

# ADSORPTION OF METALS ONTO TEA FACTORY WASTE: A REVIEW

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## ABSTRACT

Industrial waste constitutes the major source of various kinds of metal pollution in natural water. There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are Cd, Zn, Pb, Cr, Cu, and Ni. There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater. Adsorption is one of the alternatives for such cases and is an effective purification and separation technique used in industry especially in water and wastewater treatments. Cost is an important parameter for comparing the adsorbent materials. Therefore, there is increasing research interest in using alternative low-cost adsorbents. In recent years, tea factory waste (TFW) is also gaining grounds due to its potential to overcome heavy metal pollutants. Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins. In present paper a review on potential of TFW as an adsorbent for the removal of toxic metals were discussed. Characterization of various type of TFW, equilibrium studies, kinetic studies, thermodynamic studies and batch studies for the removal of toxic metals by adsorption were presented.

**Keywords:** *Adsorption, TFW, review, characterization, batch study, kinetics, equilibrium, thermodynamics.*

## 1. INTRODUCTION

Rapid industrialization has led to increase disposal of heavy metals into the environment. The tremendous increase in use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are of special concern because of their persistency. Industrial waste constitutes the major source of various kinds of metal pollution in natural water. There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are Cd, Zn, Pb and Ni. These heavy toxic metals entered into the water bodies through waste water from metal plating industries and industries of Cd- Ni batteries, phosphate fertilizer, mining, pigments, and stabilizers alloys etc. Electroplating corrosion of galvanized piping and dezincification of brass besides other industrial wastes. The metal ions i. e.  $Cd^{+2}$ ,  $Zn^{+2}$ ,  $Ni^{+2}$  and  $Pb^{+2}$  are important heavy metals in the soil water system since they are micronutrients in plants and animals including man. Mining activities, agricultural runoff, industrial and domestic effluents are mainly responsible for the increase of the metals released into the environment. Metals that are released into the environment tend to persist indefinitely, accumulating in living tissues throughout the food chain and are posing a serious threat to the environment and public health [1]. Generally, heavy metals (lead, chromium, cadmium, nickel etc.) are present in low concentration in wastewater and are difficult to remove from water. There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater [2].

These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electro precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultrafiltration, electrodialysis etc. [3]. These methods differ in their effectiveness and cost. Chemical precipitation, reverse osmosis and other methods (ultra filtration, electrochemical deposition etc.) become inefficient when contaminants are present in trace concentration [4] and do not seem to be economically feasible for such industries because of their relative high costs [5]. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and economic. For high strength and low volumes of wastewater, heavy metal removal by adsorption technique is good proposition. Adsorption is one of the alternatives for such cases [6] and is an effective purification and separation technique used in industry especially in water and wastewater treatments [7]. It is the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. Adsorption has advantages over other methods. The design is simple, and it is sludge-free and can involve low investment in terms of both the initial costs and land.

Cost is an important parameter for comparing the adsorbent materials [8]. Activated carbon has been recognized as a highly effective adsorbent for the treatment of heavy metals in wastewater, but is readily soluble under extreme pH conditions [9]. Activated carbon is most widely used adsorbent, as it has good capacity for adsorption of carcinogenic metals. However, high cost of activated carbon and 10-15% loss during the regeneration has deterred the utilization of activated carbon in the developing countries [10].

Therefore, there is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fiber, coal, sugarcane bagasse, straw, wool fiber and by products of rice mill, soybean and cottonseed hulls [11-14]. Ion exchange resins are totally effective but expensive. Coal and straw, are inexpensive but ineffective. Peat moss has been found as very effective in adsorbing heavy metals. Muhammad et al. [4] used slow sand filters to remove heavy metals (Cu, Cd, Cr, Pb). Quek et al. [5] used the sago processing waste, which is both a waste and a pollutant, to adsorb lead and copper ions from solution. Mahavi et al. [15] used tea waste as an adsorbent for the removal of heavy metals (Cd, Pb, Ni) from industrial waste. About 94-100% removal of lead, 86% for Ni and 77% for Cd were achieved using tea waste.

In last few years, a vast number of publications have been dedicated to the removal of heavy metals from waste water by using adsorption techniques with different low cost materials. In recent years, tea factory waste (TFW) is also gaining grounds due to its potential to overcome heavy metal pollutants. Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins. In other words, one-third of the total dry matter in tea leaves should have good potential as metal scavengers from solutions and waste waters since the above constituents contain functional groups. The responsible groups in lignin, tannin or other phenolic compounds are mainly carboxylate, aromatic carboxylate, phenolic hydroxyl and oxyl groups.

In India, yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production [16]. The amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted [17]. Amount of TFW produced per year after processing is about 190400 tonnes in India alone. Very few investigators have investigated TFW as an adsorbent for the removal of heavy metals.

The adsorption ability of tea waste were investigated for the removal of Cu(II) and Cd(II) from single (non-competitive) and binary (competitive) aqueous systems [17,18]. Malkoc and Nuhoglu [18] investigated the removal of nickel from aqueous solution using TFW. The effect of adsorbent dose, initial metal concentration, solution pH, agitating rate and temperature on the adsorption of nickel on TFW were studied. Mahavi et al. [15] studied the removal of cadmium, lead and nickel from industrial waste water using tea waste. Malkoc and Nuhoglu [19] studied the feasibility of TFW as an adsorbent for the removal of chromium in fixed bed. Their study indicated that the TFW can be used as an effective and environment friendly adsorbent for the treatment of chromium in aqueous solutions. Malkoc and Nuhoglu [20] investigated the fixed-bed adsorption of Ni(II) ions from aqueous solutions using TFW. The bed depth service time (BDST) model and the Thomas model were used to analyze the experimental data and the model parameters were evaluated. Thermodynamics and kinetic studies were carried out to find out the potential of TFW as an adsorbent for the removal of chromium [21]. Amarasinghe and Williams [22] used the tea waste as a low cost adsorbent for the removal of Cu and Pb from waste water. Batch experiments were conducted to determine the factors affecting adsorption and kinetics of the process. Wasewar et al. [16, 23-25] studied the adsorption of zinc onto Indian TFW.

In present paper a review on potential of TFW as an adsorbent for the removal of toxic metals were discussed. Characterization of various type of TFW, equilibrium studies, kinetic studies, thermodynamic studies and batch studies for the removal of toxic metals by adsorption were presented.

## 2. SOURCE OF TFW

In India, yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production. The amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted [17]. Amount of TFW produced per year after processing is about 190400 tonnes in India alone. The work on use of TFW as an adsorbent for the removal of toxic heavy metals has been done in India, Turkey, and Sri Lanka only. The details of the sources of TFW used by various researchers are summarized in **Table 1**.

## 3. PREPARATION OF ADSORBENT FROM TFW

A TFW from Turkey was used by Cay et al. [17] and prior to the experiments following treatment were given. Hydrolysable tannins and other soluble and colored components were removed from the crushed tea wastes by washing with hot water (80°C) for 1 h periods until a colourless solution of tea waste was spectrometrically

observed at room temperature. Decolourised and cleaned tea waste was dried in oven at 105°C and 60–170 mesh particles were used in the adsorption experiments without any further modification. A colourless solution of tea waste is normally observed in 15 washing cycle with hot water (80°C). Since adsorption of heavy metal ions was carried out in relatively cold water (25±0.3°C) in the experiments, washing of tea waste was completed in five cycles and no remarkable interfering colour was observed at room temperature.

**Table 1: Source of TFW as an adsorbent for removal of toxic metals.**

	Reference	Source	Metal
1	Cay et. al. [17]	Tea processing plants located in black sea region in Rize, Turkey.	Cu, Cd
2	Malkoc and Nuhoglu [18]	Tea plants located in black sea region in Giresun-Eynesil, Turkey.	Ni
3	Malkoc and Nuhoglu [19]	Tea plants located in black sea region in Giresun-Eynesil, Turkey.	Cr
4	Malkoc and Nuhoglu [20]	Tea plants located in black sea region in Giresun-Eynesil, Turkey.	Ni
5	Amarasinghe and Williams [22]	Black tea produced from tea plantations from central highlands of Sri Lanka “high grown tea” was used for the experiments.	Cu, Pb
6	Malkoc and Nuhoglu [21]	Tea plants located in black sea region in Giresun-Eynesil, Turkey.	Cr
7	Wasewar et al. [16]	TFW was supplied from Tea Plants located in Palampur, Himanchal Pradesh, India.	Zn
8	Wasewar et al. [24]	TFW was supplied from Tea Plants located in Palampur, Himanchal Pradesh, India.	Zn
9	Wasewar et al. [23]	TFW was supplied from Tea Plants located in Palampur, Himanchal Pradesh, India.	Zn

Mahvi et al. [15] used a very simple procedure to prepare the adsorbent. They washed TFW at the first step and then rinsed with distilled water. After drying in 100°C, it was ground and screened (using screen with mesh size 10). Prior to the experiments, Malkoc and Nuhoglu [18-21] removed other soluble dirtiness and colored components from the TFW by washing with distilled water for much times until a colorless solution of tea waste was spectrometrically observed at room temperature. Decolorized and cleaned tea waste was dried at room temperature for a few days by spreading on gauze.

Black tea produced from tea plantations from central highlands of Sri Lanka “high grown tea” was used for the experiments [22]. Soluble and colored components were removed from tea by washing with boiling water. This was repeated until the water was virtually colourless. The tea leaves were then washed with distilled water and were oven dried for 12 h at 85°C. The dried tea waste was sieved and stored in sealed polythene bags.

A similar kind of preparation method of Cay et al. [17] were used by Wasewar et al. [16, 23, 24]. TFW was supplied from Tea Plants located in Palampur, Himanchal Pradesh, India. TFW was dried first in sun light then it was crushed in a mixer to bring it in required size. Prior to experiments, hydrolysable tannins and other soluble and colored components were removed from crushed tea waste by washing with hot water (80°C) four times and the washing with dilute NaOH solution until a colorless solution of TFW was spectrometrically observed at room temperature. A colorless solution of TFW is normally observed in 15 washing cycle with hot water [17]. It was found that using NaOH solutions instead of pure hot water reduced the number of washing cycles. There may be an effect of washing with NaOH on removal of metal ions by biomass which may contribute in improvement of biosorption capacity of the biomass. This effect has been not considered in their work. Decolorized and cleaned TFW was dried in oven at 105°C and 0.15-0.25 mm particles were used in the adsorption experiments without any further modification.

#### 4. CHARACTERIZATION OF TFW

Generally, the standard procedure was used to determine the physico-chemical characteristic of TFW. The various characteristics of TFW used by various authors are summarized in **Table 2**. It can be seen from **Table 2** that the Indian TFW has the more surface area than the TFW waste from Turkey and Sri Lanka.

#### 5. EFFECT OF SOLUTION pH

The most important single parameter influencing the sorption capacity is the pH of adsorption medium. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and rejects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbent [26]. The pH of feed solution is an important controlling parameter in the heavy metal adsorption process and thus the role of hydrogen ion. It is well known that pH, besides various physicochemical effects, is an important variable in the ion exchange governed adsorption processes, by which surface charges may be changed or modified [17]. In

order to establish the effect of pH on the adsorption of heavy metals onto TFW, various batch and column experiments conducted by various researchers and are summarized in **Table 3**.

**Table 2: Physical and chemical properties of various TFW.**

Characteristics	Values			
	Cay et al. [17]	Malkoc and Nuhoglu [18-21]	Amarasinghe and Williams [22]	Wasewar et al. [16, 23, 24]
Proximate analysis				
Moisture (%)	11.01	11.01	--	4.50
Ash (%)	2.97	2.97	--	3.80
Volatile matter (%)	80.24 (Insoluble components)	80.24 (Insoluble components)	--	75.10
Fixed Carbon (%)	6.04 (Water soluble components)	6.04 (Water soluble components)	--	16.6
Bulk density (kg/m <sup>3</sup> )	328	112	206	224.66
True density (kg/m <sup>3</sup> )	--	--	1105	--
Ultimate analysis (dry basis)				
C	--	--	--	46.740
H	--	--	--	7.642
N	--	--	--	0.831
S	--	--	--	0.005
Chemical analysis of ash (%)				
Insoluble Matter	--	--	--	75.34
Silica	--	--	--	2.45
Ferric	--	--	--	3.65
Alumina	--	--	--	5.66
CaO	--	--	--	11.86
MgO	--	--	--	1.04
Surface area (m <sup>2</sup> /g)				
BET	21.2 (units are not mentioned)	0.39	0.79	1.3196
Langmuir	--	--	--	2.5667
t-plot micropore	--	--	--	0.2756
t-plot external	--	--	--	1.0439
Single point	--	--	--	1.2044
BJH adsorption cumulative	--	--	--	0.8676
Pore Volume (cm <sup>3</sup> /g)				
Single point pore volume	--	--	--	0.004305
t-plot micropore volume	--	--	--	0.000107
BJH adsorption cumulative	--	--	--	0.003973
Pore size				
BET Adsorption average pore width	--	0.15 - 0.25 mm	524.22 μm (surface weighted mean diameter)	130.4903 °A
BJH adsorption average pore diameter	--	--	720.51 μm (volume weighted mean diameter)	183.168 °A
Pore size	--	--	1.92 nm	--

**Table 3: Effect of pH on adsorption of metals onto TFW.**

Reference	Metal	Contact Time	Metal conc.	Adsorbent Dose	pH Range	Optimum pH	Results
Cay et al. [17]	Cu, Cd	1 hr	5 ppm	1 gm/lit	1 - 8	5.5	After pH 5.5, recovery was almost constant for greater pHs. No pH values over 8.0 were studied since precipitation of heavy metals occurs. Optimum is very close to original pH
Malkoc and Nuhoglu [18]	Ni	2 hr	100 mg/lit	10 gm/lit	2 - 5	4	Significantly decreased by reducing the pH values to 2.0 Effect related with zeta potential.
Malkoc and Nuhoglu [19]	Cr	Column study	100 mg/lit	Bed depth: 30 cm, Bed dia: 2 cm	2 - 5	2	The amounts of Cr(VI) ions adsorbed per unit weight of beds for pH 2.0, 3.0, and 5.0 were 33.71, 28.07 and 23.76 mg g <sup>-1</sup> , respectively. The treated volume considerably decreases from about 9600 (breakthrough time 480 min) to 7200 ml (breakthrough time 360 min) as the solution pH increases from 2.0 to 5.0.
Malkoc and Nuhoglu [20]	Ni	Column study	100 mg/lit	Bed depth: 30 cm, Bed dia: 2 cm	2 - 5	4	The removal efficiency was higher at pH 4.0 and for the pH of 2.0, 3.0, 4.0 and 5.0, 17.46, 32.93, 40.25 and 30.68% of total nickel(II) applied to the column was adsorbed by the TFW beads, respectively
Amarasinghe and Williams [22]	Cu, Pb	1.5 hr	100 mg/lit	0.1 gm/lit	2 - 7	5 - 6	At pH 2–3 range the adsorption was very low and rapidly increases between pH 4 and 5.
Malkoc and Nuhoglu [21]	Cr	1 hr	100 mg/lit	10 gm/lit	2 - 5	2	The adsorption efficiency increased from 37% at pH 5.0 to 99% at pH 2.0. On changing the pH of Cr(VI) solution from 2.0 to 5.0, the amount adsorbed decreased from 9.9 to 3.7 mg g <sup>-1</sup> at room temperature
Wasewar et al. [23]	Zn	2.5 hr	50 mg/lit	4 gm/lit	2 - 12	4.2	Between pH 2.0 and 4.2 sharp increase in the percentage removal and the becomes almost constant for pH values larger than 4.2.

Cay et al. [17] found that the adsorption percentages are very low at strong acidic medium. After pH 3, uptakes increase sharply up to pH 5.5 and thereafter they stay almost constant for greater pHs. No pH values over 8.0 were studied since precipitation of heavy metals occurs. The optimum pH for Cu(II) and Cd(II) in single and binary systems was graphically determined as 5.5 [17].

The batch adsorption studies at different pH values were carried out in the range of 2.0–5.0 for adsorption of Ni onto TFW [18]. The maximum adsorption of nickel(II) ions were observed at pH 4.0 and significantly decreased by reducing the pH values to 2.0. Malkoc and Nuhoglu [18] observed that the removal of Ni(II) increased rapidly at pH 4.0–5.0 and reached upto 82.4% at pH 4.0. While the residual concentration of Ni(II) ions was 17.6 mg/l at pH 4.0, this value was 20 mg/l at pH 5.0. At pH < 3.0, H<sup>+</sup> ions compete with Ni(II) ions for the surface of the adsorbent which would hinder Ni(II) ions from reaching the binding sites of the sorbent caused by the repulsive forces. At pH > 5.0, the Ni(II) ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate [27].

Malkoc and Nuhoglu [18] discussed the concept of zeta potential to understand the effect of pH on the adsorption of Ni onto TFW. The electrical potential at the surface of a particle is zeta potential. It can be determined by the measurement of the velocity of particles in the electric field. At 3.0, 4.0, 5.0, 6.0 and 7.0 the zeta potentials of TFW were -14.5, -23.8, -22.5, -21.5 and -19.5mV, respectively. The zeta potential values could not be measured due to the high ionic strength at pH 2.0. All samples indicated negative charge values that should be favorable to the attraction

between active sites and positive charges of metal ions, resulting in electrostatic interaction. The TFW at pH 4.0 gave the greatest zeta-potential value.

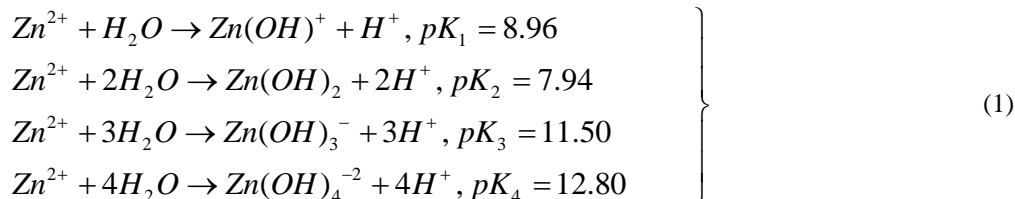
The column adsorption studies at different pH values were carried out in the range of 2.0–5.0 for adsorption of Cr onto TFW [19]. For Cr(VI) adsorption onto TFW, the highest maximum bed capacity and the longest breakthrough time was obtained at the lowest examined pH value. The maximum of Cr(VI) adsorption occurs at pH 2.0. It was observed that with decrease in the influent feed solution pH, the breakthrough curves shifted from left to right, which indicated that more Cr(VI) ions were removed. The amounts of Cr(VI) ions adsorbed per unit weight of beds for pH 2.0, 3.0, and 5.0 were 33.71, 28.07 and 23.76 mg/l, respectively. It is well known that the dominant form of Cr(VI) at this pH value is the acid chromate ion species ( $\text{HCrO}^-$ ) and increasing the pH will shift the concentration of  $\text{HCrO}^-$  to other forms,  $\text{CrO}_2^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ . At very low pH values, the surface of adsorbent would also be surrounded by the hydrogen ions which enhance the Cr(VI) interaction with binding sites of the adsorbent by greater attractive forces. As the pH increased, the overall surface charge on the adsorbent became negative and adsorption decreased [29]. Also, as pH of feed Cr(VI) concentration increased, breakthrough time or treated volume decreased. The treated volume considerably decreases from about 9600 (breakthrough time 480 min) to 7200 ml (breakthrough time 360 min) as the solution pH increases from 2.0 to 5.0 [19].

In Ni(II) adsorption onto TFW, the highest maximum bed capacity and the longest breakthrough time was obtained at pH 4.0 [20]. The hydroxyl groups of TFW have effective binding sites for metal ions, forming stable complexes by coordination. The interaction between the functional groups in TFW and Ni(II) ions may be responsible for pH increase in the initial stages and as the saturation of the bed proceeds, the pH decreased. A dramatic change in the effluent pH was observed. For the influent solution with pH 2.0, 3.0, 4.0 and 5.0, the effluent pH was sharply increased to 3.1, 3.8, 4.7 and 5.6, respectively. It was that adsorption of hydrogen ions from the solution and dissolution of some impurities from the adsorbent surface could result in increase in the effluent pH [29]. As continued to flow through the column, the effluent pH dropped to the influent pH value. The equilibrium nickel(II) uptake and amount of total sorbed nickel(II) increased with increasing pH of inlet solution from 2.0 to 4.0. The removal efficiency was higher at pH 4.0 and for the pH of 2.0, 3.0, 4.0 and 5.0, 17.46, 32.93, 40.25 and 30.68% of total nickel(II) applied to the column was adsorbed by the TFW beads, respectively.

Amarasinghe and Williams [22] studied the adsorption of Cu and Pb onto TFW in the pH range 2–7. It was found that the maximum removal of metals in the pH range 5–7. At pH 2–3 range the adsorption was very low and rapidly increases between pH 4 and 5. This phenomenon can be explained by the surface charge of the adsorbent and the  $\text{H}^+$  ions present in the solution. At low pH the cations compete with the  $\text{H}^+$  ions in the solution for the active sites and therefore lower adsorption. The surface charge of the biomass materials was a strong function of the pH. Zeta potential of tea waste particles at pH 3, 4, 5 and 6 are -14, -24, -23 and -22mV respectively [18]. Therefore at high pH values surface of the adsorbent has a higher negative charge which results higher attraction of cations. These data are in agreement with the results obtained for other biomass materials such as coffee residues [30], orange waste [31], coca shells [32], sago waste [5], and saw dust [33, 34] by many workers. At very high pH values the metal complex forms and results precipitation and therefore the separation may not be due to adsorption [33, 35, 72]. Malkoc and Nuhoglu [21] carried out the batch experiments in pH range 2 – 5 for adsorption of Cr onto TFW. The maximum uptake levels of Cr(VI) were observed at pH 2.0. The uptake of Cr(VI) increased with a decrease in the solution pH. The adsorption efficiency increased from 37% at pH 5.0 to 99% at pH 2.0. On changing the pH of Cr(VI) solution from 2.0 to 5.0, the amount adsorbed decreased from 9.9 to 3.7  $\text{mg g}^{-1}$  at room temperature. The electrical potential at the surface of a particle is zeta potential. It can be determined by the measurement of the velocity of particles in the electric field. At pH 3.0; 4.0; 5.0; 6.0 and 7.0 the zeta potentials of TFW were -14.5; -23.8; -22.5; -21.5 and -19.5mV, respectively. The zeta potential values could not be measured due to the high ionic strength at pH 2.0, but it was considered that these values were slightly positive. These measurements were conducted at 25°C [21].

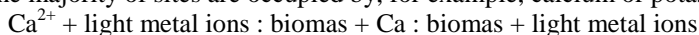
The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process and thus the role of hydrogen ion concentration was examined from solutions at different pH, covering the range of 2 – 12 [16, 23, 24]. Zinc ion exists in different forms in aqueous solution and the stability of these forms is dependent on the pH of system. The optimum pH for TFW-Zn system was found to be 4.2 with removal of about 99% metal from solution with initial zinc concentration of 50  $\text{mg/dm}^3$ . This may be because at pH values below 2.0, the electrostatic force of repulsion between adsorbent (TFW) and adsorbate ( $\text{Zn}^{2+}$ ) is prominent. At pH above 6.0, there is a possibility of  $\text{Zn}^{2+}$  precipitation on the surface of the adsorbents by nucleation [36]. Between pH 2.0 and 4.2 sharp increase in the percentage removal and the becomes almost constant for pH values larger than 4.2. This might be due to the fact that metal ions start replacing hydrogen ions from adsorbent surface. Similar results were reported by Gabaldon *et al.* [37]. The effect of pH on the adsorption isotherm may be attributed to the interaction between ions in solution and complexes formed at the adsorbent surface. Bodek *et al.* [38] reported the presence of different species of Zn (II) in the aqueous solution depending on the pH of solution. The speciation diagram in support of this

has been reported by Carrott *et al.* [39] which can be obtained using the reaction and equilibrium constants given by Baes and Messmer [40]:



Thus, the predominant ionic species is  $\text{Zn}^{2+}$  at  $\text{pH} < 7$ , whereas, Zn (II) is present mainly as  $\text{Zn}^{2+}$  and  $\text{Zn}(\text{OH})_2$ , and in lesser quantity as  $\text{Zn}(\text{OH})^+$  at  $\text{pH}$  between 8 and 9. Since all the experiment were carried at a maximum  $\text{pH}$  of 4.2, the predominant Zn (II) species found in solution and adsorbed on TFW surface was Zn (II).

At lower  $\text{pH}$  value, the  $\text{H}^+$  ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter, which compete with the  $\text{M}^{2+}$  ions for the adsorption sites of waste tea. Decrease in adsorption at higher  $\text{pH}$  is due to the formation of soluble hydroxyl complexes. The heavy metal cations are completely released under circumstances of extreme acidic conditions [18, 42]. Untreated biomass generally contains light metal ions, such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Treated biomass generally implies one of two chemical alterations. The first is protonation of the biomass with a strong acid, such as HCl whereby the proton displaces the light metal ions from the binding sites. In the second, the biomass is reacted with an aqueous solution of a given ion at high concentration so that the majority of sites are occupied by, for example, calcium or potassium [18, 43]:



In order to assure the optimal performance of the biomass, ionic form should be used for removing heavy metals and what chemicals should be selected for desorbing the metals [18, 43].

**Table 4: Effect of adsorbent dose on adsorption of metals onto TFW.**

Reference	Metal	Contact Time	Metal conc.	pH	Dose Range	Optimum dose	Results
Cay et al. [17]	Cu, Cd	1 hr	5 ppm	5.5	0.2 – 4 gm/lit	1 gm/lit	The total amount of metal ions removed from the solutions increases by the amount of adsorbent. This is an expected result because as the adsorbent concentration increases, the number of adsorbent particles surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces.
Mahvi et al. [15]	Cd, Ni, Pb	1 hr	5 – 100 mg/lit	--	5 – 15 gm/lit	--	94% removal of lead from a 5 mg/L solution was possible by applying 0.5g teawaste whereas the similar amount of adsorbent was not enough to treat a 100 mg/L lead solution to more than about 76%. But by increasing the amount of teawaste to 1.5g it was possible to increase the efficiency of adsorption to about 96.5% for the same solution (100 mg/L Pb). So we would have better treatment by using excess teawaste. As this adsorbent is cheap and available there would be no problem to increase its consumption
Malkoc and Nuhoglu [18]	Ni	2 hr	200 mg/lit	4	5 – 15 gm/lit	10 gm/lit	The increase in adsorbent dosage from 5.0 to 15 g L-1 resulted in an increase from 49.5 to 79.5% in adsorption of nickel(II) ions. This is observed at $\text{pH}$ 4.0 and significantly decreased by reducing the $\text{pH}$ values to 2.0. At lower $\text{pH}$ value, the $\text{H}^+$ ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter, which compete with the $\text{M}^{2+}$ ions for the adsorption sites of waste tea.
Malkoc and Nuhoglu [19]	Cr	Column study	100 mg/lit	2	Bed depth: 5 - 30 cm, Bed dia: 2 cm	--	The maximum bed capacities for different bed depth, 5, 10, 20 and 30 cm, were 34.97, 40.41, 49.93 and 56.96 mg g-1, respectively.
Malkoc and Nuhoglu [20]	Ni	Column study	100 mg/lit	4	Bed depth: 10 - 30 cm, Bed dia: 2 cm	--	The maximum bed capacities for different bed depth 10, 20 and 30 cm were 10.57, 11.67 and 13.6 mg/g, respectively.
Amarasi-	Cu, Pb	1.5 hr	100, 200	--	1.25 –	--	Percentage of lead ion removal increased from 37 to



nghe and Williams [22]			mg/lit		7.5 gm/lit		94% when the adsorbent dose per 200 ml of solution was increased from 0.25 to 1.5 g. A similar trend was observed by Cu adsorption. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose.
Malkoc and Nuhoglu [21]	Cr	1 hr	100 mg/lit	2	5 – 15 gm/lit	--	It is evident that adsorption increases with the increase in the mass of sorbent and the uptake capacity of Cr(VI) decreased from 48.82 mg g <sup>-1</sup> (61% removal) to 23.51 mg g <sup>-1</sup> (88% removal) with the increasing TFW concentration from 5 to 15 g L <sup>-1</sup> . This is because at the higher dosage of sorbent due to increased surface area, more adsorption sites are available causing higher removal of Cr(VI).
Wasewar et al. [23]	Zn	4 hr	50 mg/lit	4.2	1.2 – 20 gm/lit	4 gm/lit	The percent adsorption is increased with increase in TFW dose from 0.06 g to 1.00 g per 50 cm <sup>3</sup> solution. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. The optimum value of adsorbent dose found to be 0.2 g per 50 cm <sup>3</sup> of solution.

## 6. EFFECT OF ADSORBENT DOSE

Effect of the amount of TFW on metal adsorption was studied at fixed pH by various authors. The results of effect of adsorbent dose on the adsorption of various metals onto TFW are summarized in **Table 4**. The total amount of metal ions removed from the solutions increases by the amount of adsorbent. This is an expected result because as the adsorbent concentration increases, the number of adsorbent particles surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. [17, 23].

In some cases the amount of metal ions adsorbed per unit weight of adsorbent ( $q$ ) decreases with the adsorbent dose. This is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of ' $q$ ' indicating the adsorption sites remain unsaturated [22].

## 7. EFFECT OF CONTACT TIME

The percentages of Cu(II) and Cd(II) removed from single and binary systems as a function of time was presented by Cay et al. [17] (2004). The adsorbed amount of single and binary metal ions increases from 30 to 60 min time, after that a maximum removal is reached. Therefore, they selected 60 min as a suitable contact time for both metal ions in single and binary systems. [17]

Wasewar et al. [23] studied the effect of contact time on the adsorption of Zn onto TFW. Initially the removal was very rapid in first 25 minutes, then adsorption rate gradually decreases and removal reaches equilibrium in around 30 minutes. The time required to reach equilibrium was dependent on initial concentration of zinc. For the same concentration the percentage removal of zinc increases with increase in contact time till equilibrium attained in 30 minutes.

## 8. EFFECT OF INITIAL CONCENTRATION OF METAL

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases [18, 44].

Nickel(II) adsorption capacities of TFW were presented as a contact time [18]. When the initial nickel(II) ion concentration increased from 50 to 300 mg/lit, the residual Ni(II) concentration of solution increased from 5.8 to 159 mg/lit. The removal of Ni(II) ions increased rapidly with time up to 20 min and thereafter increased slowly. While initial metal concentration was 100 mg/lit, the uptake of Ni(II) ions was 8.12 mg/g at 30 min and 8.24 mg/g at 120 min. According to results, the adsorption equilibrium reached at 120 min. The amount of nickel(II) ions adsorbed per unit mass of the biosorbent increased with the initial concentration of metal ions. When the initial nickel(II) ion concentration increased from 50 to 300 mg/lit, the initial adsorption capacity of TFW increased from 4.413 to 14.04 mg/g. [18]

Malkoc and Nuhoglu [19] carried out the column studies for the adsorption of Cr onto TFW. The breakthrough curves of Cr(VI) ion concentrations were obtained at increasing initial feed Cr(VI) ions concentrations in the range 50–200 mg/l at constant flow rate, pH and bed height. Adsorbent of waste tea gets saturated early at high concentration. The breakthrough time considerably decreases from about 660 min to less than 360 min as the



concentration increases from 50 to 200 mg/lit. A rise in the inlet metal concentration reduces the treated volume before the fixed bed adsorption bed gets saturated. A high metal concentration may saturate the TFW more quickly, thereby decreasing the breakthrough time. Also, it is clear that the maximum bed capacity of Cr(VI) decreased with the increase in the initial concentration of Cr(VI). For tested different initial Cr(VI) concentration, maximum bed capacities at 50, 75, 100 and 200 mg/lit Cr(VI) concentrations were 27.67, 34.46, 40.41 and 43.67 mg/lit, respectively. Decreasing the feed Cr(VI) concentration increases the treated volume of feed metal concentration that can be processed, and shifts the breakthrough curve to the right. The driving force for adsorption is the concentration difference between the solute on the sorbent and the solute in the solution. A high concentration difference provides a high driving force for the adsorption process and this may explain why higher adsorption capacities were achieved in the column fed with a higher Cr(VI) concentration. The relatively low Cr(VI) retention for adsorbent can be attributed to the difference in the surface morphology. Adsorbent particles do not have many micro- or macropores, so its low surface area also results in lower sorption capacity [26].

An increase of the initial Ni(II) concentration from 50 to 200 mg/L, when other experimental conditions are kept constant, the corresponding adsorption bed capacity appears to increase from 7.31 to 11.17 mg/g [20]. Higher initial nickel concentrations caused a faster breakthrough. A decreased inlet nickel(II) concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient [45]. At the highest Ni(II) concentration (200 mg/L) the waste tea bed saturated quickly leading to earlier breakthrough and exhaustion time. Highest uptake and low total Ni(II) removal are obtained at the highest Ni(II) concentration. Also more positive and steep breakthrough curve was obtained for 200 mg/L Ni(II). The driving force for biosorption is the concentration difference between the metal on the waste tea and the metal ion in the solution [26]. Thus the high driving force due to the high Ni(II) concentration resulted in better column performance.

Pb and Cu ion removal percentage increased when the initial ion concentration decreased [22]. At low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, amount of metal adsorbed per unit weight of adsorbent,  $q$ , is higher at high concentrations.

Malkoc and Nuhoglu [21] carried out the biosorption of Cr(VI) ions at different initial chromium ion concentrations ranging from 50 to 400 mg/lit, at pH 2, at 360 rpm with 60 min of contact time using TFW. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake [45]. Uptake of the Cr(VI) also increased with increasing the initial metal concentration tending to saturation at higher metal concentrations. When the initial Cr(VI) concentration increased from 50 to 400 mg/lit, the uptake capacity of TFW increased from 5 to 30 mg/g. As at very low pH values, the surface of adsorbent would also be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the adsorbent by greater attractive forces. As the pH increased, the overall surface charge on the adsorbent became negative and adsorption decreased.

Wasewar et al. [23] studied removal of Zn (II) for various initial concentrations (25-200 mg/lit) of zinc by TFW (0.2 g/50 cm<sup>3</sup>) at different contact times. The percent adsorption was decreased with increase in initial concentration but actual amount of Zn (II) adsorbed per unit mass of adsorbent (TFW) increased with increase in initial concentration in test solution. This was because of the decrease in resistance for the uptake of solute from solution with increase in metal concentration.

## 9. EFFECT OF AGITATION RATE

Malkoc and Nuhoglu [18] carried out the adsorption studies with a magnetic shaker at pH 4.0 and initial nickel(II) concentration of 100 mg/L. The agitation speed varied from 3.0 to 8.0 rps (180, 360, 480 rpm). As agitating rate increased from 3.0 to 8.0 rps, adsorption capacity of TFW increased from 7.89 to 8.59 mg/g. The adsorption removal efficiency increased weakly with increasing agitation rate because an agitation rate of 150 rpm was enough to remove nickel. When the agitation speed was increased from 180 to 480 rpm, the removal of nickel(II) ion increased from 78.9% to 85.9%.

## 10. EFFECT OF TEMPERATURE

The effect of temperature on the adsorption of Ni(II) ions was presented by Malkoc and Nuhoglu [18] for the adsorption of Ni onto TFW. The sorption capacity for initial metal concentration 300 mg/L increased from 14.04 to 17.1 mg/g with the temperatures increasing from 25 to 60°C. The effect of temperature is fairly common and increasing the mobility of the metal cation. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the TFW enabling metal cation to penetrate further. At 25°C for a nickel concentration of 50 mg/L after a 60 min of sorption time, while nickel concentration was measured as 5.87 mg/L,

for 60°C no nickel was remained. The equilibrium uptake and adsorption yield of nickel(II) onto waste of tea factory was also affected by temperatures. The maximum adsorption yields were determined as 88.30, 95.30 and 100% at 50 mg/L initial nickel(II) concentration for 25, 45 and 60°C, respectively. It was indicated that nickel(II) adsorption capacity increased with increasing temperature from 25 to 60°C. Similar results were observed for nickel(II) adsorption yields of TFW and the adsorption yields increased with increasing temperature. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the adsorption of nickel(II) ions by waste tea may involve not only physical but also chemical sorption. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

## 11. KINETICS

Various kinetic models (pseudo-first-order model, pseudo-second-order, intraparticle diffusion model etc.) are available to find out the best fit kinetic model for the adsorption of metal onto TFW.

Lagergren rate equation (Pseudo-first order model) is one of the most widely used sorption rate equation to present the adsorption process. The pseudo-first-order equation is [46]:

$$\frac{dq}{dt} = k_f (q_e - q) \quad (1)$$

where  $q$  is the amount of adsorbate adsorbed at time  $t$  (mg/g),  $q_e$  is the adsorption capacity in equilibrium (mg/g),  $k_f$  is the rate constant of pseudo-first-order model (1/min), and  $t$  is the time. After definite integration by applying initial conditions at  $t = 0, q = 0$  and at  $t = t, q = q$ , the equation becomes:

$$\log(q_e - q) = \log q_e - \frac{k_f}{2.303} t \quad (2)$$

The straight line plot of  $\log(q_e - q)$  against  $t$  gives the value of adsorption rate constant ( $k_f$ ). Only one study [16] is available on kinetics using pseudo-first order model for adsorption of metal onto TFW. The values of adsorption rate constant ( $k_f$ ) for removal of metals onto TFW are given in **Table 5**. These values indicated that the adsorption rate was very fast at the beginning of adsorption of zinc onto TFW.

**Table 5: Lagergren rate equation (Pseudo-first order model) kinetic parameters for removal of various metals by adsorption onto TFW.**

Pseudo-first-order constant, Zn, Wasewar et al. [16]				
Conc. (mg/lit)	25	50	100	200
$k_f$ (1/min)	0.0170	0.0191	0.0147	0.0256

The pseudo-second-order model can be represented in the following form [47]:

$$\frac{dq}{dt} = k_s (q_e - q)^2 \quad (3)$$

where  $k_s$  is rate constant of pseudo-second-order model (g/mg min). After integrating equation for boundary conditions at  $t = 0, q = 0$  and at  $t = t, q = q$ , the following form of equation can be obtained:

$$\frac{t}{q} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (4)$$

The initial sorption rate in mg/gm min, as  $t \rightarrow 0$  can be defined as

$$\left( \frac{dq}{dt} \right)_{initial} = k_s q_e^2 \quad (5)$$

The initial sorption rate, the equilibrium adsorption capacity ( $q_e$ ), and the pseudo-second-order rate constant  $k_s$  can be determined from plot of  $t/q$  versus  $t$ .

Amarasinghe and Williams [22] studied the kinetics of adsorption Cu and Pb onto TFW. They found that pseudo-second order model provided better correlation than pseudo first order model. The kinetic parameters obtained in their studies are summarized in **Table 6**. The initial adsorption rate increases with the initial solution concentration for both Cu and Pb. The rate constant decreases with the solution concentration. At high concentration the difference between the metal ion concentration in the solution and that on the solid-liquid interface, which is the driving force for the adsorption is high and therefore higher initial adsorption rates are shown at higher solution concentrations.

Pb shows higher adsorption rate compared to Cu for all concentrations. The results also show that the initial adsorption rate is high for smaller particles despite there being no significant difference in rate constants. [22]

**Table 6: Pseudo-second order kinetic model parameters for removal of various metals by adsorption onto TFW.**

<b>Conc. (mg/lit)</b>	200	100	50	25
<b>Metal and Reference</b>	Cu, Amarasinghe and Williams [22]			
$(dq/dt)_{initial}$ (mg/g min)	5	3	3	2
$k_s$ (g/mg min)	0.0133	0.017	0.0427	0.1268
<b>Metal and Reference</b>	Pb, Amarasinghe and Williams [22]			
$(dq/dt)_{initial}$ (mg/g min)	11	10	6	--
$k_s$ (g/mg min)	0.0091	0.0283	0.0586	--
<b>Metal and Reference</b>	Zn, Wasewar et al. [16]			
$(dq/dt)_{initial}$ (mg/g min)	12.5000	14.3062	23.9808	26.4550
$k_s$ (g/mg min)	0.0215	0.0403	0.1664	0.6899

Contradictory results were found for the adsorption of Zn onto TFW [16]. The initial adsorption rate decreases with the initial solution concentration for Zn. The rate constant decreases with the solution concentration. At high concentration the difference between the metal ion concentration in the solution and that on the solid-liquid interface, which is the driving force for the adsorption is high and therefore higher initial adsorption rates are shown at higher solution concentrations.

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism and the kinetic results can be then analyzed by using intraparticle diffusion model. According to this model, the plot of uptake versus the square root of time should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step [48]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously [49].

An empirically found functional relationship, common to most adsorption processes, is that uptake varies almost proportionally with  $t^{1/2}$ , the Weber-Morris plot, rather than with the contact time  $t$  [50].

$$q = k_{id}t^{1/2} + C \quad (6)$$

Where  $k_{id}$  is the intraparticle diffusion rate constant Values of intercept  $C$  give the idea about the thickness of boundary layer.

Wasewar et al. [16] fitted adsorption data in intraparticle diffusion model. The idea about the thickness of boundary layer can be obtained from the values of intercept  $C$  i.e., the larger the intercept the greater is the boundary layer effect [51]. The deviation of straight line from origin may be due to difference in initial and final stages of adsorption. Further such deviation of straight line from origin indicated that pore diffusion was not the sole rate controlling step [52]. Also, it was observed that there were two separate regions: the initial portion attributed to bulk diffusion and linear portion intraparticle diffusion. The values of  $k_{id,1}$  and  $k_{id,2}$  as obtained from intercepts of straight lines were listed in Table 7. Again it may be suggested both film and pore diffusion were effective in the removal process to different extent. Macro pore diffusion was much larger than micro pore diffusion rate.

**Table 7: Intra-particle diffusion model parameters for removal of zinc by adsorption onto TFW (Wasewar et al.) [16].**

<b>Conc. (mg/lit)</b>	200	100	50	25
$k_{id,1}$ (mg/g min)	0.0257	0.1557	0.2786	1.4560
$k_{id,2}$ (mg/g min)	0.0072	0.0232	0.1199	0.1136

## 12. EQUILIBRIUM ISOTHERMS

The analysis and study of equilibrium data is very important in view to develop a model equation which can accurately represent the results and could be used for the design purposes. Freundlich [53], Langmuir [54], Redlich-Peterson [55] and Temkin [56] isotherm models were used to describe the equilibrium characteristics of adsorption of metal onto TFW.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm contains a factor that explicitly takes into the account adsorptive-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

### Freundlich Isotherm

Linearized form of Freundlich isotherm is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Cay et al. [17] carried out equilibrium study for the adsorption of Cu and Cd onto TFW. An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the sorbent and can also be used to find the capacity of adsorbent. Experimental data were fitted in Freundlich isotherm and estimated parameters are summarized in **Table 8**. For the adsorption of Ni onto TFW [18], from **Table 8**, the magnitude of  $K_F$  showed a high nickel adsorptive capacity of TFW from aqueous solution at 45 and 60°C temperatures studied and increased with the rise in temperature. The highest  $K_F$  value was found as 5.31 at 60°C. Application of Freundlich model to the equilibrium data for Cu and Cd indicates the monolayer coverage of TFW by the ions of Cu and Cd, but this was to non-distinct or multiple sites of adsorption unlike the Langmuir model which is to distinct localised adsorption sites [71]. It is well known that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the adsorption process. [17]

**Table 8: Freundlich isotherm parameters for removal metals by adsorption onto TFW.**

Metal	Temp. (°K)	$K_F$ (mg/g)/(mg/lit) <sup>1/n</sup>	1/n	R <sup>2</sup>	Reference
Cu	298	2.8379	0.845	0.992	Cay et al. [17]
Cd	298	3.9537	0.983	0.982	
Ni	298	0.258	1.0706	0.9228	Malkoc and Nuhoglu [18]
	318	3.858	0.3165	0.9681	
	333	5.31	0.25	0.9673	
Cu	295	0.7012	0.7427	0.9845	Amarasinghe and Williams [22]
Pb	295	9.6532	0.3885	0.9614	
Cr	298	6.153	0.2766	0.8320	Malkoc and Nuhoglu [21]
	318	10.04	0.2069	0.8110	
	333	12.93	0.2049	0.8516	
Zn	303	5.8305	0.0904	0.9177	Wasewar et al. [16]
	318	6.5571	0.1193	0.9684	
	333	6.3624	0.1386	0.9684	

Amarasinghe and Williams [22] carried out the equilibrium studies using Freundlich isotherm. The results indicated (**Table 8**) a higher adsorption of Pb compared to Cu for the experimental conditions under observation. This may be explained by the hydration enthalpy which is the energy that permits the detachment of H<sub>2</sub>O molecules from cations and then reflects the easiness for the ion to interact with the functional groups on TFW particles. The more a cation is hydrated the stronger its hydration enthalpy and then less it could interact with the adsorbent [22, 57, 58]. Hydration enthalpies of Pb and Cu are -1481 and -2100 kJ/kg, respectively. This indicates theoretically high affinity of Pb cations to the adsorbent and hence higher removal of Pb compared to Cu. The values obtained for Cr [21] from the Freundlich model at different temperatures showed a maximum adsorption capacity ( $K_F$ ) of 12.93 at 60°C. The values obtained for Zn(II) from the Freundlich model at different temperatures showed a maximum adsorption capacity of 6.36 mg/g at 333 K with an affinity value ( $n$ ) equal to 7.31 [16].

### Langmuir Isotherm

Linearized form of Langmuir isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (8)$$

Langmuir isotherm was used by various authors for the adsorption of various metals onto TFW and their results are summarized in **Table 9**. Malkoc and Nuhoglu [18] studied adsorption of Ni onto TFW. They found that Langmuir isotherm constants and the monolayer saturation capacities, increased from 15.26 to 18.42 mg/g as the temperature of solution increased ranging from 25 to 60°C. Thus, the equilibrium adsorption capacity of TFW was found to be 18.42 mg/g under optimized conditions. A higher value of  $K_L$  implies a shift of the adsorption equilibrium to the right at 60°C. Increase of  $K_L$  with temperature shows that there is a chemical interaction between adsorbent and nickel.

The effect of isotherm shape can be used to predict whether a sorption system is 'favorable' or unfavorable'. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor,  $R_L$ , which describes the type of pattern and is defined as  $R_L = 1/(1 + K_L C_i)$  (where  $C_i$  is the initial concentration and  $K_L$  is the Langmuir constant) indicates the nature of adsorption as [59, 60]:

If	$R_L > 1$	Unfavorable
	$R_L = 1$	Linear
	$0 < R_L < 1$	Favorable
	$R_L = 0$	Irreversible

To confirm the favorability of the adsorption process, Malkoc and Nuhoglu [18, 21] calculated the separation factor ( $R_L$ ). The average values of  $R_L$  are summarized in **Table 9**. The values of  $R_L$  less than 1, as given in **Table 9** demonstrated the adsorption can be deemed favorable. At all studied temperatures, the  $R_L$  values were decreased with increasing initial metal concentration. This indicated that sorption was more favorable for the higher initial metal concentration than for the lower one.

**Table 9: Langmuir isotherm parameters for removal metals by adsorption onto TFW.**

Metal	Temp. (°K)	$K_L$ (lit/mg)	$q_m$ (mg/g)	$R_{L,ave}$	$R^2$	Reference
<b>Cu</b>	298	5.6207	6.1350	--	0.827	Cay et al. [17]
<b>Cd</b>	298	0.1048	20	--	0.694	
<b>Ni</b>	298	0.088	15.26	0.0942	0.9921	Malkoc and Nuhoglu [18]
	318	0.093	17.73	0.09	0.9996	
	333	0.098	18.42	0.086	0.9999	
<b>Cu</b>	295	0.0076	48	--	0.9947	Amarasinghe and Williams [22]
<b>Pb</b>	295	0.0494	65	--	0.9579	
<b>Cr</b>	298	0.0378	27.24	0.117	0.9477	Malkoc and Nuhoglu [21]
	318	0.0286	36.90	0.169	0.9139	
	333	0.0125	54.65	0.277	0.9937	
<b>Zn</b>	303	0.0753	10.1833	0.2099	0.9951	Wasewar et al. [16]
	318	0.0747	12.5471	0.2112	0.9936	
	333	0.0726	14.2045	0.2160	0.9917	

According to the Langmuir model, the maximum Cr adsorption capacity was obtained at 60°C with a value of  $q_m$  of 54.65 mg/g [21]. The equilibrium sorption capacity was found to increase from 27.24 to 54.65 mg/g for an increase in the solution temperatures from 25 to 60°C. It is clear that the sorption of Cr) on TFW is an endothermic process. However, the sorption constant decreases from 0.0378 to 0.0125 L/mg, as temperatures vary from 25 to 60°C [21]. Wasewar et al. [16] obtained the maximum Zn(II) adsorption capacity at 333 K as 14.2 mg/g. The results revealed that the sorption capacity increased from 10.18 to 14.2 mg/gm with the temperature increasing from 303 to 333 K. It was clear that the sorption of Zn(II) on TFW was an endothermic process. The effect of temperature was fairly common and increasing the mobility of the metal cation. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the TFW enabling metal cation to penetrate further [28].

#### **Redlich-Peterson Isotherm**

Redlich-Peterson model combines element of Langmuir and Freundlich model. The mechanism of Redlich-Peterson adsorption model is a hybrid and does not follow ideal monolayer adsorption. The Redlich Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator.

It approaches Freundlich model at high concentration and it is accordance with the low concentration limit of Langmuir equation. Furthermore, Redlich-Peterson model incorporates three parameters into an empirical isotherm, and therefore can be applied either in homogeneous or heterogeneous system due to high versatility of the equation. It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (9)$$

where  $K_R$  and  $a_R$  are Redlich-Peterson isotherm constants (lit/mg) and  $\beta$  is the exponent which lies between 1 and 0, where  $\beta = 1$

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \quad (10)$$

It becomes Langmuir equation, when  $\beta = 0$

$$q_e = \frac{K_R C_e}{1 + a_R} \quad (11)$$

Equation (11) can be linearized as in equation (12).

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \quad (12)$$

So far only Wasewar et al. [16] used Redlich-Peterson isotherm for the analysis of equilibrium data for the adsorption of metal onto TFW. Wasewar et al. [16] used Redlich-Peterson isotherm to represent the adsorption mechanism of zinc onto TFW. Plotting the left hand side of above equation against  $\ln C_e$  to obtain isotherm constant is not applicable because of three unknowns,  $a_R$ ,  $K_R$  and  $\beta$ . Therefore, the parameters of equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with solver add-in function of Microsoft Excel [16]. The Redlich-Peterson isotherm parameters and the correlation coefficients were significantly higher than both Langmuir and Freundlich values for Zn adsorption onto TFW. The values of isotherm constant were presented in **Table 10**.

**Table 10: Redlich-Peterson isotherm and Temkin isotherm parameters for removal Zn by adsorption onto TFW (Wasewar et al.) [16].**

Temp. (K)	Redlich-Peterson constants				Temkin constants		
	$K_R$ (lit/g)	$a_R$ (lit/mg)	$\beta$	$R^2$	$K_T$ (lit/mg)	$B_1$	$R^2$
303	7.8274	1.0924	0.9471	0.9999	14697.399	0.6340	0.9866
318	3.9547	1.1130	0.8160	0.9951	70.858	1.2095	0.9748
333	2.6462	4.1658	0.9645	0.9998	48.789	1.4287	0.9818

#### Temkin Isotherm

Temkin isotherm contains a factor that explicitly takes in account adsorbing species- adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all molecules in the layer decreases with coverage due to adsorbate-adsorbate interaction and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Temkin isotherm is represented by following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (13)$$

Equation (13) can be linearized as in equation (14).

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (14)$$

Where  $B_1 = \frac{RT}{b}$

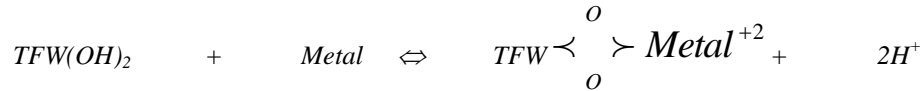
Regression of  $q_e$  versus  $\ln C_e$  enables the determination of isotherm constants  $K_T$  and  $B_1$ .  $K_T$  is equilibrium binding constant (lit/mg) corresponding to maximum binding energy and constant  $B_1$  is related to the heat of adsorption.

So far only Wasewar et al. [16] used Temkin isotherm for the analysis of equilibrium data for the adsorption of metal onto TFW. They removed Zn by adsorption onto TFW. The values of isotherm constant were presented in **Table 10**.

The available results indicated that the capacity of TFW for the adsorption of metals increases with temperature which was typical for the adsorption of most metal ions from their solution [16]. When the system was in a state of equilibrium, the distribution of metal between the TFW and the metal solution was of fundamental importance in determining the maximum sorption capacity of TFW for the metal ion from the isotherm.

The actual mechanism for the adsorption of metals onto TFW is not known well, it is thought that ion exchange, complexation and electrostatic interactions play an important role in the whole adsorption process of TFW [17].

Cay et al. [17] suggested the following ion exchange mechanism based on model of metal binding and proton releasing reaction for the adsorption of Cu and Cd onto TFW:



Their experimental pH measurements of the original metal solutions, before and after adding TFW shows that ion exchange is only a part of the whole adsorption process since the ratio of the theoretical and experimental pH changes deviated considerably from unity. [17]

#### **Error Analysis of Equilibrium Isotherm**

Due to the inherent bias resulting from linearization, five different error functions of non-linear regression basin were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data.

#### *The Sum of the Squares of the Errors (SSE)*

This error function, SSE [62] is given as:

$$SSE = \sum_{i=1}^n (q_{e,estm} - q_{e,exp})_i^2 \quad (15)$$

Here,  $q_{e,estm}$  and  $q_{e,exp}$  are, respectively, the estimated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g) and  $n$  is the number of data point. This is the most commonly used error function. SSE has one major drawback in that it will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because of the magnitude of the errors, which increase as the concentration increases.

#### *The Sum of the Absolute Errors (SAE)*

SAE [62] is given as

$$SAE = \sum_{i=1}^n |q_{e,estm} - q_{e,exp}|_i \quad (16)$$

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data.

#### *The Average Relative Error (ARE)*

ARE [62] is defined as

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{(q_{e,exp} - q_{e,estm})}{q_{e,exp}} \right|_i \quad (17)$$

This error function attempts to minimize the fractional error distribution across the entire concentration range.

#### *The Hybrid Fractional Error Function (HYBRID)*

HYBRID [62] is given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(q_{e,exp} - q_{e,estm})}{q_{e,exp}} \right]_i \quad (18)$$

This error function was developed to improve the fit of the ARE method at low concentration values. Instead of  $n$  as used in ARE, the sum of the fractional errors is divided by  $(n-p)$  where  $p$  is the number of parameters in the isotherm equation.

**Table 11: Isotherm error analysis for adsorption of Zn (II) onto TFW. (Wasewar et al.) [16]**

Isotherm Temperature	HYBRID	MPSD	SSE	SAE	ARE
303K					
Langmuir	15.6475	15.6483	8.2394	5.8577	10.4317
Freundlich	0.9754	3.7298	0.0416	0.3474	0.6503
Tempkin	3.8789	0.5962	0.4302	1.3495	2.5859
318K					
Langmuir	7.8062	7.8877	2.2451	3.1136	5.2041
Freundlich	4.9095	4.3488	0.9777	2.1932	3.2730
Tempkin	5.5196	6.0236	1.7060	2.4175	3.6798
333K					
Langmuir	3.4715	3.7110	0.8681	1.6971	2.3143
Freundlich	3.3700	3.4828	0.8202	1.7377	2.2467
Tempkin	4.8125	4.4938	1.3482	2.4498	3.2083



### Marquardt's Percent Standard Deviation (MPSD)

MPSD [62] has been used by a number of researchers in the field to test the adequacy and accuracy of the model fit with the experimental data. It has some similarity to the geometric mean error distribution, but was modified by incorporating the number of degrees of freedom. This error function is given as:

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left( \frac{(q_{e,\text{exp}} - q_{e,\text{estm}})}{q_{e,\text{exp}}} \right)^2} \quad (19)$$

It is very difficult to select the best fit adsorption isotherm. Therefore five different error functions (sum of squares of the errors (SSE), sum of the absolute errors (SAE), average relative error (ARE), hybrid functional error function (HYBRID), Marquardt's Percent Standard Deviation (MPSD)) of non-linear regression basin were employed to find out the best-fit isotherm model to the experimental equilibrium data. Only one study is available for the case of TFW. Wasewar et al. [16] used five error functions for the adsorption of Zn onto TFW. The values of the five error functions are presented in **Table 11**. By comparing the values of the error functions, it was found that Freundlich isotherm fitted well to the observed data for Zn (II) adsorption onto TFW.

### 13. THERMODYNAMIC STUDY

Based on fundamental thermodynamic concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously [63]. The equilibrium constant ( $K$ ) of the adsorption is defined as:

$$K = C_{\text{ad,eq}} / C_{\text{eq}}$$

where  $C_{\text{ad,eq}}$  and  $C_{\text{eq}}$  are the concentration of metal on the adsorbent and residual metal concentration at equilibrium, respectively. In this case, the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant ( $K$ ) of the adsorption system [64].

Thermodynamic data such as adsorption free energy can be obtained from both Langmuir and Temkin equation using following equation [65, 66]:

$$-\Delta G^\circ = RT \ln(K) \quad (20)$$

The thermodynamic parameters for adsorption of Zn (II) were calculated by using following equations;

$$\left. \begin{aligned} -\Delta G_{\text{ads}}^\circ &= RT \ln(K) \\ \Delta H^\circ &= -R \left[ \frac{T_2 T_1}{(T_2 - T_1)} \right] \ln \frac{K_{L_2}}{K_{L_1}}, \\ \Delta S^\circ &= -\frac{(\Delta G^\circ - \Delta H^\circ)}{T} \end{aligned} \right\} \quad (21)$$

Where  $K$ ,  $K_{L_1}$  and  $K_{L_2}$  are the equilibrium constants at temperatures  $T$ ,  $T_1$  and  $T_2$ ; respectively, obtained from Langmuir or Temkin isotherms.

Malkoc and Nuhoglu [18, 21] and Wasewar et al. [16] determined the thermodynamic parameters for the adsorption of Ni, Cr, and Zn onto TFW respectively and are summarized in **Table 12**. The free energy of the process at all temperatures was negative and changed with the rise in temperature. The negative values of free energy at all temperatures studied are due to the fact that adsorption process is spontaneous. The positive value of  $\Delta S$  suggests increased randomness at the solid/solution interface during the adsorption of metal ions onto adsorbent. Positive values of  $\Delta H$  indicate the endothermic nature of the adsorption process. The change of the standard free energy decreases with increase in temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.

**Table 12: Thermodynamic parameters for adsorption of metal onto TFW.**

Metal and Reference	T (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/mol K)
Ni Malkoc and Nuhoglu [18]	298	-3.82	17.07	70.27
	318	-5.34		
	333	-6.27		
Cr Malkoc and Nuhoglu [21]	298	-0.29	4060	0.0146
	318	-0.60		
	333	-1.70		
Zn Wasewar et al. [16]	303	-0.0095	11554.5	31247.3
	318	-0.0099		
	333	-0.0104		

#### 14. DISPOSAL OF TFW AFTER ADSORPTION

Disposal of the exhausted adsorbent loaded with heavy metal ions creates another environmental problem such as acid rains can wash out the adsorbed heavy metal ions [17]. This problem may be overcome to some extent by using one of the elimination methods (e.g. elution, incineration and pyrolysis) proposed by Gaballah and Kilbertus [67], previously. The elution of heavy metals is the most common elimination method, allowing both recovery of solutions of heavy metal ions at higher concentrations for inertisation and recycling of the adsorbent for subsequent uses.

Cay et al. [17] calculated the percent recoveries of the heavy metal ions by the elution method for single and binary systems. Percent recoveries calculated were  $97.23 \pm 1.40$  and  $98.07 \pm 0.98\%$  for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in single,  $96.49 \pm 1.73$  and  $96.38 \pm 1.36\%$  for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in binary systems, respectively. It was found that, the TFW may be recovered for consecutive uses with advantage. Additional studies on life time of adsorbent showed that tea waste may be efficiently used at least three cycles without changing retention capacity significantly.

It has been reported that the sorption process of trace metals are not reversible. Several explanations have been proposed in the literature [68].

TFW has a calorific value of about 21.69 MJ/kg [16]. It can be utilized for making blended fuel briquettes which could be used as a fuel in the furnaces. The bottom ash obtained after its combustion can be blended with the cementitious mixtures. Setting and leaching tests on cementitious mixtures have shown that the bottom ash can be incorporated into the cementitious matrices to a great extent (75% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products [69].

In many parts of the world where tea waste is available at low or no cost, regeneration is not required and the metal laden biomass can be disposed by incineration [70].

#### 15. CONCLUSION

Based on the above study following conclusions were drawn:

1. TFW were successfully used for the removal of various toxic metals (Zn, Cr, Ni, Cu, Cd, Pb).
2. Three different kind of TFW waste from India, Sri-Lanka and Turkey were used.
3. TFW characterization shows high surface area for the adsorption.
4. Effect of pH was studied by various authors in the range of 1-12 and optimum was found in the range of 4-6.
5. Effect of adsorbent dose were studied in the range of 0.2 gm/lit to 20 gm/lit. Optimum dose was varied as the studied range was varied.
6. Only one study was found for the application of pseudo-first order model for the adsorption of Zn onto TFW.  $k_f$  was obtained in the range of 0.0170 – 0.0256 1/min.
7. For pseudo-second order kinetics, the value of  $k_s$ , model parameter were found in the range of 0.0091 – 0.1664 g/mg min and the value of initial sorption rate was observed in the range of 2 – 26.5 mg/g min.
8. Intra-particle diffusion model was used to present the kinetic data for the removal of zinc by adsorption onto TFW. Model parameters were found in the range of 0.0072 - 1.456 mg/g min.
9. Freundlich isotherm parameters  $K_F$  and  $1/n$  were found in the range of 0.258 – 12.93 (mg/g)(mg/lit)<sup>1/n</sup> and 0.205 – 1.07 respectively for temperature range 298 – 333 K for adsorption of various metals onto TFW.
10. Langmuir isotherm parameters  $K_L$ ,  $q_m$ , and  $R_L$  were evaluated as 0.0076 – 0.105 lit/mg, 6 – 65 mg/g, and 0.086 – 0.277 respectively for temperature range 298 – 333 K for adsorption of various metals onto TFW.
11. Only one study was found for the use of Redlich-Peterson isotherm and Temkin isotherm for the adsorption of Zn onto TFW. Various model parameters  $K_R$ ,  $a_R$ ,  $\beta$ ,  $K_T$  and  $B_T$  were obtained in the range of 2.64 – 7.83 lit/g, 1.09 – 4.16 lit/mg, 0.816 – 0.964, 48 – 14697 lit/mg, and 0.634 – 1.429 respectively for temperature range 303 – 333 K for adsorption of Zn onto TFW.
12. Five types of error functions (HYBRID, MPSD, SSE, SAE, and ARE) were used for the analysis of equilibrium data of adsorption of Zn onto TFW.
13. The negative values of free energy at all temperatures studied were observed which is due to the fact that adsorption process is spontaneous. The positive value of  $\Delta S$  suggests increased randomness at the solid/solution interface during the adsorption of metal ions onto adsorbent. Positive values of  $\Delta H$  indicate the endothermic nature of the adsorption process. The change of the standard free energy decreases with increase in temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.
14. TFW has a high calorific value and hence can be utilized for making blended fuel briquettes which could be used as a fuel in the furnaces. The bottom ash obtained after its combustion can be blended with the cementitious mixtures. Setting and leaching tests on cementitious mixtures have shown that the bottom ash can be

incorporated into the cementitious matrices to a great extent (75% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products.

## NOMENCLATURE

$a_R$	R-P isotherm constant (lit/mg)
$b$	Tempkin isotherm constant (--)
$C_e$	Concentration of adsorbate in solution at equilibrium (mg/lit)
$k_f$	Rate constant of pseudo-first-order model, (1/min)
$k_s$	Rate constant of pseudo second-order, (g/mg min)
$k_{id}$	Intraparticle diffusion rate constant (mg /g min <sup>1/2</sup> )
$K$	Equilibrium constant (1/min)
$K_L$	Langmuir isotherm constant, (lit/mg)
$K_F$	Freundlich isotherm constant (lit/mg) <sup>1/n</sup>
$K_R$	Redlich Peterson constant, (lit/mg)
$K_T$	Tempkin isotherm constant, (lit/mg)
$n$	Affinity value of Freundlich isotherm constant (--)
$q_e$	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)m
$q_m$	Limiting adsorbing capacity, (mg/g)
$q$	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg/g)
$q_{e, estm}$	Estimated value of amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)m
$q_{e, exo}$	Experimental value of amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)m
$R$	Universal gas constant (--)
$R_L$	Separation factor
$t$	Adsorption time (min)
$T$	Temperature (K)
$\beta$	Exponent which lies between 1 and 0 in R-P isotherm
$\Delta G^\circ$	Gibbs free energy, (kJ/mol)
$\Delta H^\circ$	Enthalpy, (kJ/mol)
$\Delta S^\circ$	Entropy, (J/mol K)

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