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Adsorption of Cd (II) Ions from Synthetic Waste Water by Tea Waste

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Abstract

A batch adsorption study was carried out to evaluate the suitability of tea waste (TW) as a low cost adsorbent for the removal of Cd (II) metal ions from synthetic waste water. The effect of pH,temperature, sorbent dose and initial metal ion concentration along with the study of equilibrium and thermodynamics 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 Cd (II). The equilibrium data was fitted into Langmuir and Freundlich models.The Langmuir model described the sorption isotherm best. The Langmuir adsorption capacity was found to be 14.10 mg/g at pH 6 .Thermodynamics study revealed the spontaneous and exothermic nature of the process.The results showed that the tea waste (TW) has a good potential to be used as a low cost sorbent for Cd(II) ions removal.

Keywords: Adsorption, tea waste, Cadmium, Equilibrium, Thermodynamics

Introduction

As a result of fast expansion of industries the release of toxic heavy metals into water streams are causing much concern now. The heavy metals with an atomic density greater than 6 g/cm^3 like nickel, lead, cadmium, copper, mercury and chromium are toxic to human beings and other living species if their concentrations exceed certain limits[1,2,3,4].

The undesirable amount of Cadmium ions Cd (II) are found in the effluents of various industries like metallurgy, paint & pigments, electroplating, petroleum refining, battery manufacture [5,6,7,8]. Cd(II) is non biodegradable and tends to accumulate in living organisms. The higher amount of Cadmium than the permissible level causes detrimental effects in bone tissues, gets accumulated in the kidneys causing its malfunction and disrupting protein metabolism.In Japan in 1955 the consumption of rice containing high concentrations of cadmium led to a surge in the Itai-Itai disease [9].

Various methods have been used for the removal of Cadmium ions Cd (II) from waste water such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, membrane technologies etc [10,11,12,13,14,15].In the recent past years tea waste has been reported to be one of the most promising low cost adsorbent for heavy metals removal from waste water. [16,17].A great amount of tea waste is produced in the world Fig.1.[18] and is usually discarded into the environment which could be effectively used as a low cost adsorbent.

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

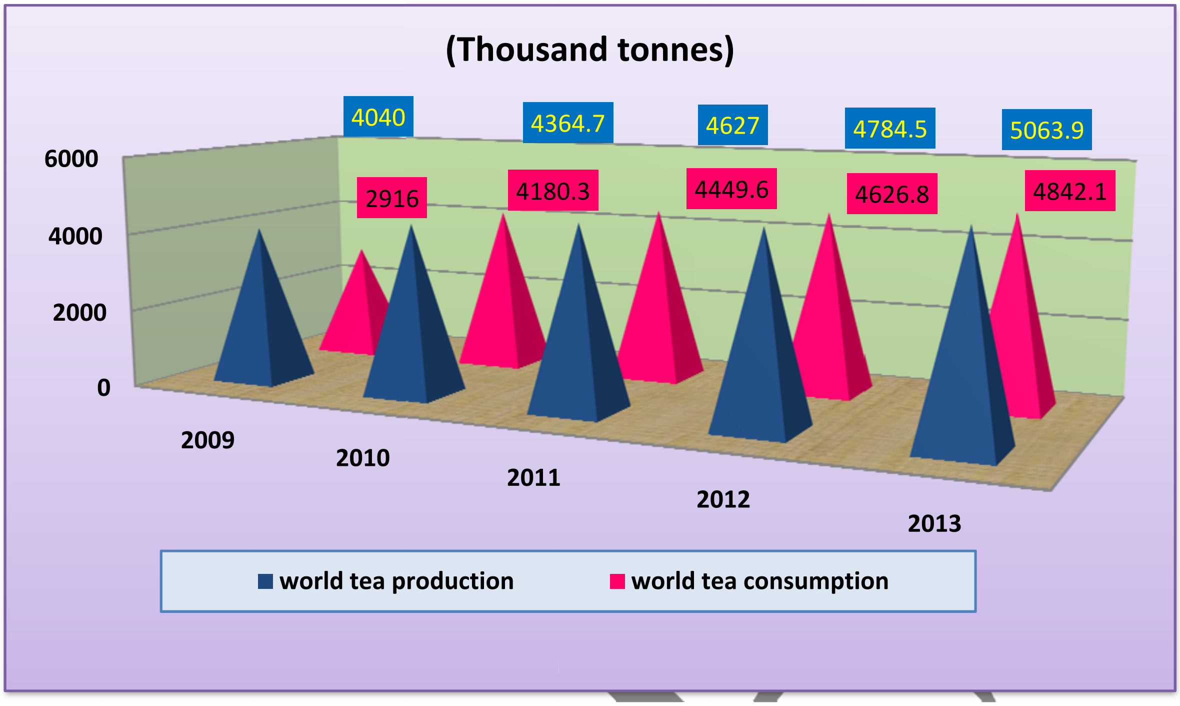


Fig.1. World Tea Production and Consumption

Materials and methods

Instruments Used

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 Cd(II) 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 Cd(II) ions.pH meter model PHEP Hanna Instrument, Italy was used for pH measurements. Scanning Electron Microscope (ZEISS EV018) was used for surface structure study.

Chemicals and reagents

Standard stock solution of 1000 ppm was prepared by dissolving $CdCl_2.2.5H_2O$ (Thomas Baker) in double distilled water. Suitable dilutions of Cd(II) solutions were prepared from it. The pH of the solution was adjusted using HNO_3 and NaOH solutions.

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 tannin colour the raw tea waste was first subjected to steam treatment under 70 kPa pressure for 30 min using a pressure cooker. This process was repeated several times until the tea waste became fully colourless. This steam treated tea waste was then dried in an oven for 24 hours at (80 ± 5^0C) temperature, and 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.

Batch Adsorption Experiments

The samples of Cd(II) ion solution of 100 ml were prepared by diluting the stock solutions into desired concentrations (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 HNO_3 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. 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_e at equilibrium of TW and percentage sorption of Cd(II) was calculated according to the following equations

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\%\ \text{of Removal (R)} = \frac{(C_0 - C_e)}{C_0} x100 \quad (2)$$

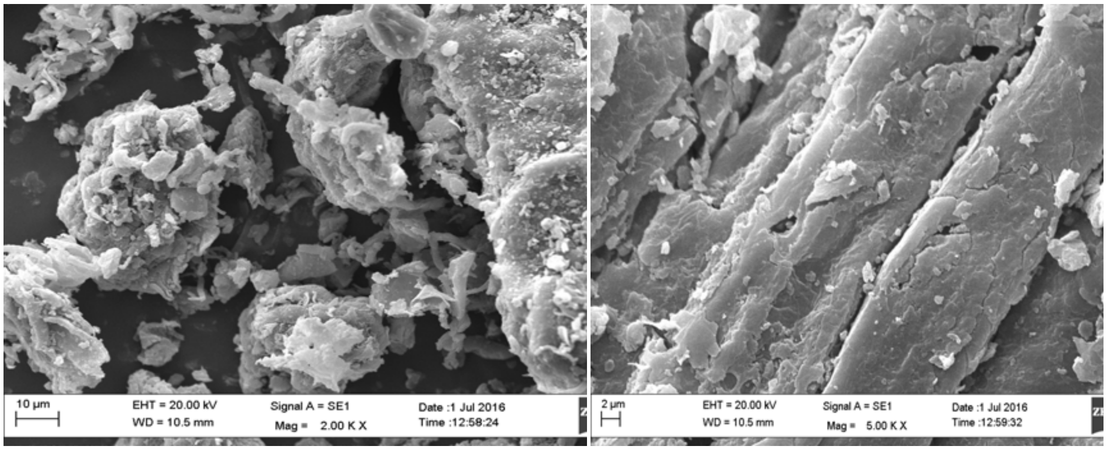
Where C_o- initial concentrations of Cd (II) ion solution, (ppm), C_e- concentrations of Cd (II) ion solution at equilibrium,(ppm), M- amount of adsorbent (g), q_e- amount of adsorbate Cd (II) ions adsorbed per unit weight of the sorbent at equilibrium,(mg /g), V- volume of Cd (II) solution (ml).

Results and discussion

Characterization of the Adsorbent

SEM Analysis

The SEM micrographs of TW surface before and after Cd (II) ions adsorption are shown in Fig.2. (a) and (b) respectively. The porous and irregular surface layer structure of the TW can clearly be observed. It is consisted of irregular particles which might provide TW good adsorbing properties.The surface seems more covered after adsorption. This might be due to adsorbed Cd (II) ions on it [19].



(a) Tea waste before adsorption (b) Tea waste after adsorption of Cd(II)

Fig.2. SEM images of tea waste

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra was recorded in the frequency range of 4000-500 cm $^{-1}$wave number and is shown in Fig.3. The spectrum shows a number of peaks due to absorption of different functional groups present on

TW. The intensity of the peaks for Cd (II) loaded TW was shifted slightly. The absorption peak from 3447 is shifted to 3458 which exhibits the stretch of O-H group. The another peak shown at the 2933 is slightly shifted to 2945 is showing the C-H stretch while shift in C-O stretch is from 1660 to 1670. It shows that carboxyl and hydroxyl groups were main contributors in Cd(II) metal ion uptake [19]. Based on FTIR spectra, it can be concluded that the chemical nature of TW does not alter and it remains almost the same after Cd(II) adsorption.

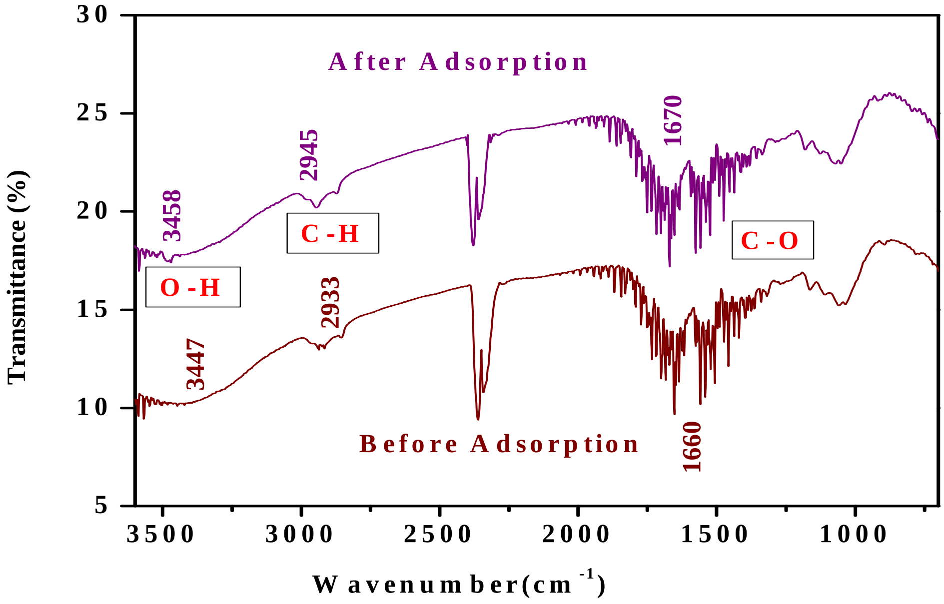


Fig.3. FTIR spectrum of TW before and after adsorption. Red letters are the functional groups likely involved in Cd(II) binding.

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ZETA potential

The pH_{zpc} (zero-point charge of pH) lies near pH 2.4[19].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 Cd (II) ions above pH 2.4 due to opposite polarity[19].

The physico-chemical of TW are shown in Table.1. [19]

Table.1 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

Effect of parameters

Effect of initial Cd (ll) ion Concentration

The effect of initial Cd (II) ion concentration on the percent removal of Cd(II) is shown in Fig.4.The initial concentration was varied from 20 ppm to 200 ppm in 10 samples of Cd(II) ion solution. It shows that there is a decrease in the metal removal % by the sorbent TW gradually. Initially it starts from a maximum value of 81.2 % at 20 ppm concentration. Then it reaches upto a minimum of 58.3 % at 200 ppm concentration. The reason 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 removal % might be due to the non availability of new adsorption sites and increase in the number of ions competing for available binding sites of the TW [20].

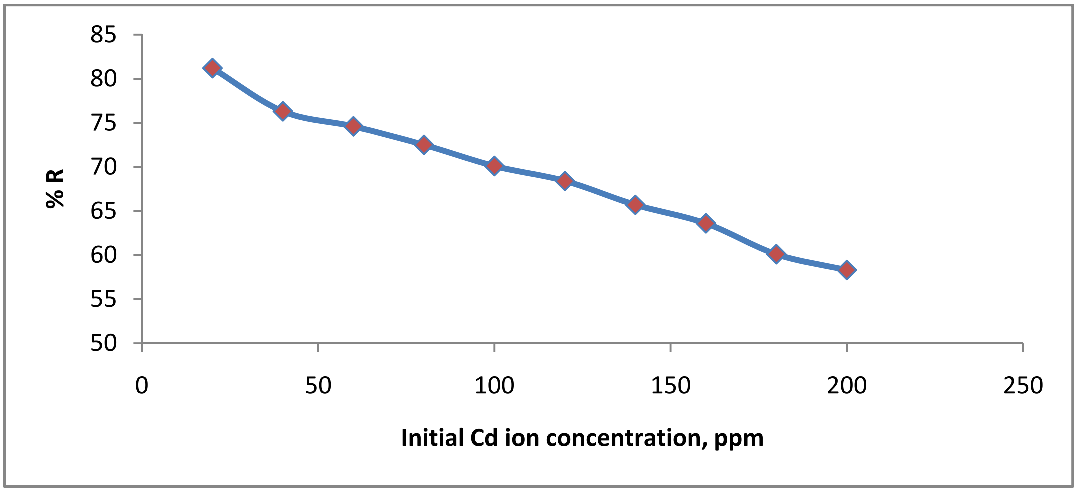

Fig. 4. Change in (%) removal of Cd with initial Cd (ll) ion concentration 20-200 ppm (TW dose 1.0 g/100 ml Cd ion solution,150 rpm,pH 6,303 K,time 2 h)

Effect of adsorbent dose

The effect of dose of TW on the sorption of Cd (II) ions is shown in Fig.5. The TW dose was varied from 0.2 to 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 81.8 % uptake was achieved at around 2 g dose. Initially, the rate was fast as the adsorption sites were occupied almost fully by the available metal ions. But the rate became slow after 1.0 g of adsorbent dose.

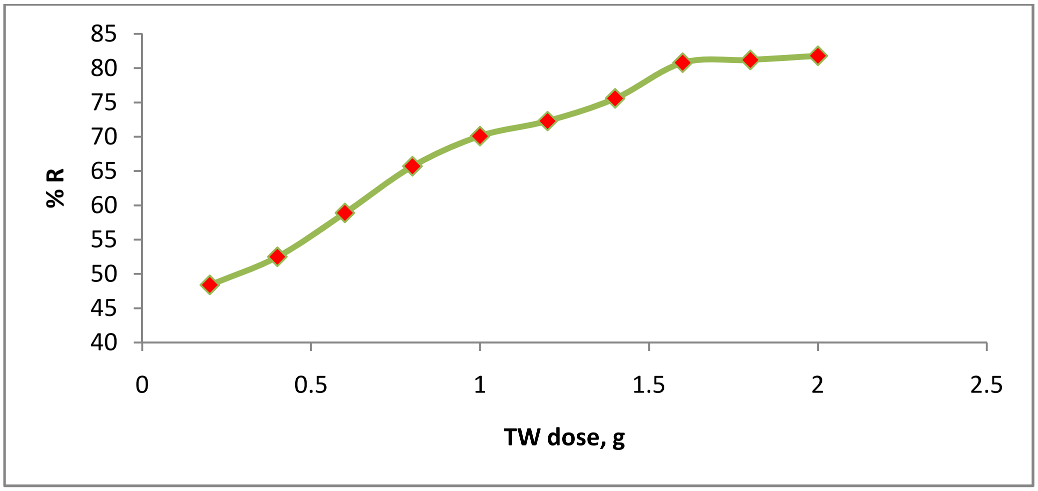

Fig.5.Change in (%) removal of Cd with dose of TW (initial concentration Cd ion solution 100 ppm,150 rpm, pH 6, 303 K, time 2 h)

Effect of pH value

The effect of pH on the Cd (II) adsorption is shown in Fig.6.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 Cd (II) metal cations. The protons then compete with metal ions for TW and thereby decreases the interaction of Cd (II) metal ions with the sorbent.. Whereas at higher pH above 2.4, it attract positively charged metal ions and binding occurs[19]. The maximum equilibrium uptake for Cd (II) ions was found to be at pH 6.After pH 8 hydroxide precipitation starts taking place.

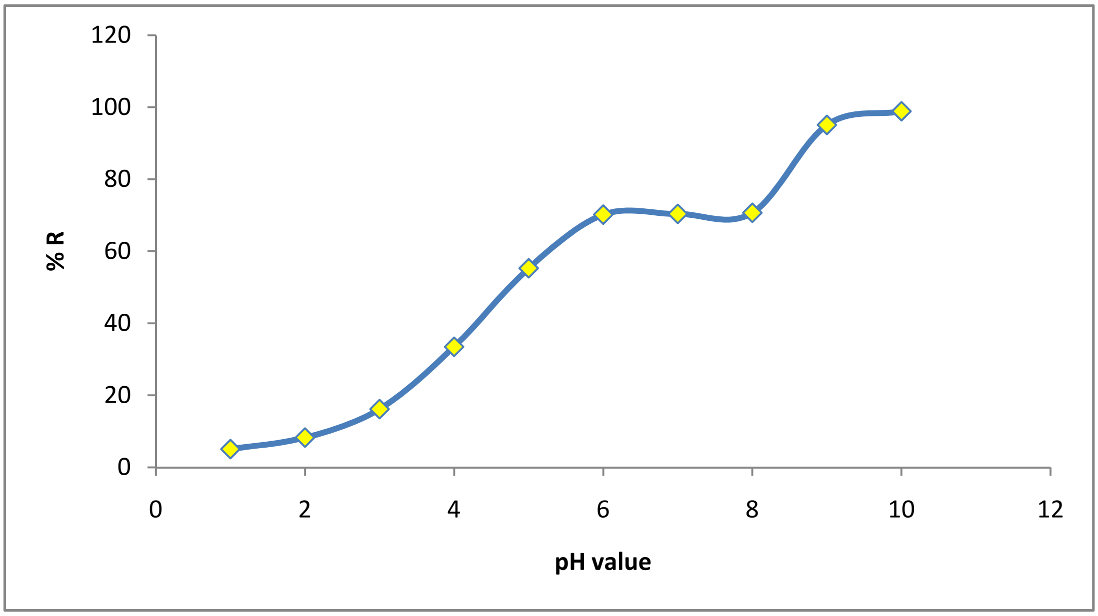

Fig.6. Change in (%) removal of Cd with pH value
(initial concentration Cd ion solution 100 ppm , TW dose 1.0 g/100 ml, 150 rpm, 303 K, time 2 h)

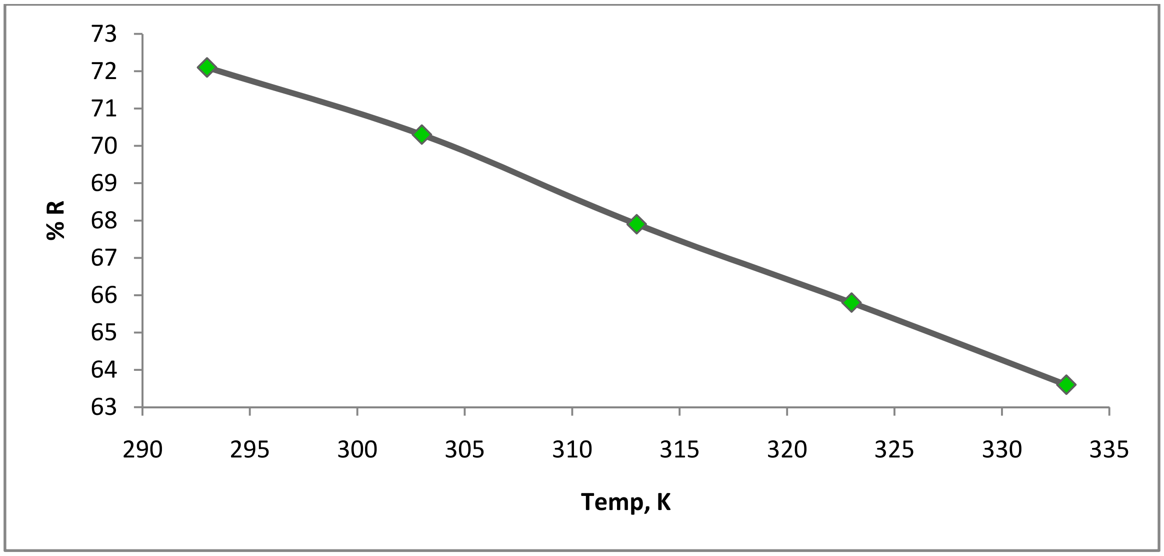

Fig.7. Change in (%) removal of Cd with Temperature
(initial concentration Cd ion solution 100 ppm,150 rpm, TW dose1.0 g/100 ml, pH6, time 2 h)

Effect of temperature

The effect of temperature on the metal adsorption is shown in Fig.7.The adsorption experiments were conducted at five different temperatures (293,303,313,323,333K). The maximum removal % of Cd (II) was found to be 72.1 % at 293 K. At higher temperatures, removal % gradually decreased. The decrease of removal percentage at higher temperatures may be due to the decrease in the active binding sites in the sorbent TW.This might be because of certain changes in structures with temperature in the adsorbent TW . This is indicative of an exothermic process.

Adsorption Isotherm .

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 [19]

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

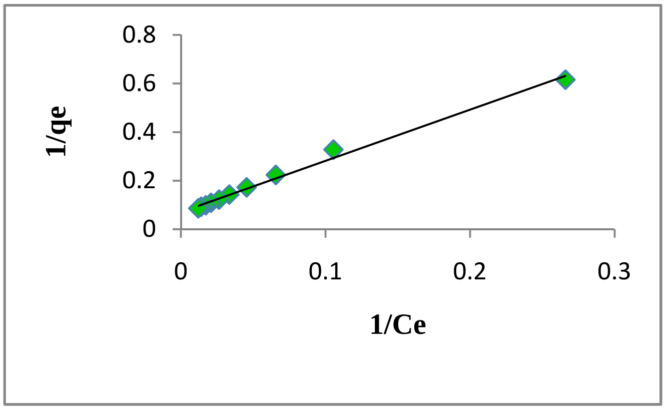

Fig.8. Langmuir isotherm for the adsorption of Cd(II) on TW
(Initial Conc. 20-200 ppm, pH 6, sorbent dose 1.0 g/100 ml ,303 K)

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.Also

$R_{L,}$ (L/mg) separation factor can be calculated $R_L = \frac{1}{(1+K_L C_0)}$ (4)

Where, K_L- Langmuir constant related to the free energy of adsorption (L/mg), q_m- maximum adsorption capacity (mg/g), R_L- Langmuir separation factor, 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.2.

The Freundlich Isotherm Model

This model is used for multilayer adsorption, with non-uniform distribution of adsorption heat over the heterogeneous surface[19]. The linear form of Freundlich equation is

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

If the value of Freundlich constant n is from 1-10 it depicts favourable adsorption.

Where, K_F- Freundlich constant related to adsorption intensity,(mg/g)(L/mg)$^{1/n}$ and n- constant indicative of the intensity of adsorption, n >1 shows good adsorption.The plot of this model is shown in Fig.9 and the calculated parameters of the Freundlich model are presented in Table.2. The higher ($R^2 = 9.991$) value and lower n value from Table.2. suggests that the Langmuir model describes the adsorption data more effectively .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 Cd (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 14.10 mg/g.

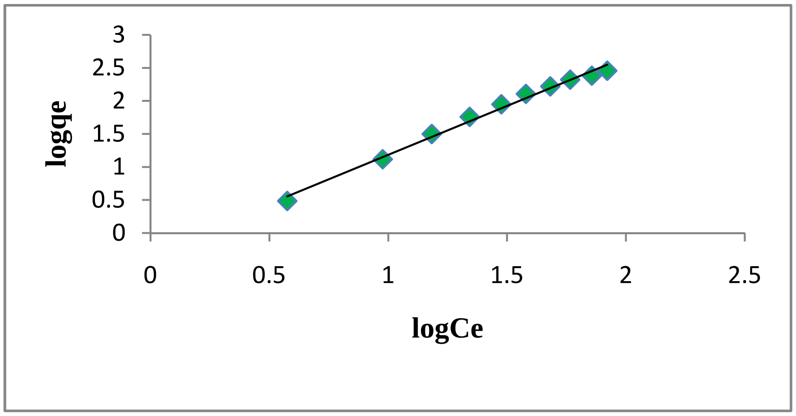

Fig.9. Freundlich isotherm for the adsorption of Cd (II) on TW
(Initial Conc.20 -200 ppm , pH 6, TW dose 1.0 g/100 ml ,303 K)

Table.2. Various isotherm constants for adsorption of Cd (II) on TW

S.No.	Adsorption isotherm	Parameters	Parameters values	R^2
1	Langmuir	q_m, (mg/g)	14.10	0.991
		K_L , (L/mg)	0.03	
		$R_{L,}$ (L/mg)	$0.1 < R_L < 0.4$	
2	Freundlich	n,	0.68	0.990
		K_F (mg/g)	0.50	

Thermodynamics of adsorption

The temperature was varied from 293 to 333K. Thermodynamic parameters[2,5] such as change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined from the following equations :

$$K_d = \frac{q_e}{C_e} \quad (6)$$

$$\Delta G^0 = -RT \ln K_d \quad (7)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where K_d- equilibrium constant, ΔG^0- Gibb's free energy (kJ/mol), ΔS^0-entropy(kJ/mol), ΔH^0-enthalpy(kJ/mol) and R- ideal gas constant

The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot $\ln K_d$ vs 1/T of the Fig.10 and are listed in Table.3. The negative value for enthalpy change (ΔH^0) indicates that this is an exothermic sorption process. The affinity of tea waste TW for Cd (II) ions is shown by the positive value of entropy (ΔS^0) whereas, the negative value of (ΔG^0) confirms[5] that the sorption process is spontaneous at the selected range of temperature.

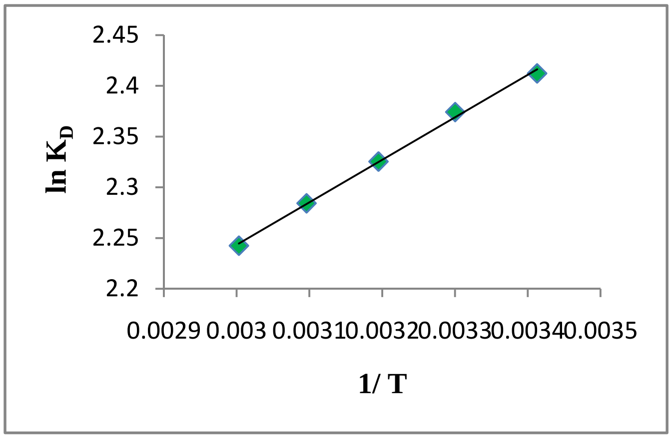

Fig.10. Van't Hoff plot for adsorption of Cd (II) on TW
(initial concentration Cd ion solution 100 ppm, TW dose1.0 g/100 ml, 150 rpm, pH6)

Table.3. Thermodynamic parameters for adsorption of Cd (II) on TW

S.No.	T (K)	ΔG^0 (KJ/mol)	ΔH^0(KJ/mol)	ΔS^0 (KJ/mol)
1	293	-5.9	-3.5	0.0082
2	303	-5.9		
3	313	-6.1		
4	323	-6.1		
5	333	-6.20		

Conclusions

The removal % of Cd (II) with TW was found to be more than 81%.Analysis of FTIR showed that the main functional groups of TW participating in Cd(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 14.10 mg/g and thermodynamic study revealed that adsorption was a spontaneous and exothermic process.

Therefore tea waste (TW) could be effectively used as a low cost adsorbent for the removal of Cd(II) metal ions from synthetic waste water.For further study pre-treatments of tea waste TW is recommended to enhance its capacity and removal efficiency.

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