Adsorption Study of Nickel Ni (II) Ions from Aqueous Solution on Tea Waste

Sudeep Asthana[1], A.O.Kedia[2], Shweta Gupta[3]

[1,2,3] *University School of Chemical Technology, GGSIP University, New Delhi, (India)*

ABSTRACT

A batch adsorption study was carried out to evaluate the suitability of tea waste (TW) as a low cost sorbent for the removal of Ni (II) metal ions from aqueous solution. The effect of pH, contact time, sorbent dose and initial metal ion concentration along with the study of equilibrium and kinetics were investigated. Batch studies revealed that the pH for efficient adsorption was 6, and the adsorption equilibrium was achieved within 2 h Tea waste (TW) had a highly porous surface structure was revealed in Scanning electron microscopy (SEM).Fourier transform infrared spectroscopy (FTIR) analysis showed that carboxyl and hydroxyl functional groups were mainly responsible for the adsorption of Ni (II). The equilibrium data were fitted into Langmuir and Freundlich models.The Langmuir model described the sorption isotherm best. The Langmuir adsorption capacity was found to be 14.09 mg/g at pH 6 . Two kinetic models, pseudo-first-order, pseudo-second-order were employed to explain the sorption mechanism. The pseudo-second-order model is the best fit with correlation coefficient of 0.999. The results showed that the tea waste (TW) has a good potential to be used as a low cost sorbent for Ni(II) ions removal.

Keywords: Adsorption, tea waste, Nickel, Equilibrium, kinetics

I. INTRODUCTION

Due to rapid industrialization, the disposal of toxic heavy metals into water streams has become a significant threat to human health and environment. The heavy metals of utmost concern are nickel, lead, cadmium, copper, mercury and chromium.

The undesirable amount of Nickel ions Ni (II) are found in the effluents of various industries like metallurgy, paint & pigments, electroplating, petroleum refining, battery manufacture [1,2,3,4]. Nickel is non biodegradable and tends to accumulate in living organisms. The higher amount of Nickel than the permissible level causes various diseases like skin dermatitis, renal infection, diarrhoea, lung cancer [5]. The permissible concentration of Ni (II) is 0.1 ppm [6, 7].

Various methods have been used for the removal of heavy metals from waste water such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, membrane technologies etc, [8,9,10,11,12,13].Recently the tea waste has been reported to be one of the most promising low cost adsorbent for heavy metals removal from waste water. [14,15].A great amount of tea waste is produced in the world and is usually discarded into the environment which can be used as a low cost adsorbent.

The present study is carried out to evaluate the feasibility and extent of adsorption of Ni (II) on tea waste (TW), the effect of various parameters on the adsorption process of Ni(II) and to study the isotherm and kinetics of the adsorption process.

II. MATERIALS AND METHODS

2.1. Instruments

For the specific surface area (SSA) and pore volume determination of tea wastes Surface Area Analyser (BET) Thermo Finnigan Italy, was used. Atomic Absorption Spectrophotometer (AAS 4141) ECIL, India, using air acetylene flame was used for the determination of Ni ions in the samples, Fourier transform infrared spectroscopy (FTIR) analysis was done on an FTIR spectrophotometer (Varian 600 UMA) with the absorption spectrum between 400 and 4,000 cm^{-1}.The FTIR spectra were analyzed and compared before and after loading with Ni ions.pH meter model PHEP Hanna Instrument, Italy was used for pH measurements. Scanning Electron Microscope (ZEISS EV018) was used for surface structure study. Zeta potential measurements were taken by SurPASS Electro Kinectic Analyser (Anton Paar).

2.2. Chemicals and reagents

Standard stock solution of 1000 ppm was prepared by dissolving $Ni(NO_3)_2.6H_2O$ (Thomas Baker) in double distilled water. Suitable dilutions of Ni(II) solutions were prepared from it. The pH of the solution was adjusted using HNO_3 and NaOH solutions.

2.3. Tea Waste

Tea waste (TW) of brand name Tata Tea was collected in bulk from GGSIP University, New Delhi, India, hostel mess and was used for adsorption experiments. To remove residual tea colour (tannins) the raw tea waste was first subjected to steam treatment under 70 kPa pressure for 25 min using a pressure cooker. This process was repeated several times until the supernatant became fully colourless. This steam treated tea waste was then dried in an oven for 24 hours at (80 ± 5^0C) temperature, and then it was grinded by a grinder. The grinded tea wastes particles were sieved to obtain particle size finer than 0.149 mm and stored in an air tight container for further use.

2.4. Batch Adsorption Experiments

The sample of Ni ion solution of 100 ml was prepared by diluting the stock solutions into desired concentration (20 ppm to 200 ppm). The fixed dose of tea waste adsorbent (1.0 g) was then added to this sample. The pH value (6) of the sample solution was adjusted by adding 0.1 M HCl or NaOH solutions. The sample flask was kept at 303 K temperature, at a constant stirring speed of 150 rpm in a temperature controlled orbital shaker for a contact time of 2 h for equilibrium. The samples were filtered thereafter and the residual concentration was determined using atomic absorption spectrophotometer(AAS).Each batch experiment was conducted two times and the average values were taken in the data analysis.The adsorption capacity q_t at equilibrium of TW and percentage sorption of Ni(II) was calculated according to the following general equation:-

$$q_t = \frac{(C_0 - C_e)V}{M} \tag{1}$$

$$\% \ of \ Removal \ (R) = \frac{(C_o - C_e)}{C_o} X \ 100 \tag{2}$$

III. RESULTS AND DISCUSSION

3.1 Characterization of the Adsorbent

3.1.1. SEM Analysis

The SEM micrographs of TW surface before and after Ni (II) ions adsorption are shown in Fig.1. (a) and (b) respectively. The porous and irregular surface layer structure of the TW can clearly be observed. It is consisted of

irregular particles ranging from 2 to 20 µm.This structure might provide TW good adsorbing properties. After adsorption the surface seems more covered. This might be due to adsorbed Ni(II) ions on it.
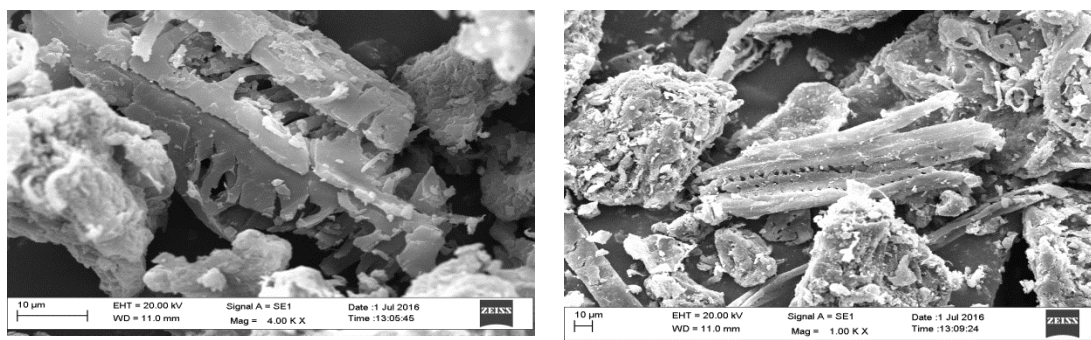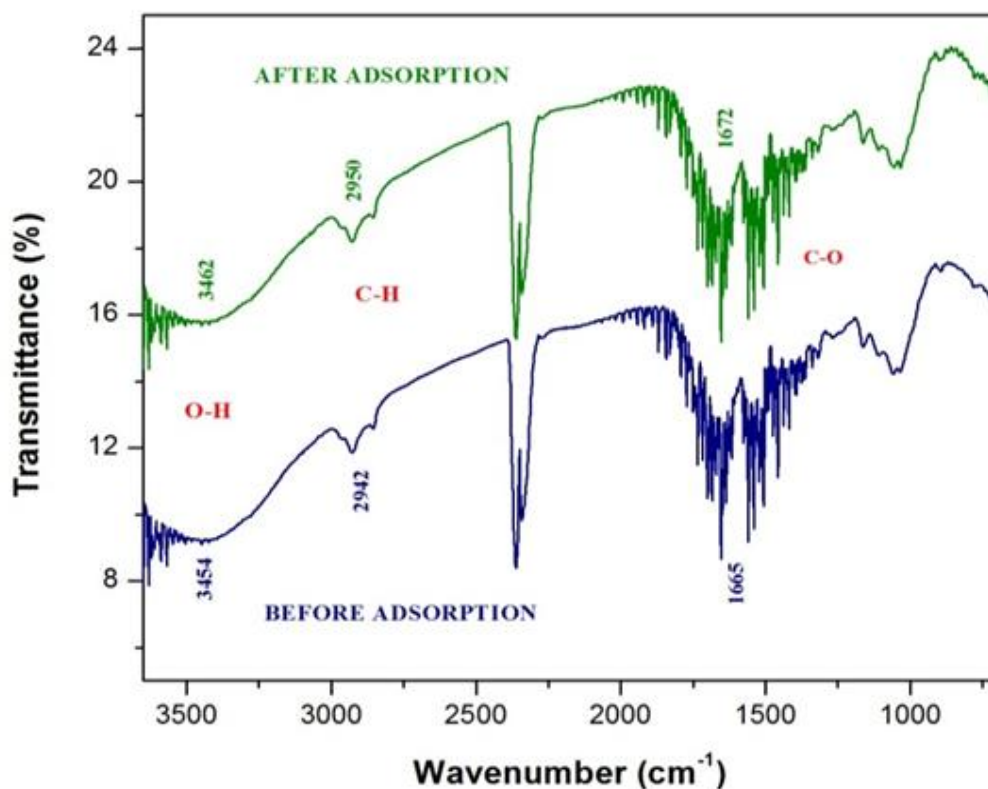

(a) Tea waste before adsorption   **(b) Tea waste after adsorption**

Fig.1. SEM images of tea waste

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

3.1.3. ZETA potential

The Zeta potential is a parameter which describes the surface charging behaviour of the substance at different pH values of the solution. The variation of Zeta potential with pH value of tea waste TW at room temperature, 303 K, is shown in Fig.3. The pH_{zpc} (zero-point charge of pH) lies near pH 2.4.It means that the surface of TW is positively charged below pH 2.4 and negatively charged above pH 2.4. Therefore the surface of TW adsorbent favours the adsorption of positively charged Ni (II) ions above pH 2.4 due to opposite polarity.
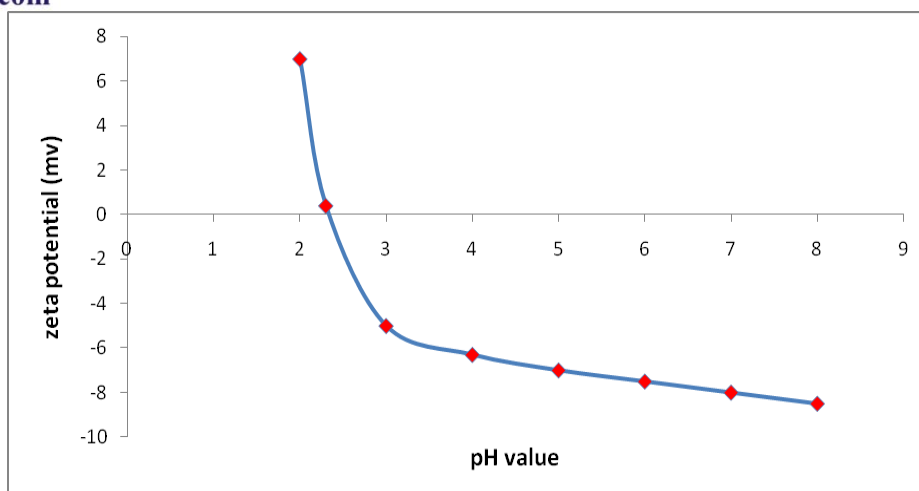
Fig. 3. Zeta potential of TW as a function of solution pH

3.1.4. BET Surface Area and pore volume

The specific surface area of TW was determined from the surface area analyzer using nitrogen gas by the Brunauer, Emmett and Teller (BET) method. The surface area of TW was found to be 122.03 (m^2 / g) and the pore volume was 0.132 cm^3/g.

Table.1.

Measured physico-chemical properties of adsorbent TW

S.No.	Items	Value
1.	pH $_{Zpc}$ (Zero point charge)	2.4
2.	Specific Surface area BET (m^2 / g)	122.03
3.	Average particle size (mm)	0.150
4.	Pore Volume (cm^3 / g)	0.132

3.2. Effect of parameters

3.2.1. Effect of initial Ni (ll) ion Concentration

The effect of initial Ni (II) ion concentration on the percent removal of Ni(II) is shown in Fig.4.The initial concentration was varied from 20 ppm to 200 ppm in 10 samples of Ni(II) ion solution. It shows that there is a
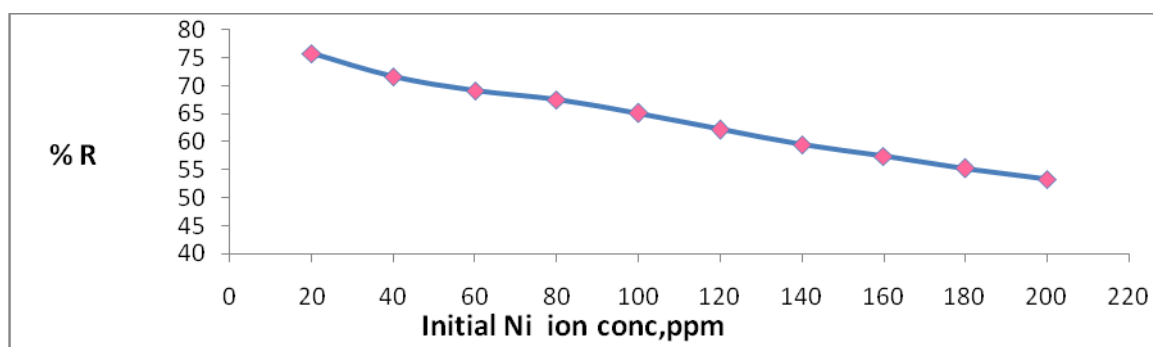

Fig. 4. Change in (%) removal of Ni with varying initial Ni (ll) ion concentration 20-200 ppm

(TW dose 1.0 g/100 ml Ni ion solution , 150 rpm , pH 6 , 303 K , contact time 2 h)

gradual decrease in the metal uptake by the sorbent TW. Initially it goes up to maximum value of 75.8 % at 20 ppm concentration. Then it decreases upto 53.3 % at 200 ppm concentration. This might be due to the fact that initially more fresh adsorption sites are available on the sorbent TW and gradually they are occupied and becomes partly saturated. At higher concentration low adsorption yield may be due to the non availability of new adsorption sites and increase in the number of ions competing for available binding sites in the sorbent [16].

3.2.2. Effect of adsorbent dose

The effect of dose of TW on the sorption of Ni (II) ions is shown in Fig.5. The TW dose was varied from 0.2 to
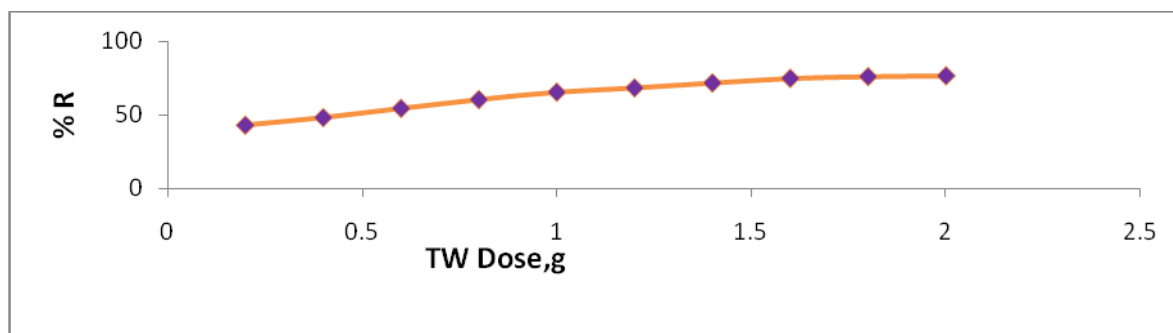

Fig. 5. Change in (%) removal of Ni with varying dose of sorbent TW (initial concentration Ni ion solution 100 ppm ,150 rpm , pH 6 , 303 K contact time 2 h)

2 g in 10 samples As the TW dose increases from 0.2 to 2 g, the number of sites for sorption also increases and 95-96 % uptake was achieved at around 2 g dose. Initially, the adsorption sites are occupied almost fully by the available metal ions. But the rate of increase was slower at higher sorbent dose after 1.0 g and the adsorption process reaches almost to equilibrium.Therefore further studies were performed with 1.0 g of sorbent dose.3.2.3. Effect of contact time

The effect of contact time on the extent of adsorption of Ni (II) is shown in Fig.6. The removal of Ni was increased from 38.7 % to 67.6 % with increase in contact time   from 0.25 h to 7 h. The equilibrium was achieved within 2 h. The fact that initially for the adsorption of Ni ion large number of vacant sites were available , which slowed down later due to the exhaustion of remaining surface sites and repulsive forces between solute molecules and bulk phase.According to these results, the contact time was fixed at 2 h for the rest of the batch experiments to ensure the equilibrium conditions.
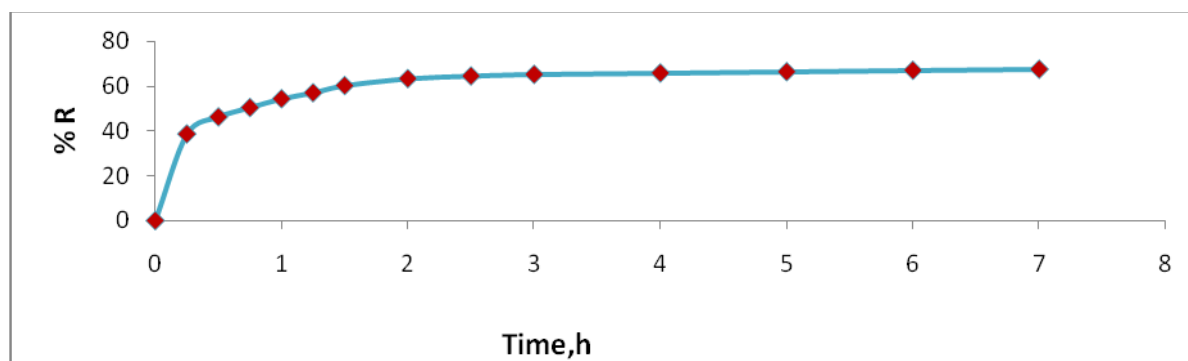

Fig. 6. Change in (%) removal of Ni with varying Contact time

(initial conc. Ni ion solution100 ppm ,150 rpm, pH 6,303K ,sorbent dose 1.0 g/100 ml)

3.2.4. Effect of pH value

The effect of pH on the Ni adsorption is shown in Fig.7.The pH value of the sample was varied from 1-10 in 10 samples. At the lower pH values the removal is very low because at pH less than 2.4 (pH$_{zpc}$ at zero point charge) the surface charge of the TW becomes positive, which restricts the approach of positively charged Ni(II) metal
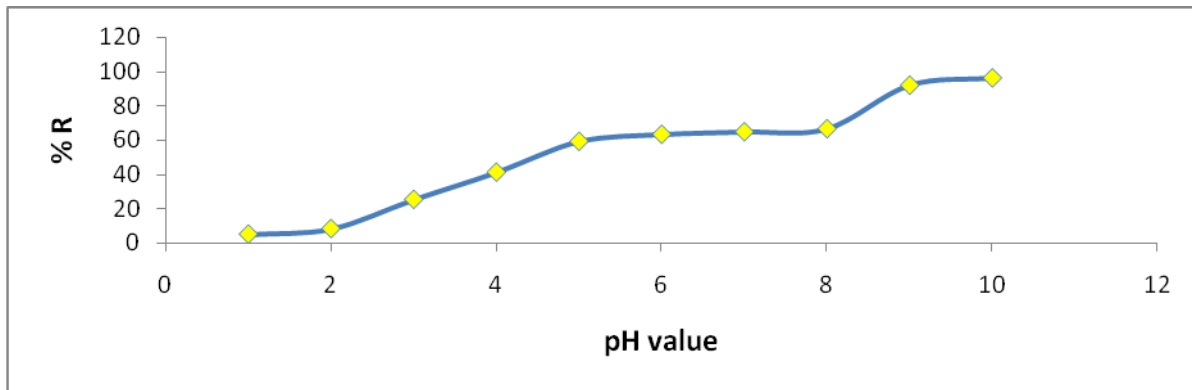

Fig.7. Change in (%) removal of Ni with varying pH value

(initial concentration Ni ion solution 100 ppm , TW dose 1.0 g/100 ml, 150 rpm, 303 K, contact time 2 h)

cations. The protons then compete with metal ions for TW and thereby decreases the interaction of Ni (II) metal ions with the sorbent.. Whereas at higher pH above 2.4, it attract positively charged metal ions and binding occurs. The maximum equilibrium uptake for Ni (II) ions was found to be at pH 6.Therefore pH 6 value was selected as the optimum value for the adsorption experiments.3.3. Adsorption Isotherm.

3.3.1.The Langmuir Isotherm Model

Langmuir isotherm model assumes the monolayer adsorption, homogeneous surface and negligible interaction forces between adsorbed molecules . The linear form of Eq is

$$\frac{1}{q_e} = \frac{1}{q_m K_L \, C_e} + \frac{1}{q_m} \qquad (3)$$

Where, q_m and K_L can be found from the linear plot of $1/q_e$ vs $1/C_e$ from the Fig.8.

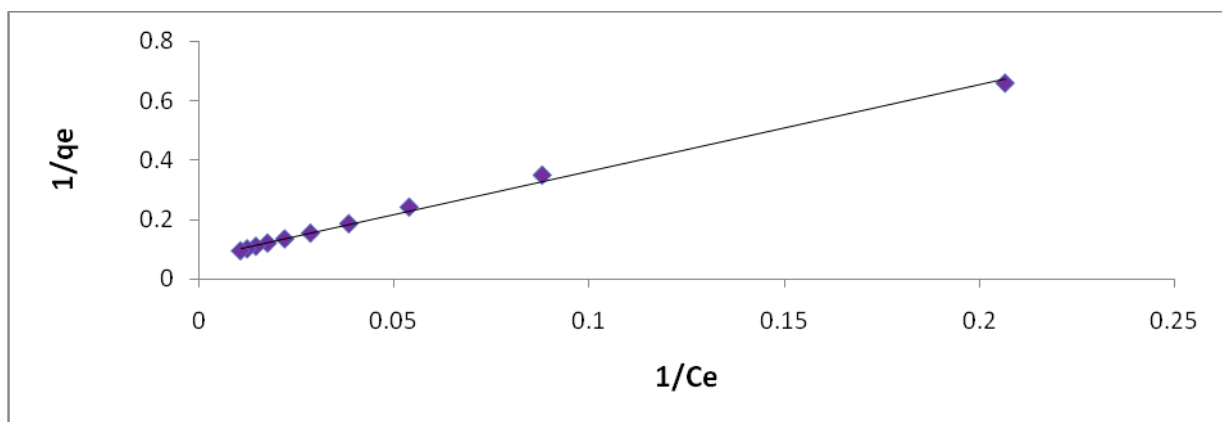The calculated parameters of the Langmuir model are presented in Table.3.

Fig.8. Langmuir isotherm for the adsorption of Ni(II) on TW

(Initial Conc. 20-200 ppm, pH 6, sorbent dose 1.0 g/100 ml ,303 K)

3.3.2. The Freundlich Isotherm Model

 This model is used for multilayer adsorption, with non-uniform distribution of adsorption heat over the heterogeneous surface. The linear form of Freundlich equation is

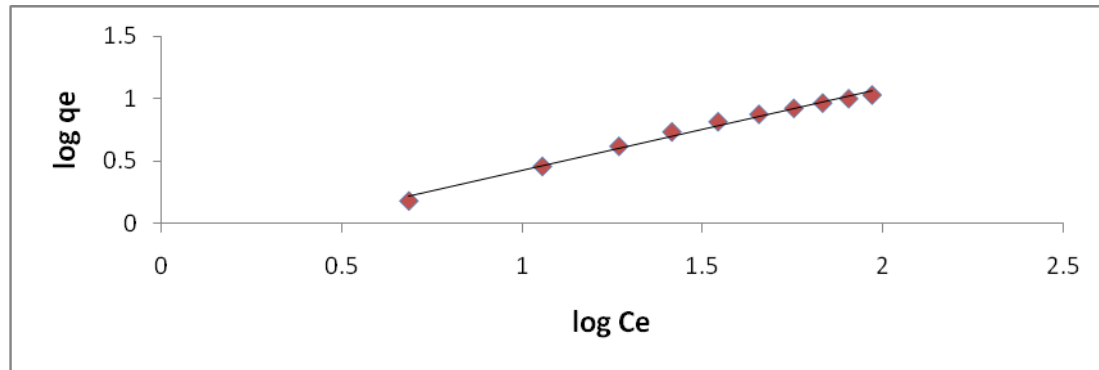$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e \tag{4}$$

Fig.9. Freundlich isotherm for the adsorption of   Ni (II) on TW (Initial Conc.20 -200 ppm , pH 6, TW dose 1.0 g/100 ml ,303 K)If the value of Freundlich constant *n* is from 1-10 it depicts favourable adsorption.

The plot of this model is shown in Fig.9 and the calculated parameters of the Freundlich model are presented in Table.2.

Table.2.

Various isotherm constants for adsorption of Ni (II) on TW

S.No.	Adsorption isotherm	Parameters	Parameters values	R^2
1	**Langmuir**	q_m, **(mg/g)**	**14.09**	**0.996**
		K_L , **(L/mg)**	**0.0245**	
		R_L, **(L/mg)**	**$0.1 < R_L < 0.5$**	
2	Freundlich	*n*,	1.761	0.991
		K_F (mg/g)	0.815	

The higher (R^2 = 9.996) value from Table.2. suggests that the Langmuir model describes the adsorption data more effectively .It is well known that the Langmuir equation assumes a homogeneous surface and a good fit of this equation means the adsorption is monolayer adsorption . This suggests that the adsorption of Ni (II) on the TW mainly takes place at specific homogeneous sites and is confined to one layer adsorption. The maximum Langmuir adsorption capacity was found to be 14.09 mg/g.

3.4. Adsorption Kinetics

3.4.1.Pseudo first order model: The linear form of Lagergren equation [16] is given as

$$log\ (q_e - q_t) = log q_e - \frac{K_1\ t}{2.303} \tag{5}$$

Figure.10 shows the plot of this model. The pseudo first-order rate constant K_1 and q_e (cal.) values were determined from the slope and the intercept of the plot and are listed in Table 3.
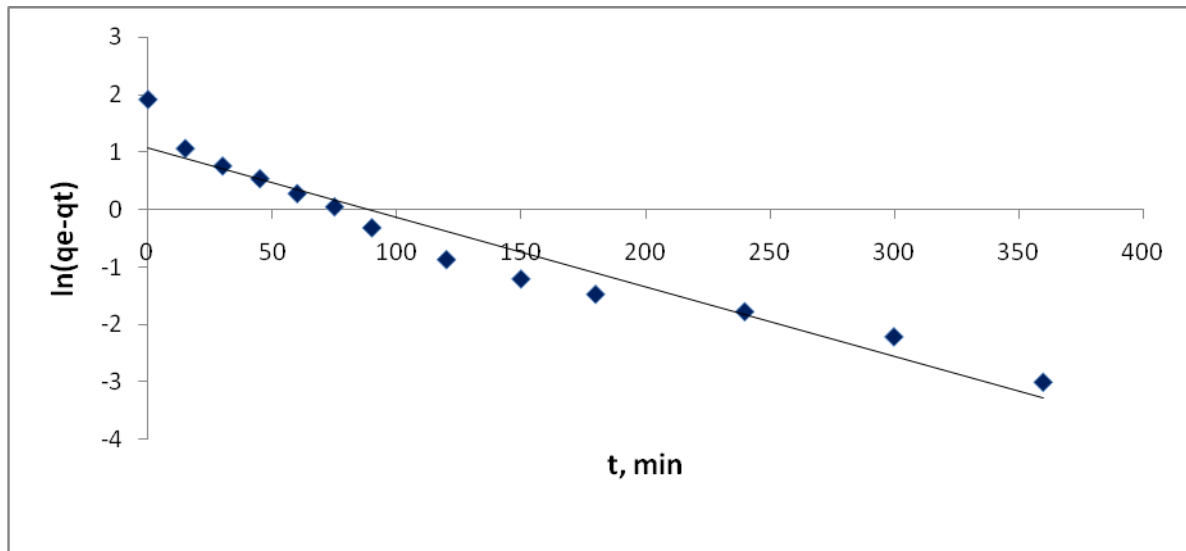

Fig.10. Pseudo first order kinetics for adsorption of Ni (II) on TW

(TW dose : 1.0 g/100 ml,150 rpm , pH 6,303 K)

3.4.2.Pseudo second order model

It is described by the following equation

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^{\,2}} + \frac{t}{q_e} \qquad\qquad (6)$$

The plots of t/q_t vs t are shown in Figure.11 The values of q_e (cal.) and rate constant K_2 were determined from the slope and intercept of the plot and are listed in Table 3.
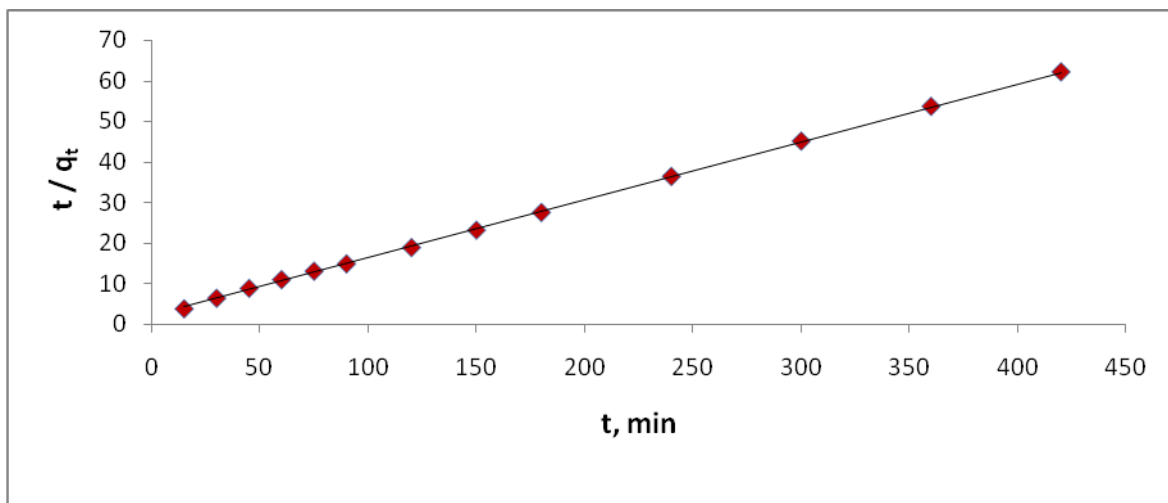

Fig.11. Pseudo second order kinetics for adsorption of Ni (II) on TW

(TW dose 1.0 g/100 ml, 150 rpm , pH 6 ,303 K)

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Table.3.

Kinetic parameters for adsorption of Ni (II) on TW

S. No	Kinectic Model	parameters	R^2
1	Pseudo first order	q_e, mg / g = 6.76	0.932
		K_1, min^{-1} = 0.0276	
		q_e,(cal) mg / g = 11.75	
2	**Pseudo second order**	**K_2 , g / mg^{-1} min^{-1} =0.0095**	**0.999**
		q_e, (cal), mg/g = 7.04	

The results from kinetic models shows that the experimental data fitted well to the pseudo-second-order kinetic model with a high R^2 value (R^2 = 0.999).Similar results were also reported in previous studies.Therefore the adsorption follows Pseudo second order rate kinetics.

IV. CONCLUSIONS

The removal rate of Ni (II) with TW was found to be more than 75%.Analysis of FTIR showed that the main functional groups of TW participating in Ni(II) binding were OH, CH, and C-O groups. The equilibrium data fitted well with Langmuir isotherm model with high correlation coefficient and the adsorption capacity was found to be 14.09 mg/g.The kinetic data fitted well for pseudo second order model.

These finding reveals that tea waste (TW), can be effectively used as a low cost adsorbent for the removal of Ni (II) heavy metal from aqueous solution. Because tea consumption is worldwide and tea wastes can easily be acquired, tea waste has a high potential for practical applications in treating Ni (II) contaminated wastewaters. For further study pre-treatments of tea waste TW is recommended to enhance its capacity and removal efficiency.

V. ACKNOWLEDGMENT

Nomenclature

C_o initial concentrations of Ni (II) ion solution, (ppm)

C_e concentrations of Ni (II) ion solution at equilibrium,(ppm)

K_L Langmuir constant related to the free energy of adsorption (L/mg)

K_F Freundlich constant related to adsorption intensity,(mg/g)(L/mg)$^{1/n}$

K_1 rate constant of pseudo first-order kinetics

K_2 rate constant for pseudo second-order kinetics

M amount of sorbent TW (g)

n constant indicative of the intensity of adsorption, n >1 shows good adsorption

q_e amount of adsorbate Ni (II) ions adsorbed per unit weight of the sorbent TW at equilibrium,(mg /g)

q_m maximum adsorption capacity of TW (mg/g)

q_t amount of adsorbate Ni (II) ions adsorbed per unit weight of the sorbent TW at time t minutes, (mg /g)

R_L Langmuir separation factor

TW   tea waste

V volume of Ni (II) solution (ml)

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