsorbent in 100 mL of deionised water and conductivity was measured at every 2 h interval for a total period of 12 h. Density of the adsorbents was found by specific gravity estimation method[6]. The adsorbent was packed in a dry 25 mL bottle and weighed. The mean value was obtained by repeating the experiment for five times to calculate the

density of the adsorbent. Weight loss of the adsorbent was determined by standard methods. The samples were sieved using the British Standard Sieves BSS 52, BSS 30 and BSS 25 to obtain particles of various sizes. The actual size of the particles was determined using Occular Micrometer.

Surface area determination The surface area of the adsorbent was measured by p-nitrophenol method[7]. p-Nitrophenol was recrystallized twice from water and 0.695g was weighed and 50mM stock solution was prepared. Various concentrations, 3, 4, 5, 6, 7, 8 and 9 mM of p-nitrophenol were prepared from the stock solutions. In a typical experiment 1 of adsorbent sample with 0.36-0.48mm of particle size was mixed with 3mM concentration of p-nitrophenol in a 100mL flask and the mixture was mechanically shaken at 301K until adsorption equilibrium was reached. Similar procedure was repeated for all other concentrations of p-nitrophenol and adsorption was followed. After an hour of agitation time the flasks were set aside for 15 minutes to allow the adsorbent for complete settlement. The supernatant solution was decanted and absorbance was measured at 400nm wavelength in the UV-Visible spectrophotometer. The experiments were repeated for adsorbents with particles of varying sizes. Surface area was determined using the relation. $S.A = x_m \, N \, A \, (m^2/g)$ where x_m is the monolayer capacity in moles per gram, N the Avagadro number, A the area of surface occupied by each solute molecule in sq.cm.

2.2 Adsorption Studies

Batch adsorption experiments were carried out by agitating 0.4 g of the adsorbent with 200 ml of nickel(II) ion solutions of desired concentrations and pH 5 at room temperature using an mechanical shaker at 150 rpm. The effect of pH was studied by adjusting pH of the solution using 1 N HCl or 1 N NaOH solution the pH was measured using a pH meter. The effect of initial metal ion concentrations was carried out by shaking 5, 9,13,17,21 and 25mg/L with 400mg of adsorbent with 200ml of metal solution and pH 5 at room temperature. All the investigations were carried out in duplicate to avoid any discrepancy in experimental results

and metal solution controls were kept throughout the experiment to maintain quality control. The percentage of metal adsorption by the adsorbents was using the equation(1).

$$Adsorption\ (\%) = C_0\text{-}C_e/C_0 \times 100 \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of metal ion (mg/L) in the solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent using equation(2)

$$q = (C_0\text{-}C_e)X\ v/m \qquad (2)$$

where q is the amount adsorbed(mg/g), m is the weight of sorbent, v is the volume of metal solution. The amount of metal ion sorbed at equilibrium, q is calculated using equation 2.

3. Results and Discussion

Table 1: Physical properties of Raw Cabbage

Parameters	Raw Cabbage(RC)
pH	5.2
EC (µS/cm)	0.367
Density (g/ml)	0.439
Particle size (mm)	0.38-0.46
Surface area (m²/g)	109.9

Adsorbent characterization
The Scanning Electron Microscope (JSM-5610 model) machine was used to determine the structure of the adsorbent material. The morphological difference of the surface of the RC and metal ion loaded-RC are shown in **Figure 1**. SEM analysis revealed that there were significant changes on the surface texture and the porosity of the adsorbent has holes and small openings found on the surface indicate that these increase the contact areas which facilitate pore diffusion during adsorption. A foam like net anchored on the surface of the adsorbent corresponding to the adsorbed heavy metal ion on the surface[8].
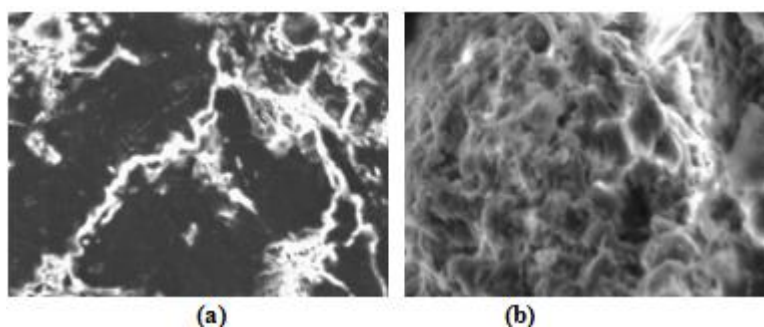

Figure 1: SEM images of (a) raw cabbage and (b) metal ion loaded raw cabbage

Effect of pH
The removal of metal ions from aqueous solution by adsorption was depended on the pH of the solution since it affected adsorbent surface charge, degree of ionization of the functional groups and metal ion speciation[9]. At lower pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the later. The heavy metal cations are completely released

under circumstances of extreme acidic conditions. To find a suitable pH for the effective adsorption of Ni(II) ions, experiments were performed over a pH range of 3.0 to 9.0. The variation of amount of metal ion adsorbed with initial pH is given **Figure 2** for an initial nickel(II) ion concentration of 5 mg/L at 301K. Maximum nickel(II) adsorption was obtained at pH 5. This optimum pH obtained of 5.0 was used in all subsequent adsorption

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studies. It is observed from the figure that the initial pH of a solution played a major role in nickel adsorption. Under low pH conditions the adsorption of nickel(II) ions is not significant since the metal binding sites on the RC surface were closely associated with H_3O^+ which restricted the approach of the positive nickel(II) ions due to repulsive forces[10]. However the adsorption capacity increase as pH increased since more metal binding sites were exposed with negative charges which attracted the positive Ni(II) ions into the surface of the adsorbent[11].
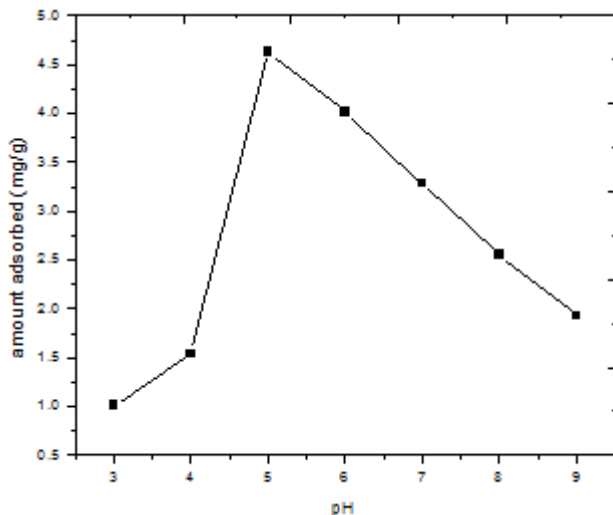

Figure 2: Effect of pH on the equilibrium nickel(II) ion sorption capacity of RC. Condition: initial metal concentration = 5mg/L, dosage 400mg, particle size 0.38-0.46mm and room temperature

Effect of contact time and initial concentration

The contact time is one of the factors for the development of surface charges at the solid solution interface. At a fixed pH, initial metal ion concentration and temperature, the result on the effect of varying the sorption time is presented in **Figure 3**. The adsorption rate was seen to increase rapidly at the initial stage and optimum adsorption was attained within 20 minutes. However, the maximum adsorption was obtained in 60 minutes. The fast initial uptake capacity is due to the availability of abundant active sites for sorption which became saturated with time[12].

The initial concentration of adsorbate also plays an important role as a given mass of the adsorbent can adsorb only a fixed amount of the solute. The effect of initial nickel(II) ion concentration on adsorption by RC is presented in **Figure 4**. The removal of the Ni(II) ions by RC increased from 1.54 to 5.75 mg/g by increasing the concentration of the metal ion from 5 to 25mg/L at temperature 301K and pH 5. The uptake capacity of RC for this metal ion increased with increase in initial concentration of nickel(II) ions. This is due to the presence of more metal ions in solution available for sorption. This increase in concentration increased the driving force overcoming resistances to mass transfer between the adsorbent and adsorbate species which led to the increase in adsorption observed[13]. The time variation curves for adsorption are simple, smooth and continuous, indicating the formation of monolayer coverage on the surface of adsorbent[14].
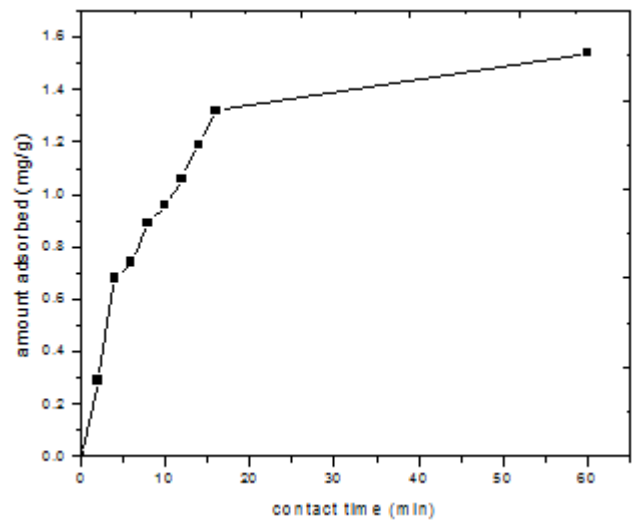

Figure 3: Effect of contact time on the adsorption of nickel(II) ions. Condition; pH=5.0, Concentration of metal ion:5mg/L, dosage 400mg, particle size 0.38-0.46mm and room temperature
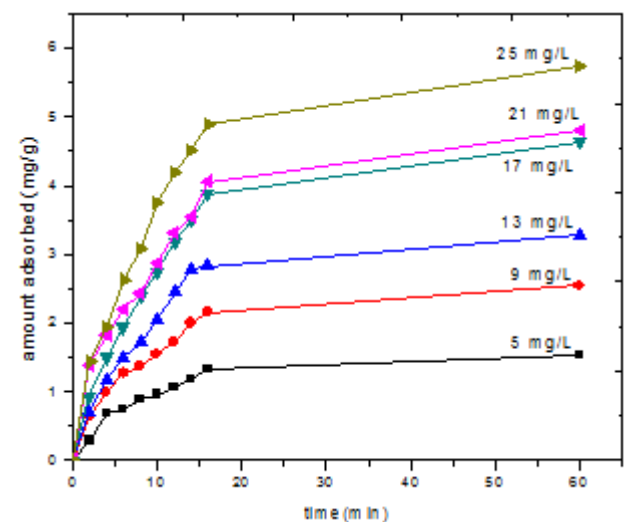

Figure 4: Effect of initial concentration of nickel (II) ion removal by RC. Conditions: pH 5, dosage 400mg, particle size 0.38-0.46mm and room temperature

Effect of adsorbent dosage

The effect of variation of adsorbent dosage amount on the removal of metal ions by RC is shown in **Figure 5**. The percent removal of nickel was found to increase with an increase in the mass of adsorbent. Highest nickel removals were 77.3 to 80.8% for the initial nickel concentration of 5 mg/L at the adsorbent doses were 400 and 800mg/200ml under the optimized conditions. This may be attributed to overlapping or aggregation of adsorbent surface area available to ion and an increase in diffusion path length[15]. Also, due to lack of active binding site, the lower removals were obtained at low adsorbent does[16].
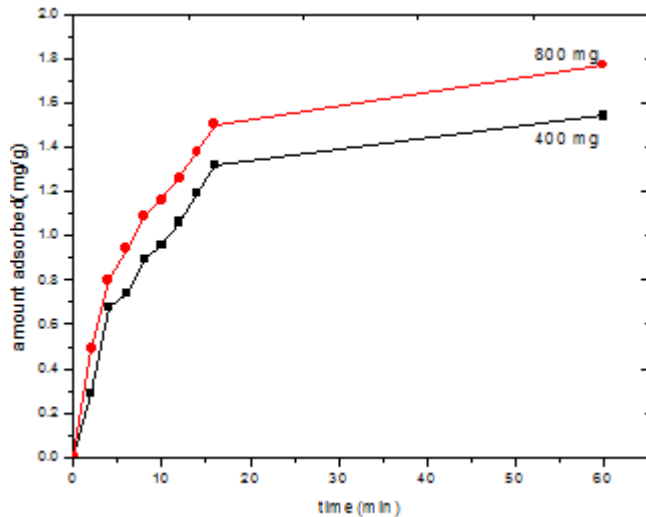
Figure 5: Effect of adsorbent dosages on removal of nickel. Condition: pH 5, initial concentration of metal solution 5mg/L, particle size 0.38-0.46mm and room temperature

Effect of particle size

Nickel (II) solution was agitated with 400 mg of RC in three different experiments (initial concentration: 5 mg/L; particle sizes: 0.05-0.06 (BSS52), 0.38-0.46 (BSS30) and 0.65-0.91mm (BSS25) mm at room temperature and pH 5) in which the uptake was found to be 1.93, 1.54 and 1.37 mg/g respectively. **Figure 6** shows that decrease of the particle size increases the adsorption of nickel(II) on RC. According to Weber and Morris the breaking of larger particle tends to open tiny cracks and channels on the particle surface, providing additional surface area which is useful in the adsorption process[17]. In general, the rate of removal of metal ion increases with the decrease in particle size of the adsorbent and the time required for 50% removal is also less while particles of smaller size is used. This relationship clearly demonstrates the advantage of powdered adsorbent materials over the granular particles from kinetic view point, indicating the external transport limits the rate of adsorption. The presence of larger number of smaller particles provides the sorption system a larger surface area available for nickel(II) removal and it also reduces the external mass transfer resistance.
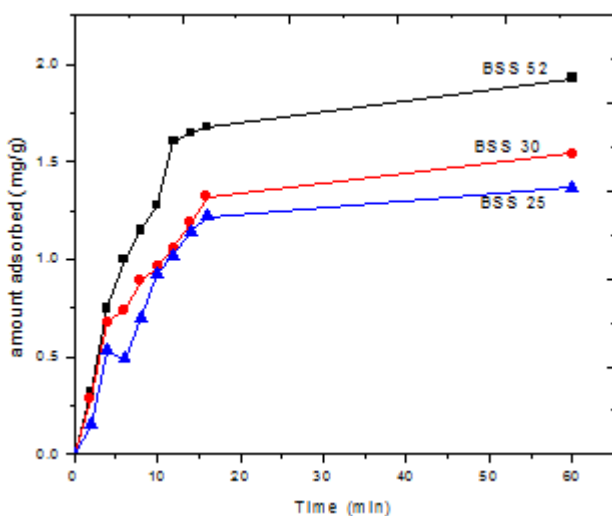

Figure 6: Effect of particle size on removal of nickel Condition: initial metal ion concentration 5mg/L, pH 5, dosage 400mg/200ml and room temperature.

Activation Energy and Thermodynamic Parameters

To determine the thermodynamic properties and thermal effects on the adsorption, the temperature variation experiments were conducted at 294, 301and 308K, with an initial nickel concentration 5mg/L and 400mg of RC. The effect of temperature on adsorption is shown in **Figure 7**, which illustrates that the increase of the amount of the adsorbate is a function of temperature. This temperature dependence of adsorption process may be explained on the basis of thermodynamic parameters calculated using standard thermodynamic relationships. The thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations[18,19].

$$K_c = C_i/C_e \qquad (3)$$
$$\Delta G^0 = -RT\ln K_c \qquad (4)$$
$$\log K_c = \Delta S^0/2.303R - \Delta H^0/2.303RT \qquad (5)$$
$$\ln K = \ln A - E_a/RT \qquad (6)$$

where C_e is the equilibrium concentration in solution in mg/L and C_i is the equilibrium concentration on the sorbent in mg/L and K_c is the equilibrium constant. The Gibbs free energy (ΔG^0) for the adsorption of nickel onto RC at all temperatures was obtained from equation 4 and are presented in Table 2. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot $\log K_c$ against 1/T(figure not given) and are also listed in table 2. Where K is rate constant, Ea is activation energy and A is Arrhenius pre-exponential factors (J/mol) and activation energy was calculated by plotting 1/T versus logK.

Table 2: Thermodynamic parameters for adsorption of nickel(II) onto raw cabbage

Temp (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	E_a (kJ/mol)
294	-1.112	50.02	0.1737	-28.45
301	-2.399			
308	-3.456			

From table 2 the value of R^2 (0.999) obtained showed a good agreement between the entropy change and temperature. The negative values of ΔG^0 measured at 294, 301, and 308 K indicate spontaneous nature of adsorption process for nickel(II) ion. The value of ΔG^0 confirms the maximum adsorption at higher temperatures, because there is a gradual decrease in ΔG^0 value with rise in temperature. The positive value of enthalpy change, ΔH^0, shows the adsorption is endothermic and the positive value of ΔS^0. A highly disordered process was also indicated by the positive value of ΔS^0. Similarly, the positive enthalpy change showed an endothermic adsorption process, which implies an increase in adsorption capacity with temperature increase. The E_a value calculated from the slope of the plot was found to be -28.45kJ/mol. (lesser Ea value faster the reaction) The negative value of E_a indicates that lower solution temperatures favours metal ion removal by adsorption onto RC surface and the adsorption process is endothermic in nature.
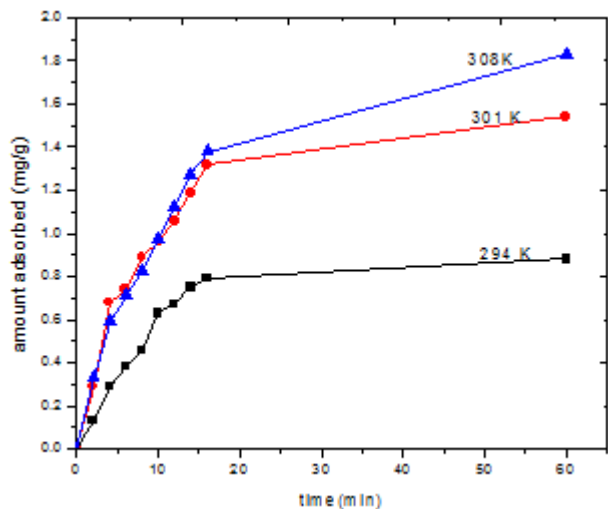
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Figure 7: Effect of temperature of nickel (II) ion removal by RC. Conditions: pH 5, initial concentration 5 mg/L, dosage 400mg/200mL and particle size 0.38-0.46mm

Adsorption Isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study Freundlich, Langmuir and Temkin models were used to describe the equilibrium data. The results are shown in **Table 3** (and the modeled isotherm are plotted in figure 8,9 and 10).

The Langmuir Isotherm

The Langmuir Isotherm model[20] was used to describe observed sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The linear forms of the equation can be written as:

$$C_e/q_e = 1/Q_o b + C_e/Q_o \qquad (7)$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ions (mg/L), Q_o (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive site, „b‟ (L/mg) is the Langmuir constant related to the energy of adsorption. The Langmuir Isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monoloayer coverage on the RC surface. The plots of specific sorption (C_e/q_e) against the equilibrium concentration(C_e) for nickel(II) are shown in **Fig.8** and the linear isotherm parameters, Q_o, b and the coefficient of determinations are presented in Table 3. It was observed that the Langmuir adsorption Isotherm is satisfactory describes the sorption of nickel(II) from aqueous solution using RC as indicated by the high correlation coefficient (r^2) of 0.9875. The applicability of the Langmuir Isotherm indicates good monolayer coverage of nickel(II) ions on the RC which consequently suggests the formation of a monolayer on the adsorbent surface in the given concentration range[21]. The fact that the Langmuir Isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites on the adsorbent since the Langmuir equation assumes that the surface is homogenous. The shape of the

Langmuir Isotherm can be used to predict whether a sorption system is favourable or unfavourable in a batch adsorption process. The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor(R_L) that can be defined by the following relationship[22].

$R_L = 1/1+bC_o$ The values of R_L indicated the type of Langmuir isotherm to be irreversible(R_L=0), favourble ($0<R_L<1$), linear (R_L=1), or unfavourable ($R_L>1$). The values of R_L obtained in this study were found to lie between 0 and 1, indicating favourable adsorption.

The Freundlich Isotherm

The Freundlich Isotherm is applicable to non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as[23].

$$Log\ q_e = log\ K_F + 1/n\ log\ C_e \qquad (8)$$

Where K_F is the Freundlich constant related to sorption capacity($mgg^{-1}Lg^{1/n}$) and „n‟ is related to the adsorption intensity of the adsorbent[24]. Where K_F and n can be determined from the linear plot of log q_e vs log C_e. The evaluated constants are given in **Table 3**.

Table 3: Isotherm model constants and correlation coefficients for Ni(II) ions from adsorption from aqueous solution using RC

Langmuir Isotherm	Freundlich Isotherm	Temkin Isotherm
Q_0 = 0.6292	K_F = 2.396	B_T = 2.109
b = 1.04	n = 1.206	K_T = 0.970
R_L = 2.89	r^2 = 0.9717	r^2 = 0.976
r^2 = 0.9875		

The Freundlich exponent,"n‟ should have values lying in the range of 1 to 10 for classification as favourable adsorption[25]. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The experimental data from the batch sorption study of the metal ions on RC was plotted logarithmically in **Figure 9**. The linear Freundlich isotherm constants for Ni(II) on RC is presented in Table 3. The Freundlich isotherm parameter „n‟ measures the adsorption intensity of metal ions on the RC. The high „n‟ value of Ni(II) ion indicate the preferential sorption of metal ion probably due to its smaller ionic radius and shows the ability of the RC to remove the metal ions from solution even at high concentration. The ultimate adsorption capacity K_F of the adsorbent was calculated from the isothermal linear regression equation. The K_F value 2.396($mgg^{-1}Lg^{1/n}$) suggesting and conforming that Ni(II) has greater adsorption tendency towards the RC. Similar results are reported[26].

Temkin Isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption in characterized by a uniform distribution of the bonding energies up to some maximum binding energy.

The Temkin isotherm is represented as

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$q_e= B_T \ln K_T + B_T \ln C_e$ (9)

$qe = RT/b_T \ln K_T + RT/b_T \ln C_e$ (10)

where T is the absolute temperature(K), R is the gas constant(8.314 J/kmol), K_T is the equilibrium binding constant(L/mg), b_T is the variation of adsorption energy(kJ/mol) and B_T is Temkin constant related to the best of adsorption(kJ/mol). The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for the adsorbates[27]. The Temkin isotherm plot for the nickel(II) ions is presented in **Figure 10** and the parameters is given in Table 3. The Temkin adsorption potential, K_T of RC of Ni(II) is 0.970(L/mg), the Temkin constant, b_T related to heat of sorption for the metal ion is 2.108kJ/mol.
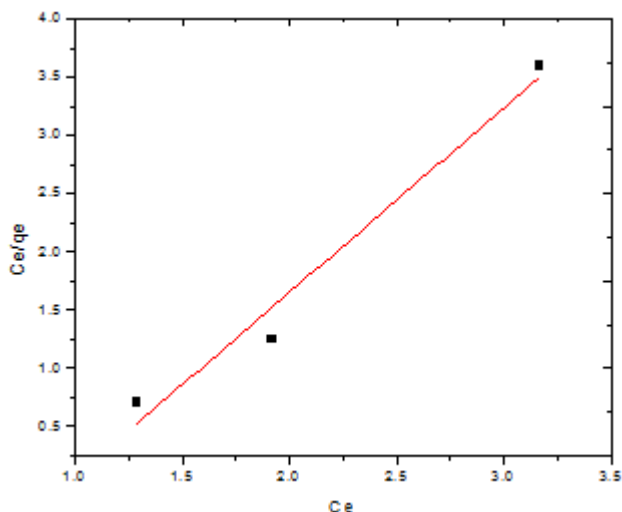

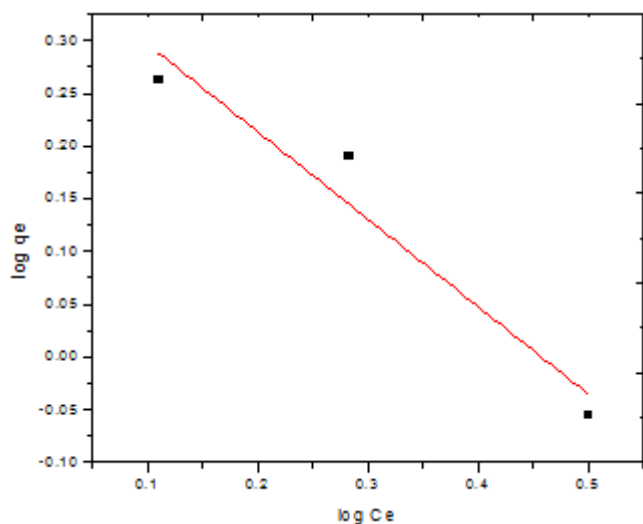**Figure 8:** Langmuir adsorption isotherm for adsorption of nickel(II) ions on RC

Figure 9: Freundlich adsorption isotherm for adsorption of nicke(II) ion on RC
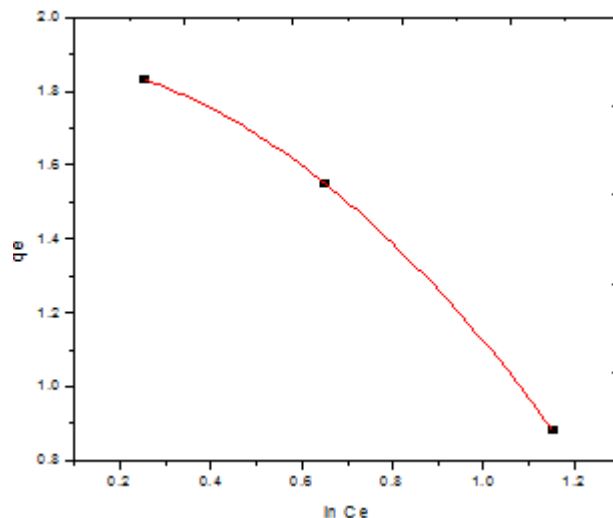

Figure 10: Temkin adsorption isotherm for adsorption of nickel(II) ions on RC

Batch Kinetic Studies

Kinetic studies are significant for any kind of biosorption processes. Adsorption kinetics not only describes the adsorption mechanism of metals on adsorbents but also describe the metal adsorption rate which controls the contact time of metals at the solid-liquid interface[28]. Various kinetic models have been used by various researchers whereas in this study the pseudo-first, pseudo-second order models and intraparticle diffusion were studied. Batch kinetic experiments were conducted for nickel(II) ion solutions at pH 5 with 400 mg/200 mL of adsorbent (particle size 0.38-0.46 mm) at three temperatures. Kinetics of sorption describing the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. The rate constant of adsorption of the metal ion on adsorbents is described by Lagergren[29] equation(11) or pseudo-first order and pseudo-second order equation(12)

$\log (q_e-q) = \log q_e - k_{ad}\, t/2.303$ (11)

$t/q_t = 1/k_2 q_e^2 + t/q_e$ (12)

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), „q‟ the amount of solute adsorbed at any time „t‟ (mg/g) and „k_{ad}‟ the adsorption constant and k_2 is the pseudo-second order rate constant. Linear plots of $\log(q_e-q)$ versus t suggest the applicability of the first order kinetics. The rate constants, k_{ad}, were calculated from the slope of the **figure 11**. By regression modelling, experimental curves were found to be the best fit for the data characterized by the regression coefficient(r^2). Adsorption on solid phase leads to the establishment of equilibrium between two phases, the equilibrium constant K_c was calculated equation (3).

In **figure 12** pseudo second order kinetic model of t/q_t versus „t‟. The contact time experimental results can be used to study the rate-limiting step in the adsorption process. One might then postulate that the rate-limiting step may be either film or intraparticle diffusion. The rate constant for intraparticle diffusion k_{id} (mg/g/min$^{1/2}$) is given by equation (13)

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$$q = k_{id} \, t^{1/2} \qquad (13)$$

where q is the amount adsorbed (mg/g) at time „t" (min.). k_{id} values were obtained from the slope of linear plot of „q" versus $t^{1/2}$. The rate constant, k_{ad}, k_2, equilibrium constant, K_c calculated q_e, regression coefficient(r^2) and intraparticle constant, k_{id} for all systems were calculated and given in table 4. As shown in this table, the correlation coefficients(r^2) for the first order rate equation are greater than 0.98 and substantially higher than that for the second order rate equation. This show that the adsorption of Ni(II) ion on RC can be represented by the pseudo first-order model. **Figure 13** presents intraparticle plot for Ni(II) onto RC. The calculated diffusion coefficient k_{id} values are listed in table 4. The k_{id} value was higher at the higher concentrations. Intraparticle diffusion is the sole rate-limiting step if the regression of „q" versus $t^{1/2}$ is linear and did not passing through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that intraparticle diffusion was not the only rate limiting step[30].
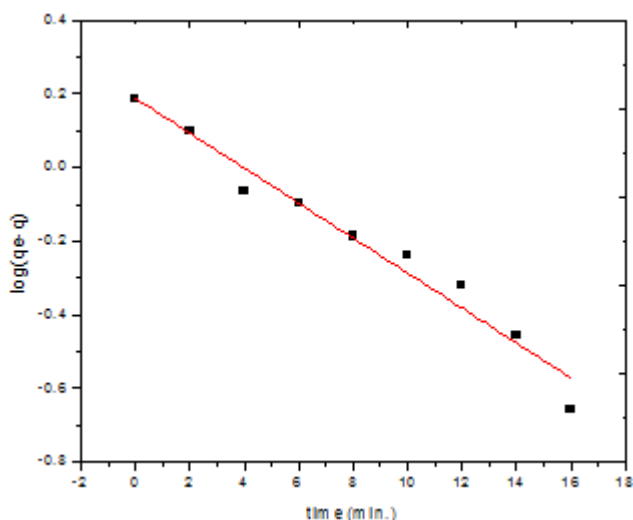

Figure 11: Pseudo-first order kinetic plots for adsorption of Ni(II) onto RC. Conditions: pH 5, dose 400mg/200mL, particle size o.38-0.46mm, initial metal ion concentration 5mg/L and temperature 301K

Figure 12: Pseudo-second order kinetic plots for adsorption of Ni(II) onto RC. Conditions: pH 5, dose 400mg/200mL, particle size o.38-0.46mm, initial metal ion concentration 5mg/L and temperature 301K
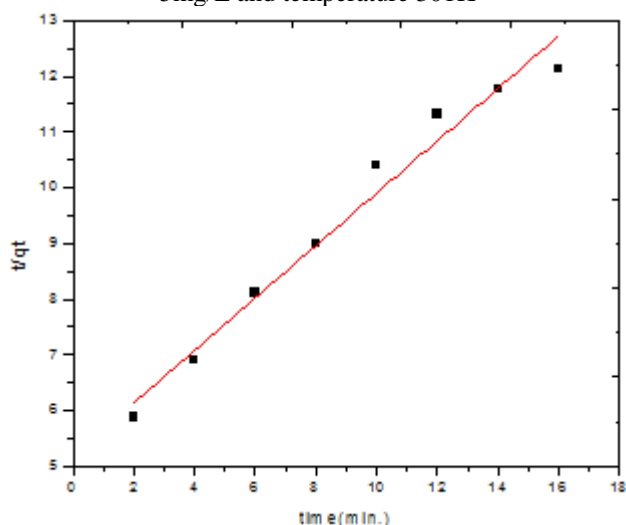
particle size o.38-0.46mm, initial metal ion concentration 5mg/L and temperature 301K

Figure 13: Intraparticle diffusion model for adsorption of Ni(II) onto RC. Conditions: pH 5, dose 400mg/200mL, particle size o.38-0.46mm, initial metal ion concentration 5mg/L and temperature 301K
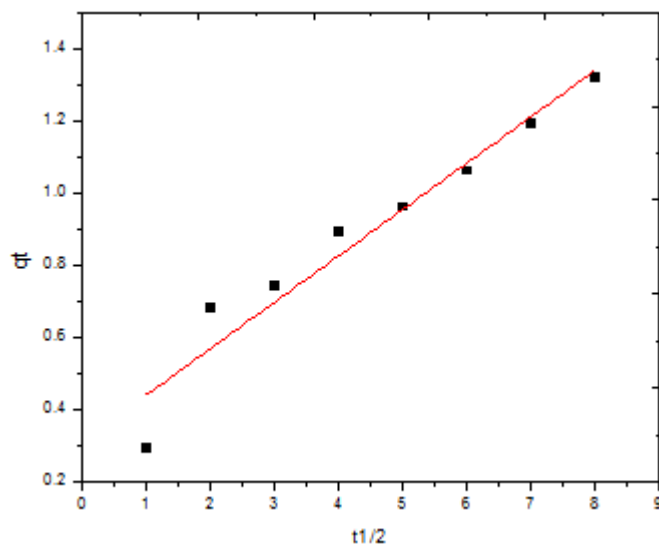
Table 4: Parameters of the kinetic models for the adsorption of Ni(II) onto RC.

Model	294K	301K	308K
Pseudo-first order			
k_{ad}	0.1428	0.1082	0.0826
r^2	0.9854	0.9834	0.9933
Pseudo-second order			
k_2	0.1538	0.1223	0.084
q_e	1.2090	1.5730	1.690
r^2	0.7610	0.9089	0.889
Intraparticle diffusion			
k_{id}	0.1005	0.1470	0.1610
r^2	0.9874	0.9634	0.9850

4. Desorption

Desorption studies were carried out as follows: In an adsorption experiment, the residual metal ion solution was filtered to separate the adsorbent and gently washed with distilled water to remove any unadsorbed chromium ion. Solid containing the metal ions was dried at 60°C and stored in a container, about, 1 g of sample was suspended in 50 mL of distilled water. Desorption rate was slow and the amount released was also very less. This indicated that the major portion of Nickel(II) ion was, probably, bound to the sorbent through stronger interactions. The percentage of removal of metal ion from the adsorbent is approximately 15%.

5. Conclusion

This study investigated the feasibility of raw cabbage used as a low cost adsorbent for the removal of Nickel(II) ion from aqueous solution. The adsorption process is also dependent on numerous factors such as the solution pH, contact time, initial concentration, adsorbent dosage, adsorbent particle size and temperature. The amount of adsorption of nickel ions increased with an increase in the

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nickel concentration, it increased with increase in contact time and adsorbent dose upto a certain level. The maximum removal was found at pH 5.0. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of Ni(II) ions onto raw cabbage. The adsorption kinetics followed pseudo-first order kinetic model with a good correlation, intraparticle diffusion was not the sole rate controlling factor. The activation energy of the adsorption process(Ea) was found to be -28.45kJ/mol^{-1} by using the Arrhenius equation, indicating exothermic nature of nickel adsorption onto RC. Thermodynamic analysis suggests that the removal of nickel from aqueous solution by raw cabbage was a spontaneous, exothermic and randomness. Therefore, the present findings suggest that raw cabbage may be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of nickel ions from wastewater.

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