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Research Article

Determination of Equilibrium Parameters of Cd(II) Adsorption by Waste Tea Leaves

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ABSTRACT

The waste tea leaves has been used as an adsorbent to remove Cd(II) ion from aqueous solution. The adsorption characteristics and corresponding groups responsible for adsorption process were investigated by Atomic Absorption Spectroscopy (AAS) and Infrared Spectroscopy (IR). The comparative studies revealed that the Base Treated Waste Tea Leaves (BTWTL) has maximum adsorption capacity compare to that of Acid Treated Waste Tea Leaves (ATWTL), Methanol Treated Waste Tea Leaves (MTWTL) and Water Treated Waste Tea Leaves (WTWTL). The batch experiments depicted that solution's pH was a key factor for the adsorption process of Waste Tea Leaves (WTL). The optimum pH (4.00) and the adsorption equilibrium could be obtained by centrifuging for 180 minutes at RT and 140 RPM. The optimum dose is 1.00 g for 50 mL aqueous Cd(II) solution which concentration was 10 ppm. IR spectroscopy analysis showed that carbonyl and hydroxyl groups were mainly responsible for the adsorption of Cd(II) and acted as the active sites. Adsorption isotherms studies showed that Langmuir isotherm and Freundlich isotherm fitted well and Temkin isotherm also fitted quite good. These suggested that Waste Tea Leaves (WTL) can be used as a potential and appealing adsorbent for the removal of Cd(II) from aqueous solutions. Which could be used for removing of Cd(II) from the waste water in future.

Keywords: Tea Leaves; Spectroscopy; Adsorbent; Equilibrium

INTRODUCTION

Rapid growth in industrialization (especially, dyeing, tannery and apparel industries) has significantly contributed to the release of toxic heavy metals into the water streams such as rivers, canals and ponds. Among these heavy metals; Hg, Pb, Cd, Cr and Ni are extremely health hazard even if the concentration of these metals is minute. These heavy metals are not biodegradable and tend to deposit in living organisms causing several diseases and disorders [1] through the food cycle. It is well known that cadmium (a highly toxic metal) is considered as a major pollutant for soil and water. It is released into the environment through mining and smelting, its use in various industrial processes and enters into the food chain when the plants uptake it from contaminated soil or water. As a result of the removal of cadmium from wastewater is currently one of the crucial environmental challenges. The conventional techniques for the removal of metal ions from aqueous solution include chemical precipitation, ion exchange, chemical oxidation-reduction, reverse osmosis, electro-dialysis, ultrafiltration, etc. which have their own limitations for example, incomplete metal removal, requirements of expensive equipment and monitoring systems, costly reagents, high energy requirement, toxic sludge generation or other waste products that require disposal [2]. Nowadays, adsorption is a physiochemical wastewater treatment process, which is gaining attention of environmentalist and chemist as a means of producing high-quality effluents, which are low in metal ion concentrations. Natural materials which are easily available in large quantities and certain waste products from industries and households have drawn attention to the

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researchers to be used as inexpensive adsorbents. Some of these are tea factory's wastes [3], eucalyptus barks [4], *Hevea brasilinesis* saw-dusts [5], beech saw-dusts [6], the agricultural byproducts of *Lentinus edodes* [7], non-living microbial biomasses [8], fresh water algae [9], clay minerals [10], phosphate rocks [11], etc. Tea is the most widely consumed beverage after the water through the world for its beneficial effects on health such as antioxidant, anti-carcinogenic, antimicrobial activities [12,13]. In Bangladesh, the consumption of tea is about 86 million kg per year so a significant amount of waste tea leaves is produced as well. The previous studies showed that tea residue is largely composed of cellulose, hemicelluloses, lignin, condensed tannins and structural proteins [14]. These components of waste tea residue have good potential as metal scavengers from solutions and wastewaters because they contain carboxylate, aromatic carboxylate and phenolic hydroxyl functional groups [15], which have relatively strong physical and chemical adsorption capacity towards the metal ions [16].

MATERIALS AND METHODS

Chemicals

Standard $Cd(NO_3)_2$ solution (1000 mg/L ± 4 mg/L), NaOH and HCl, obtained from Sigma-Aldrich, USA and all of these are analytical grade; the purity was above 99.5%, 98.9% and 37.0%, respectively.

Preparation of Cd(II) solution

Simulated waste water solutions were prepared by diluting standard $Cd(NO_3)_2$ in deionized water to obtain 10 mg/L Cd(II) solutions. The pH of the 10 ppm Cd(II) solution was 2.63. The pH adjustments of the Cd(II) solutions were done by using diluted NaOH and diluted HCl; freshly prepared solutions were used every time.

Preparation of adsorbent

Waste tea leaves were collected from tea stall, BCSIR gate, elephant road, Dhaka, Bangladesh. Afterwards, the wet waste tea leaves were dried for 6 hours. Soluble and colored components were removed thoroughly from the waste tea leaves by washing with boiling water then dried for 8 hours and it is referred as Waste Tea Leaves (WTL). Next, WTL soaked either in 0.5 M HCl, 0.5 M NaOH, 5% MeOH or deionized H_2O then washed and dried; these are referred as Acid Treated Waste Tea Leaves (ATWTL), Base Treated Waste Tea Leaves (BTWTL), Methanol Treated Waste Tea Leaves (MTWTL) and Water Treated Waste Tea Leaves (WTWTL), respectively. All washing was done by deionized water. Drying was carried out in a drying oven at 100°C-105°C.

Batch experiments

Batch experiments included the effect of washing solvents, pH, adsorbents and initial Cd(II) concentrations. All of the experiments were done at 25°C by adding known weight of WTL in 250 mL glass stoppered conical flasks on a rotary shaker at 140 rpm containing Cd(II) solutions for 180 minutes. The concentrations of Cd(II) determined by AAS and the responsible functional groups of WTL were detected by FT-IR spectroscopy.

RESULTS AND DISCUSSION

Selection of adsorbents

The four types of adsorbents (ATWTL, BTWTL, MTWTL and WTWTL) prepared from waste tea leaves were taken in equal amount in different 250 mL Erlenmeyer flask. The initial Cd(II) ion concentrations and pH of the solutions were same at each flasks and shaking with adsorbent at the same rpm for the same period of time. It was found that BTWTL exhibited the highest removal of Cd(II) than other three (Figure 1). Base treatment has sufficiently freed the active sites of the adsorbents and grinding increased the surface area promoting a great number of active sites to adsorb Cd(II) from solution. Therefore, BTWTL adsorbent was chosen and all the experiments were conducted using this adsorbent.

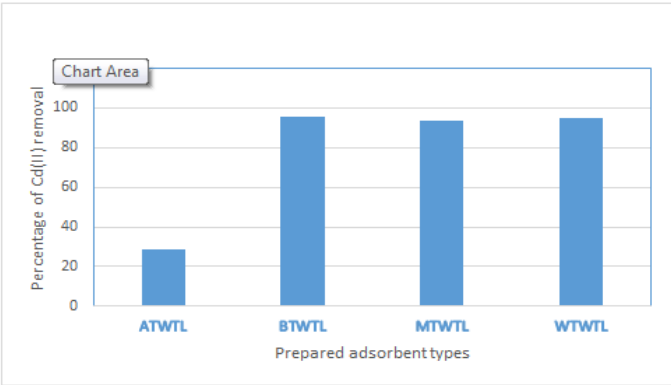

Figure 1: The bar chart illustrated the percentage of Cd(II) removal from aqueous solution for ATWTL, BTWTL, MTWTL and WTWTL. Conditions: BTWTL adsorbent 10 g/L, initial Cd(II) concentration 10 ppm, contact time 180 minutes, agitation rate 140 rpm, temperature 25°C.

Fourier Transform Infrared Spectroscopy (FTIR) analysis

The functional groups before and after adsorption of Cd(II) onto BTWTL and the corresponding infrared adsorption bands are given in Table 1. The infrared spectra were obtained using Shimadzu IRTracer-100 FT-IR spectrophotometer. The FT-IR spectra before and after adsorption of BTWTL are shown in Figures 2 and 3, respectively. Metal ions are generally adsorbed by carboxylic, phenolic, hydroxylic, carbonyl groups [17]. As shown in Figures 2,3 and Table 1, the spectra displayed a number of adsorption peaks which indicated the active functional groups present in BTWTL. The shifting of these peaks indicated that the O-H stretching, alkane C-H stretching and C=O stretching were mainly responsible for the adsorption of Cd(II) onto BTWTL [18].

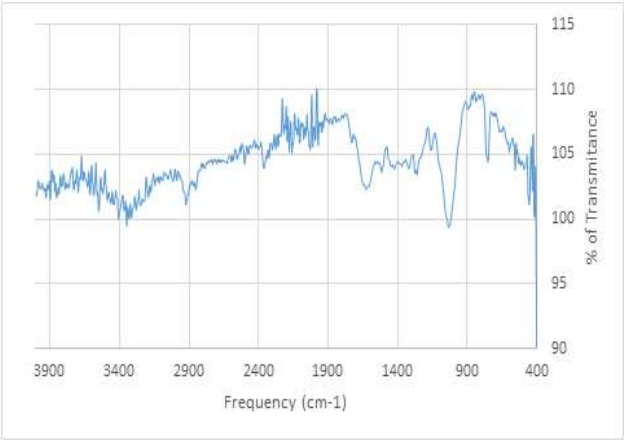

Figure 2: The FT-IR spectra of BTWTL: Before adsorption.

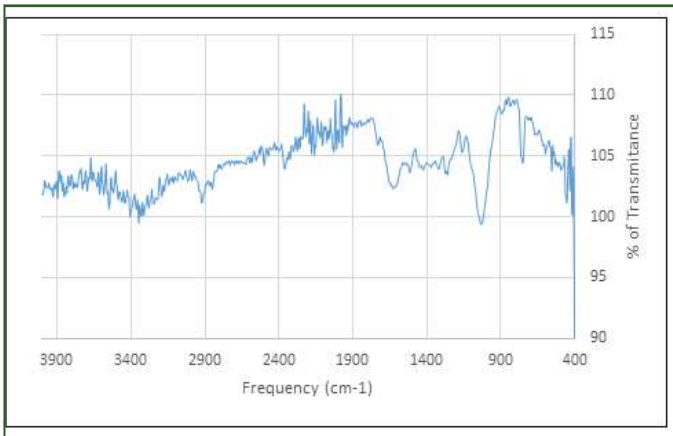

Figure 3: After adsorption. Conditions: pH 4.0, adsorbent 10 g/L, initial Cd(II) concentration 10 ppm, contact time 180 minutes, agitation rate 140 rpm, temperature 25°C.

Table 1: FTIR spectra of BTWTL before and after adsorption.

IR peaks	Frequency in cm^{-1}			Corresponding functional groups
	Before adsorption	After adsorption	Difference	
1	3348	3329	-29	O-H stretching
2	2924	2920	-4	C-H stretching asymmetric
3	2850	2850	0	C-H stretching Symmetric
4	1624	1651	26	C=O stretching
5	1033	1033	0	C-O stretching

Effect of pH on Cd(II) adsorption

To investigate the effect of pH, the adsorption of Cd(II) onto BTWTL was measured at five different pH (2.0, 4.0, 6.0, 8.0 and 10.0) for initial Cd(II) concentration of 10 ppm and the percentage of removal were presented in (Figure 3).The initial pH value of a solution might change the surface charge of an adsorbent, the degree of ionization of an adsorbate molecules and the extent of dissociation of functional groups on the active sites of an adsorbent [19], thus affecting the adsorption capacity. Therefore it plays an important role in the adsorption of Cd(II) on BTWTL. As shown in Figure 3, the adsorption capacity was only 95.60% at pH 2.0 and then it increased with increasing pH and reached up to a maximum value of 96.79% at pH 4.0. After that, it decreased very slowly up to the pH of 8.0. A similar behavior reported [20] for the adsorption of Pb(II). This phenomenon can be explained by the surface charge of the adsorbent and the presence of H^+ ions in the solution. At pH 2.0, ATTR became positively charged due to the adsorption of H^+. Thus the electrostatic force of repulsion between BTWTL and Cd(II) was prominent. In addition, the concentration of H^+ was high at low pH and they competed with Cd(II) ions in the solution for the active sites, so the adsorption was very low. At pH 4.0 BTWTL became negatively charged due to the adsorption of OH^- and the electrostatic attraction force between BTWTL and Cd(II) was significant. Moreover, as pH increased the competition of H^+ with Cd(II) ions decreased. The active sites of the surface became more negatively charged [21]. As a result, the adsorption process was favored at high pH 4.0. The precipitation of Cadmium hydroxide will play a leading role during heavy metal removal process at pH above 6.0 (Figure 4) [22].

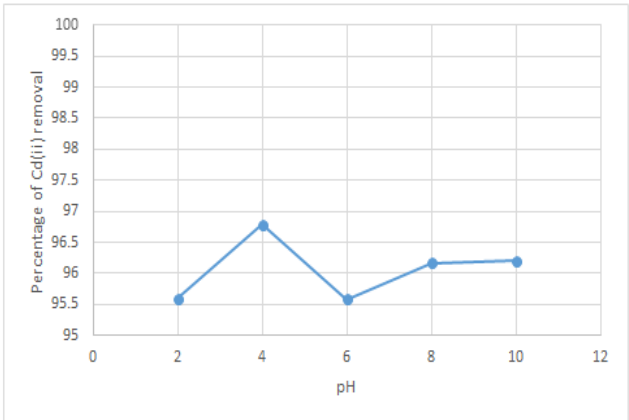

Figure 4: The effect of pH for removing Cd(II) ions, conditions: BTWTL adsorbent 10 g/L, initial Cd(II) concentration 10 ppm, contact time 180 minutes, agitation rate 140 rpm, temperature 25°C.

Effect of adsorbent

To investigate the effect of adsorbent, the adsorption of Cd(II) onto BTWTL was measured at five different adsorbent's doses (5, 10, 20 and 30 g/L) for initial Cd(II) concentration of 10 ppm and the percent removal were presented in (Figure 4). When the adsorbent's dose was increased from 5g/L to 10 g/L, the removal of metal increased from 83.3% to 96.79%. It was obvious that the percent removal of heavy metals increased rapidly with increase of the adsorbent dose due to the greater availability of the exchangeable sites or surface area. However, a little increase in metal ions removal beyond an optimum dose may be attributed to the reaching of equilibrium between adsorbate and adsorbent at the existing operating conditions [23]. The higher adsorbent dose caused screening effect of a dense outer layer of cells and blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [24]. The optimum dose for the removal of Cd(II) ions was found to be 20 g/L with removal efficiency of 97.98% (Figure 5).

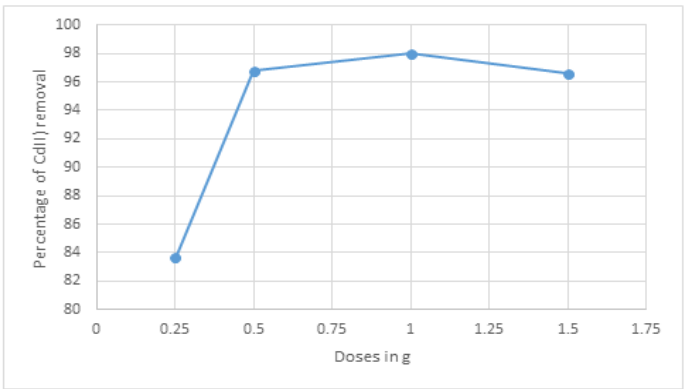

Figure 5: The effect of doses for removing Cd(II) ions, conditions: Initial Cd(II) concentration 10 ppm, contact time 180 minutes, agitation rate 140 rpm, temperature 25°C.

Effect of initial Cd(II) concentration

The driving force for overcoming the mass transfer obstacle of molecules between aqueous and solid surface could be predicted by varying the initial metal ion concentrations [25,26]. The effect of initial Cd(II) ion concentration on its removal was carried out at optimized adsorbent dose, contact time and pH by varying the metal ion concentrations from 5 ppm-40 ppm (Figure 5). Figure 5 showed that the adsorption of Cd(II) increased with the increase of metal ion concentrations from 5 ppm-30 ppm. This caused by the interaction between the adsorbate and adsorbent by creating some new adsorption sites or by increasing the rate of intra particle diffusion of Cd(II) ions into the pores of the adsorbent. The decrease in adsorption of Cd(II) for initial metal concentration of 40 ppm was caused by the increase in number of metal ions competing for available binding sites and the lack of free binding sites [27]. This also could be due to the development of a barrier by the adsorbed Cd(II) ions surrounding the molecular surface of the adsorbent molecules (Figure 6).

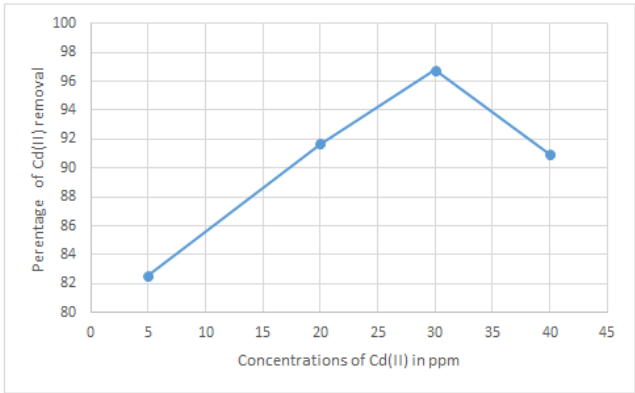

Figure 6: The effect of concentrations of Cd(II) ions, conditions: BTWTL adsorbent 10 g/L, contact time 180 minutes, agitation rate 140 rpm, temperature 25°C.

Adsorption isotherm

An adsorption isotherm is characterized by certain constant values that express the surface properties and affinities of the adsorbent. This can be used to compare the adsorptive capacities of the adsorbent for different pollutants [27] as well. The experimental data showed in Table 2 were applied to the Langmuir, Freundlich and Temkin isotherms for determining the mechanism of Cd(II) ions adsorption on BTWTL. The constant parameters of the corresponding isotherm equations for this adsorption process were calculated by regression using a linear form of the isotherm equations. The constant parameters and correlation coefficients (R^2) were tabulated in Table 3.

Langmuir isotherm model

$$\frac{1}{q_e} = \frac{1}{Q_0 K}\frac{1}{C_e} + \frac{1}{Q_0} \qquad (1)$$

Where, C_e is the equilibrium concentration, ppm, q_e is the amount absorbed at equilibrium, mg/g, Q_0 and K are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively (Tables 2,3 and Figure 7).

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL that has been used to predict if an adsorption system "favorable" or "unfavorable". The separation factor, RL defined by equation (2):

$$R_L = \frac{1}{1 + KC_0} \qquad (2)$$

Where, C_0 is the initial Cd(II) concentration, ppm, K is the Langmuir adsorption equilibrium constant, L/g.

Table 2: Experimental data for adsorption isotherm.

C_0, Initial Cd(II) conc. (ppm)	C_e, Equilibrium Cd(II) conc. (ppm)	q_e, Amount adsorbed at equilibrium (mg/g)
5	0.8705	0.4565
20	1.662	0.9169
30	2.5809	1.3709
40	3.624	1.8188

Table 3: Isotherm constants for adsorption of Cd(II) on BTWTL.

Langmuir isotherm	
Q_0, mg/g	329.9372
K, L/g	0.0016
R^2	0.9979
Freundlich isotherm	
K_f, L/g	0.5365
n	0.9724
R^2	0.9966
Temkin isotherm	
A, L/g	1.7486
B	0.9427
R^2	0.9805

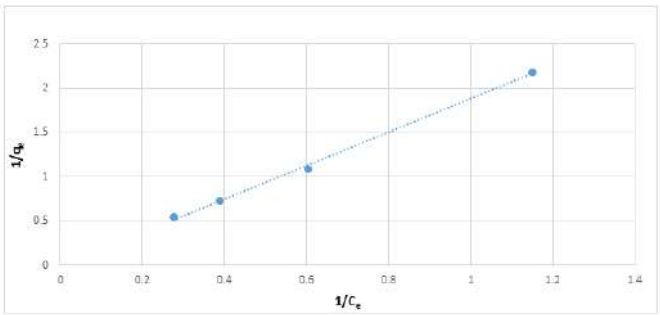

Figure 7: Langmuir isotherm.

The isotherm was unfavorable when $R_L>1$, the isotherm was linear when $R_L=1$, the isotherm was favorable when $0<R_L<1$ and the isotherm was irreversible when $R_L=0$. The values of R_L were 0.9986, 0.9973, 0.9959 and 0.9942 while initial Cd(II) concentrations were 5, 20, 30 and 40 ppm, respectively. The values of RL for adsorption of Cd(II) ions on BTWTL studied at different concentrations (between 0 and 1) indicating favorable adsorption of cadmium on BTWTL (Figure 8).

Freundlich isotherm model

$$q_e = K_f C_e^n \quad (3)$$

Where, q_e is the amount absorbed at equilibrium, mg/g, C_e is the equilibrium concentration, ppm, K_f and n are the Freundlich model constants, respectively.

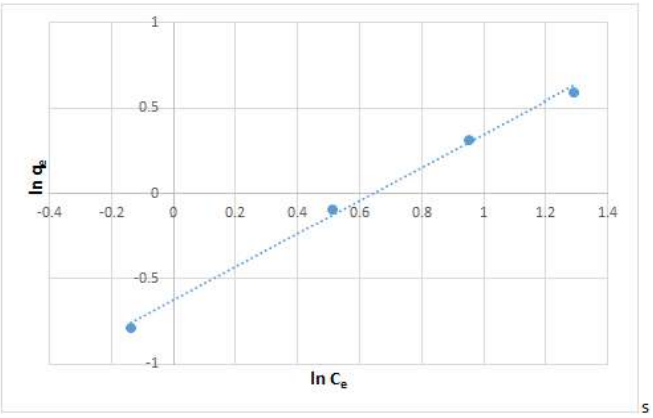

Figure 8: Freundlich isotherm.

Temkin isotherm

The derivation of the Temkin isotherm assumed that the fall in the heat of sorption was linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form. Temkin isotherm model is shown in equation (4):

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (4)$$

$$q_e = B \ln A + B \ln C_e \quad (5)$$

Where, B=(RT/b), q_e is the amounts absorbed at the equilibrium concentration, mg/g, C_e is the amount absorbed at the equilibrium concentration, ppm, T is the absolute temperature. K and R are the universal gas constants, 8.314 J/(mole K). The constant b is related to the heat of adsorption [26-28] (Figure 9).

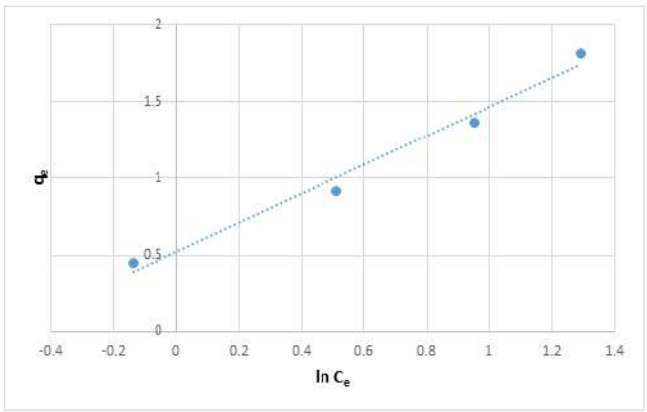

Figure 9: Temkin isotherm.

From Table 3 (based on correlation coefficients) and Figures 6-8, it was evident that the adsorption of Cd(II) onto BTWTL best fitted into the Langmuir and Freundlich isotherm model (R^2=0.9979 and 0.9966, respectively). The experimental data also fitted quite well into the Temkin isotherm model (R^2=0.9805). The Langmuir isotherm for adsorption of Cd(II) onto BTWTL was found to be linear and the correlation coefficients were extremely high as tabulated in Table 3 which was clear from Figure 6. From Figure 7, we noted that the Freundlich isotherm for Cd(II) adsorption by BTWTL was also found to be linear and the correlation coefficients were as high as that of Langmuir isotherm, as seen in Table 3. In addition, if we look into Figure 8 we can see that the Temkin isotherm was also a good fit for Cd(II) adsorption by BTWTL. The correlation coefficients were also high as shown in Table 3.

CONCLUSION

The adsorption of Cd(II) ion by BTWTL was dependent on pH, adsorbent dosage and initial metal ion concentration. The adsorption capacity was highest at pH 4.0. The optimum dosage for Cd(II) adsorption by BTWTL was found to be 20 g/L. The optimum concentration for Cd(II) ion adsorption by BTWTL was obtained as 20 ppm. Using Langmuir, Freundlich and Temkin isotherms, the adsorption of Cd(II) onto BTWTL was explained with proper causes. Langmuir and Freundlich's models demonstrated better correlation coefficients than the other model in the studied concentration. Temkin's model also showed quite good correlation coefficient. So sued tea leaves con be used as an effective adsorbent for the removal of Cd(II) ions from water, wastewater.

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