



Biosorption of Cadmium on Spent Tea: Green Chemistry Approach

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ABSTRACT

Pollution load of cadmium into the receiving waters is a threat to water resources, thus limiting the clean energy production. During recent years biosorption has gained imperative credibility because of its good performance and low cost. The present research offers an effective green chemistry approach to waste management. Tea waste, a fibrous by-product during tea processing, has been used as an adsorbent of heavy metals, however, utilization of the spent tea needs to be explored. The optimum operating conditions are found to be 20 minutes contact time, adsorbent dose of 0.05 g, and induced metal ion concentration of 50 mg/L. Biosorbent has been specifically modified by oxidation, acetylation and isopropyl alcohol to understand the mechanism of cadmium adsorption from synthetic solution. The origin of the enhancement is investigated by observing the sorption behavior and the change in surface functional group concentrations by FTIR and active sites by Boehm method. The present study recommends spent tea as a cost effective and easily available substitute for conventional carbon based adsorbents for metal removal.

Keywords: Spent tea; sorption; modification; metals

1. INTRODUCTION

An increasing development and industrialization has placed stress on the natural resources, resulted in the pollution of environment through discharge of residual water from industrial units. Discharges of industrial waste interfere with intended use of water when the level of pollutants in the water exceeds the permissible limits. The rate at which effluents are released into the water bodies, owing to rapid industrialization is of great concern (Okoye, 2010). Industrial effluents often contain elevated levels of heavy metals and cause serious environmental problems (Lodeiro et al., 2006; Gupta and Ali, 2008) and threat to

human health (Xuan et al., 2006) life and environment (Horsfall and Spiff, 2005). Not even a single product of today's consumerism is without metals in one form or the other. They are virtually present ranging from building materials to cosmetics, medicines to food products; weapons of destruction to daily use appliances.

Cadmium is a priority toxic pollutant in wastewater that is introduced into water from a wide variety of industries such as electroplating, smelting, pigments, plastic, fertilizers, pesticides, cadmium-nickel batteries, mining textile operations, and refining (Othmer, 2007; Wu et al., 2010). Cadmium has been added to the list of acknowledged endocrine disrupting chemicals.

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(Chedrese, 2006), its treatment is explored currently by exploiting two out of twelve principles of green chemistry means reduction of waste and cost (Beškoski et al., 2008). The same principle is explored by using green batteries (rechargeable lithium and nickel hydride) in comparison to dry cell batteries have innovation offset of being twice as efficient at same cost (Porter and Linde, 1995a, b).

The conventional treatment methods become less effective and more expensive when situations involving high volumes, low metal concentrations, and disposal of residual metal sludge are encountered. Still more, these methods are not suitable for small-scale industries. Recently Biosorption technology has gained important credibility because of its eco-friendly nature, excellent performance, and cost-effectiveness. New and inexpensive adsorbent materials that possess a high capacity for adsorbing heavy metals are researched. Present study is utilization of renewable resource (spent tea) as green and sustainable biosorbent for cadmium by considering management of waste through waste. The possible mode of adsorbate adsorbent interaction is evaluated through surface tailoring with the aim to transform lower-value material to higher-value products (Mulholland et al., 2000).

2. EXPERIMENTAL

2.1 Preparation and characterization of biosorbent

Black tea sample was prepared by boiling in distilled water for 5 minutes and washed with distilled water until no coloration appeared in water. The Sample was ground, sieved after oven drying at 50 °C for 24 hours and stored in desiccator. Surface morphology of untreated and metal treated sorbents was studied through SEM-EDX and FTIR spectrums. Boehm's titration procedure was employed for

determination of active sites on sorbent surface (Boehm, 2008). Thermal energy of spent tea was explored through Thermogravimetry-differential scanning calorimetry (TGA-DSC).

2.2 Batch sorption protocol

Biosorption protocol was similar to described elsewhere (Fazal and Rafique, 2012), briefly it was carried out by agitating at 100 rpm (X) mass of sorbent into 100-mL Erlenmeyer flasks containing 20 mL solution of (Y) metal ions concentration. Sorbent was separated by filtration after predetermined time interval of 1 minute until equilibrium attainment. Each data point was obtained from individual flasks to ensure uniform contact between solid and liquid till equilibrium. Contact time, sorbent dose and sorbate concentration was optimized by this practice for thermodynamic study. Removal efficiency of modified sorbents was explored by contacting 0.1 g dose in 25 mg/L of initial metal ions concentration.

2.2.1 Calculation of cations uptake by spent tea

The standard solution (1000 mg/L) of Cd(II) from cadmium sulphate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) was prepared procured from Merck. The concentration of Cd(II) ions in the sorption medium was determined using Flame Atomic Absorption Spectrophotometer.

Cations uptake by spent tea was calculated as percentage removal (%R) of Cd(II) ions by:

$$\%R = \left(\frac{C_i - C_t}{C_i} \right) 100 \quad (1)$$

The biosorption efficiency q_e (mg/g), was calculated by:

$$q_e = \left(\frac{C_i - C_e}{W} \right) V \quad (2)$$

Where C_i and C_e (mg/L) are metal ions

concentration at initial and equilibrium, respectively. V is the volume (L) of the solution and W is the weight (g) of dry sorbent.

2.3 Tailoring sorbents by surface chemical modification

2.3.1 Oxidation

The sorbent is oxidized with hydrogen peroxide by adding 8 g of sorbent in 50 mL of 1M concentrated solution. The mixture in flask is agitated at 100 rpm for 1 h.

2.3.2 Acetylation

Acetylation of amino and hydroxyl groups of the biosorbent is carried out by procedure reported by Paul et al. (1997). Sorbent (8 g) is soaked in 50 mL glacial acetic acid and agitated at 100 rpm for 1 h. Then separated by decanting and soaked in acetic anhydride containing 2 drops of concentrated H_2SO_4 for 2 min.

2.3.3 Isopropyl alcohol treatment

The sorbent (8 g) is treated with 50 mL of 20% solution of propanol for 1 hour by shaking at 100 rpm. Each modification is attempted at room temperature and treated biomass is drained to separate the solution and washed with deionized water to quench the reaction. Washing is ended when the pH of the deionized water ceased to change, afterward biomass filtered through Whatman no40 filter paper. Finally dried in an oven at 50 °C for 24 h and stored in a desiccator for further use.

3. RESULTS AND DISCUSSION

3.1 Optimization of sorption variables

Batch sorption experiments revealed 20 minutes as equilibrium contact time at 0.2 g dose

of spent tea against 50 mg/L Cd(II) ions concentration. Sorbent dose and sorbate concentration is optimized by agitating 0.05, 0.1, 0.2g dosage and 25, 50, 75 mg/L Cd(II) ions concentration through independent runs. The dose of 0.05 g and metal ions concentration of 50 mg/L is employed for temperature dependency study.

3.2 Influence of temperature

Temperature is an important indicator to assess the nature of biosorption mechanism. For this purpose, batch experiments are conducted at three temperatures, representative of one value below and one above room temperature, where 35 °C is considered as average room temperature. The results are graphically presented in Figure 1.

An inverse relationship of removal efficacy with temperature is depicted, showing decrease in biosorption capacity of spent tea with an increase of temperature. This is in agreement with the Le Chatelier's principle and that adsorption is a de-concentration phenomenon, responding to decrease in removal with increase in temperature. This behavior is clearly evident in the above mentioned case configuring the equilibrium capacity of spent tea decreases with increasing temperature. It is interesting to note that the inverse relation of temperature and sorption shows slight deviation at 35 °C and 55 °C may be justified as close competition for the adsorption sites. Present study results are significant and comparable to another study by Ahmet et al. (2008) reporting decrease in sorption from 97-82% with increase of temperature from 20-50 °C. Significance is marked in reflecting 27 times decrease than 15 times reported by Ahmet et al. (2008).

Temperature adsorption relationship is explained as being exothermic (Sarkar and Acharya, 2006) in support to present results for cadmium sorption. The fact is that pro-

gressive increase of temperature increases desorption of sorbed ions (Sarý, 2007) and thus deactivate binding sites (Ozer and Ozer, 2003), resulting in decline of removal efficacy.

3.2.1 Estimation of thermodynamic parameters

Thermodynamics of any chemical system is pivotal in determining the energies through assessment of spontaneity, favorability or reversibility of reaction as a function of temperature. For determining spontaneity of process energy and entropy, both factors must be considered (Demirbas, 2002). The distribution coefficient for adsorption process is:

$$KD = \frac{C_{ae}}{C_e} \quad (3)$$

Where C_{ae} and C_e are adsorbed and in solution phase concentrations of metal ions at equilibrium, respectively. Classical Van't Hoff equation relates the Gibbs free energy change of the adsorption process to equilibrium constant by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

The Gibbs free energy change also relates the entropy change and heat of adsorption at constant temperature according to the following equation:

$$\Delta G^\circ = -RT \ln K_D \quad (5)$$

Combination of equation (4) and (5) produces (6):

$$\ln K_D = \frac{-\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

Where ΔG° is the free energy change (kJ/mol), ΔH° the change in enthalpy (kJ/mol), ΔS° the entropy change (J/mol K), T the absolute temperature (K), R the universal gas constant (8.314×10^{-3} kJ/mol K). From linear Van't Hoff plot of $\ln K_D$ versus $(1/T)$, ΔH° and ΔS° are calculated from slope and intercept respectively.

Changes in Gibbs energy ΔG° , Enthalpy ΔH° and Entropy ΔS° at three temperatures (289 K, 308 K and 328 K) are listed in Table 1.

It can be seen that requirement of free energy for Cadmium sorption is from an external source as indicated by positive values of ΔG° at all temperatures. It also reflects the dependence of energy as a function of temperature, so higher is the temperature, more is energy requirement. It is also interesting to note that incremental jump (ΔG° 1.9 KJ/mol) is more significant in moving from 289K to 308K, than from 308K to 328K (ΔG° 0.29 KJ/mol). This might be attributed to slow filling of available sorption sites at relatively higher temperatures and consequently contributing to desorption of loaded particles. At elevated temperatures, the decreased affinity of the sorbent towards Cd(II) sorption may be due to structural differences of sorbate and sorbent used.

The standard enthalpy change for the sorption of Cd onto spent tea is (ΔH° -15.25 KJ/mol) of exothermic nature. Furthermore, feasibility of operative forces can be drawn from values of adsorption heats and functionality of physical or chemical adsorption is also valued from enthalpy values, as suggested by (Shen, 2003). The present study results indicate that binding of Cadmium is operative by both physical and chemical forces. The negative entropy changes may be interrelated to the decreased randomness at the solid-solution boundary. The study summarizes that both ΔH° and ΔS° are negative and enthalpy is less than entropy for spent tea. To revise that physical or chemical sorption is predominant mechanism, the values of activation energy (E_a) is estimated from the experimental data.

3.2.2 Activation energy

Activation energy for adsorption process can

be viewed as the energy requirement for sorbate species to overcome energy barrier for interaction with functional groups on sorbent surface. Activation energy (E_a) values are estimated from experimental data using modified Arrhenius equation,

$$\frac{\ln k(T_2)}{k(T_1)} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (7)$$

E_a values calculated from the spent tea sorption process are found to be -4.58 KJ/mol for Cd^{2+} , suggesting exothermic nature of process and signify favorable metal ion removal at lower temperature. It may be assumed that temperature increases the solubility of metal ions therefore interaction between sorbent and sorbate weakens, on one hand, and enhances between adsorbate and solvent on the other hand. As a consequence, the sorption of sorbate under study became difficult at high temperature.

The magnitude of activation energy adds to classification of adsorption nature. Physisorption involves weak forces generating values no more than 4.2 KJ/mol, while chemisorption being specific involves much stronger forces varies with temperature between 8.4-83.7

KJ/mol. Based on this criterion the results force to evaluate cadmium as physisorbed on spent tea.

3.3 Analysis of binding sites

The chemical structure of the raw biomass (RB) is of fundamental importance in understanding the adsorption mechanism. To categorize the amphoteric character and characteristic functional groups on sorbent surface, The FTIR technique and Boehm's titration method is executed. By selective neutralisation using bases NaHCO_3 , Na_2CO_3 , NaOH , and acid HCl the surface acidic and basic functional groups are characterized respectively.

Active site analysis reflected preferably acidic nature for spent tea, total acidic functional groups are 1.44 meq/g and basic sites are -1.51 meq/g. Occurrence of active sites in functional group follows the sequence as carboxylic > phenolic > lactonic. Same protocol of active sites determination is executed for sorbents altered by chemical treatments.

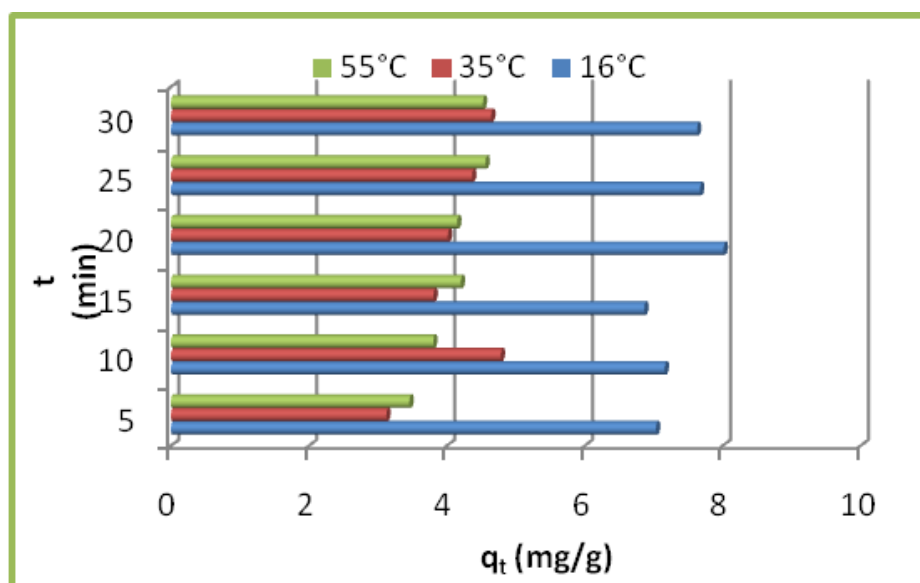


Figure1 Influence of temperature on Cd^{2+} biosorption by spent tea

Table 1 Thermodynamic parameters for Cd sorption by Spent Tea

T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol K)	E_a (KJ/mol)
289	1.16			
308	3.06	-15.25	-57.66	-4.58
328	3.35			

Table 2 Active sites of native and chemically modified Spent Tea

Sites→(meq/g)	Phenols	Lactones	Carboxyl	Total acidic	Total basic
Native	0.38	0.17	1.23	1.79	-1.51
Oxidised	1.03	0.59	1.08	2.7	-1.46
Acetylated	1.92	1.03	1.38	4.33	-1.81
Propanol treated	0.98	-0.54	1.12	1.56	-1.44

In the spectra of native spent tea (Figure 2), a broad band observed from 3000 to 3600 cm^{-1} for hydrogen bonded O-H group of phenols/ carboxyl (Fang, 2004). Similarly, peaks around 2962 cm^{-1} and 2852 cm^{-1} are indicative of -CH stretching of alkanes and aldehydes respectively. The bend at 1734 cm^{-1} and 1658 cm^{-1} corresponds to carbonyl group of lactones and amide.

The C=C presence is seen at 1448 cm^{-1} and C-N stretch of amines at 1026 cm^{-1} , 1325 cm^{-1} . Several distinct transmittances at 1261 cm^{-1} , 1145 cm^{-1} , and 1093 cm^{-1} are attributed to C-O bond stretching of carboxyl, anhydride, and alcohols in that order (Goheen and Wool, 1991). The region below 1000 cm^{-1} is the 'fingerprint zone' which corresponds to complex interacting vibration therefore the transmission cannot be clearly assigned to any particular vibration. The sharp and pointed peak at 800 cm^{-1} can be categorized for N-H bending of amines, and 875 cm^{-1} for sulfonates.

Comparison of pristine spent tea spectra with loaded biomass (LB_{Cd}) shows two new bands appearance at 1145 cm^{-1} of anhydride (C-O) and at 1521 cm^{-1} for -NO₂ aromatic nitro (Figure 2). The decrease in peak intensities after binding means the functional groups

at these wave numbers participated in the metal adsorption. Thus transmitted intensity of peaks for carboxyl (C-O) and amine (N-H) functional groups reduced more proposing them as main binding sites for cadmium removal.

The adsorption capacity of modified samples is explored and compared with raw sorbents by evaluating the maximum mass of metal adsorbed within contact time. Therefore 0.1 g mass of spent tea after modification is treated with 25 mg/L concentrated Cd(II) solution for 40 minutes of 10 minutes time interval. The sorption procedure is same as outlined in experimental section.

The enhanced percentage removal of oxidised and propanol modified biomass in comparison to raw sorbent reflects greener shade.

3.3.1 Modification of binding sites by oxidation

The oxidation of raw biomass with hydrogen peroxide exposes certain binding sites, which result increase in the accessibility of the Cd(II) ions 8% to the sorption sites in comparison to RB (Figure 3).

Nagda and Ghol, (2009) reports 2.8 folds increase in sorption capacity of Tendu waste for Congo red upon oxidation with hydrogen peroxide in reduced equilibrium time from 60 to 30 minutes. Activity of phenolic and lac-

tonic sites is enhanced, further supports the attempted modification Table 2. Total acidic sites are improved from 1.79 meq/g to 2.70 meq/g, while minor drop in basic sites is seen due to hydrogen peroxide treatment.

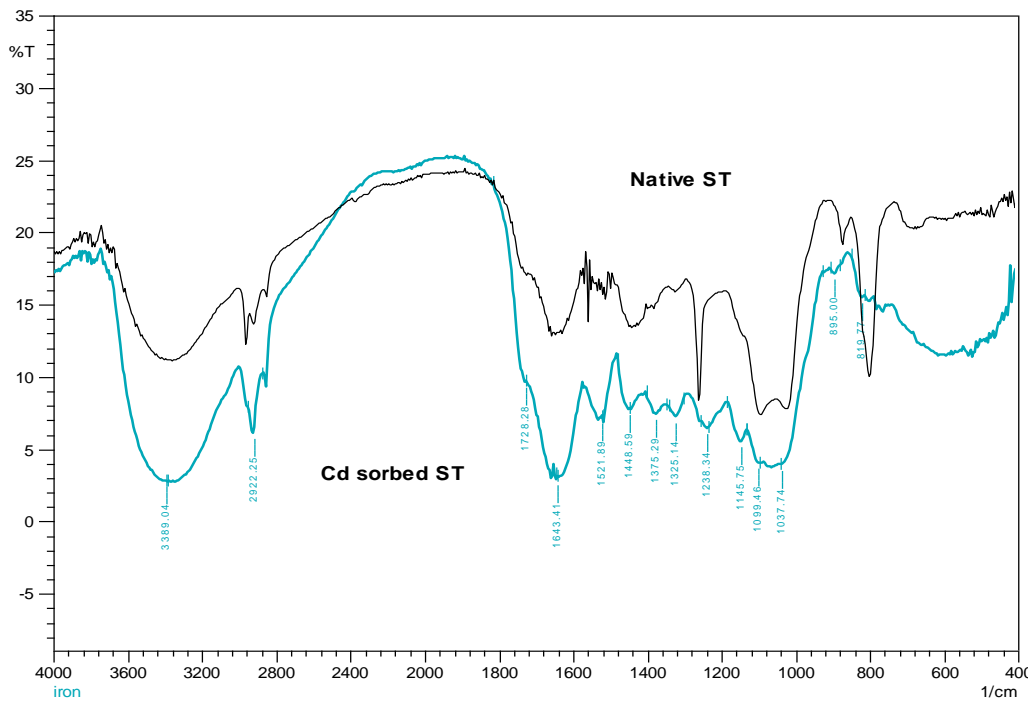


Figure 2 FTIR Spectrum of Raw Spent Tea

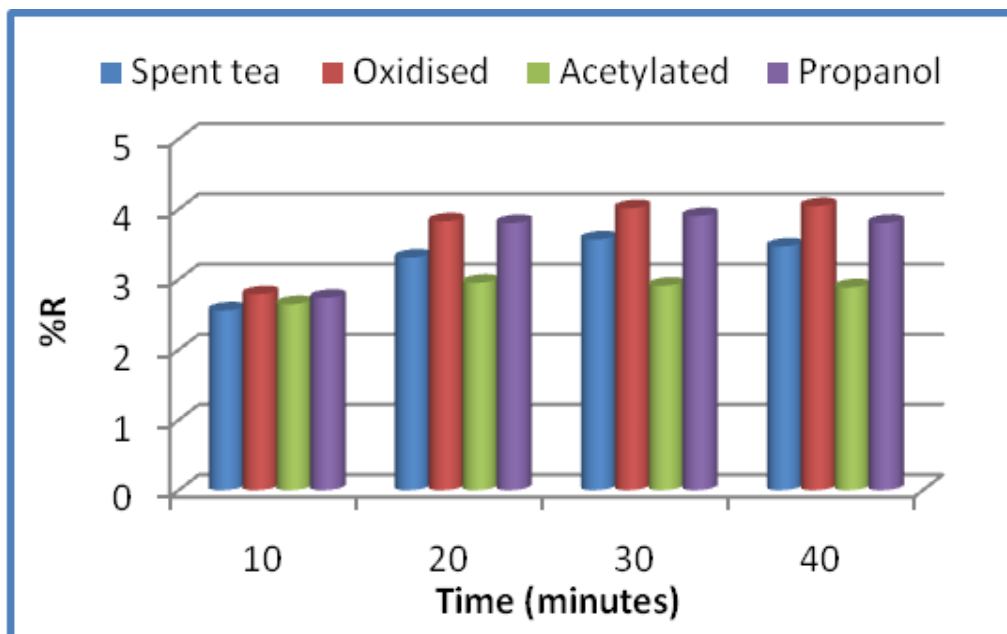


Figure 3 Comparative percentage removal of Cd onto raw and modified Spent Tea

3.3.2 Modification of binding sites by acetylation

The replacement of H^+ of $N-H_2$ by acetyl group, is marked by sharp decrease of band at 800 cm^{-1} for $N-H$ bending, in a similar fashion acetylation of amino group is executed Bai and Abraham (2002) by using acetic anhydride.

Cadmium uptake by MB acetylated reduced 8% during 40 minutes contact time Figure 3. The % sorption drop from metal ions solution after acetylation proposes the involvement of $N-H$ group in metal complexation.

3.3.3 Modification of binding sites by propanol

The change of active sites for $C=O$ is 0.17 meq/g - 0.54 meq/g , and $C-O$ is 1.23 meq/g - 1.11 meq/g (Table 2). Cadmium removal enhanced by 7% after propanol wash suggests carbonyl group ($C=O$) as active loading site (Figure 3). Similarly Li et al., (2007) reports added uptake of 214% for Cadmium by 20% propanol treated orange

peels than raw.

3.4 Characterization of spent tea

3.4.1 Thermal analysis

Characteristics features of the adsorbent are examined as a function of thermal energy using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The spectrum is reproduced in Figure 4. It shows the changes in weight over temperature as quantitative measure, proposing making and breaking of physical and chemical bonds at elevated temperatures due to dehydration or decomposition. It is also known that all weight change processes either absorb or release energy and are thus measurable under DSC. Continuous loss of mass as a function of increasing temperature is clearly pointed out in three distinct phases for spent tea. It elaborates the first phase is possibly due to dehydration and evaporation of volatile components followed by slow decomposition till 228°C beyond which very drastic weight loss is noticed.

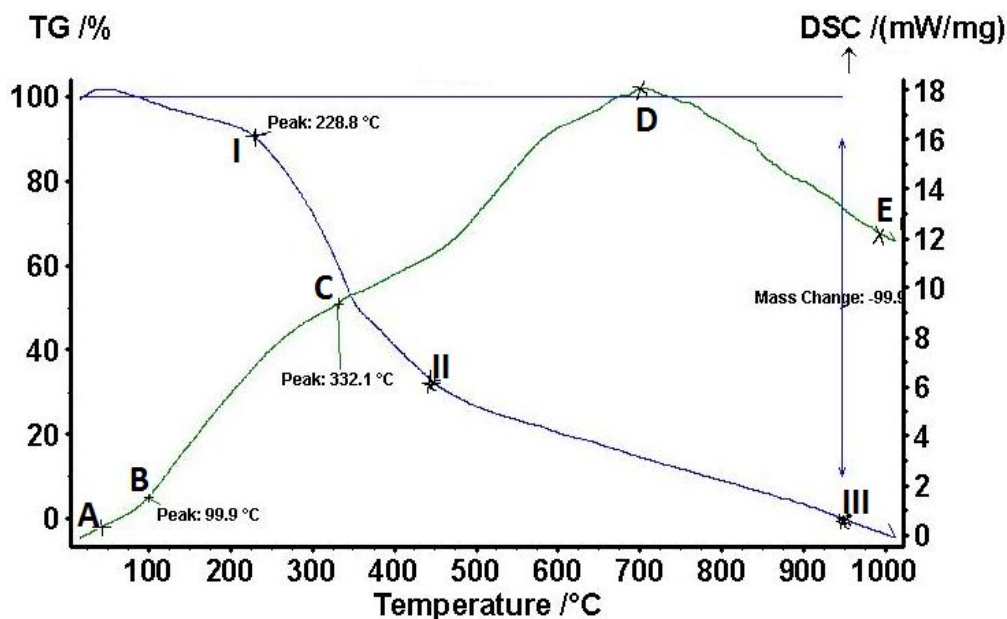


Figure 4 TG/DSC curves of Spent Tea

Third phase marks from 450 °C depicting logarithmic relationship. Decomposition initiation temperature (TD) for spent tea occurs at 228 °C representing weight loss of 10%. Result signifies that spent tea can work optimally over an extended temperature range with minimal mass loss.

DSC curves exhibit exothermic phenomenon manifesting crystallization and endothermic process indicating melting of samples. However, a short thermal lag period from A to B (see Figure 4) is attributed to thermal capacity of spent tea, followed by exothermic effect. A kink at B suggests deviation of curve from base line and transition from rigid to flexible structure. This also precludes 332.1°C as glass transition temperature (Tg). The peak temperature (D) corresponds to maximum rate of heat evolution and further crystallization in sample. It can be concluded on the bases of thermal stability that spent tea is favorable for

adsorption- desorption process at elevated temperatures.

3.4.2 Micro structure analysis

The structure analysis of sorbent is assessed using scanning electron microscopy (SEM) equipped with EDX. Generally rough surface and irregularly shaped particles dispersed in the matrix predicts feasibility for metal sorption, more porous is the surface, and greater is the diffusion. Fissures and holes in the fibers of spent tea signal the presence of meso and microspores.

SEM is also recorded for the adsorbent materials after loading with metals. Results are captured as Figure 5. Considerable changes in surface morphology after biosorption are noted as surface protuberances become less obvious and thin layer appears that may be due to deposition of metal ion.

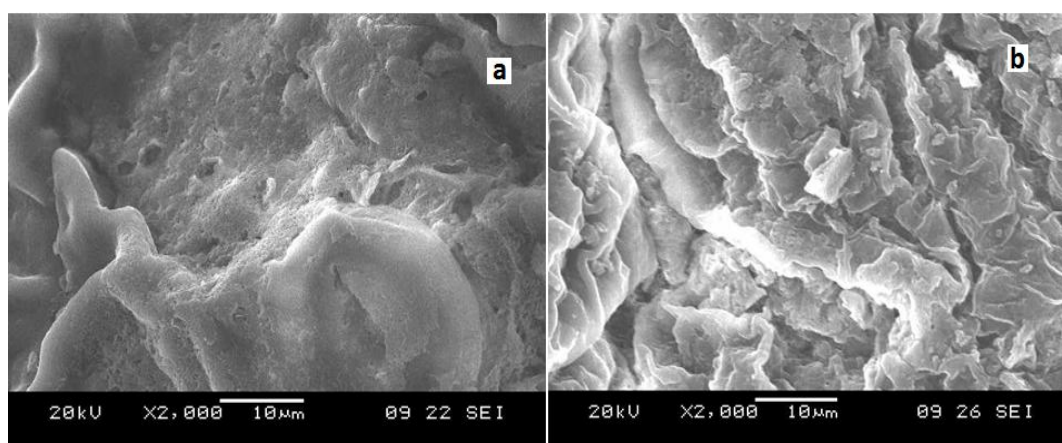


Figure 5 SEM images of Spent Tea before (a) and after (b) Cd biosorption

Table 3 EDX analysis chart of Spent Tea

<i>Sorbent</i>	<i>C</i>	<i>O</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>K</i>	<i>Ca</i>	<i>Cd</i>
<i>ST native</i>	75.72	30.73	3.82	0.24	0.34	0.52	0.56	2.29	-
<i>Cd loaded</i>	70.56	24.76	0.96	0.53	-	0.48	0.51	1.75	1.87

Surface morphology is coupled with EDX analysis for cumulative response of surface and elemental composition. Elemental analysis for native spent tea followed by loading with Cd as pollutants is summarized in Table 3. EDX analysis of native adsorbent corresponds to high signal peaks of carbon and oxygen in Phosphorus (P), aluminum (Al), and sulfur (S), are recorded as minor ingredients common to both adsorbents. The EDX data of loaded adsorbent shows significant variation and changes in morphology in comparison to unloaded one. The emergence of peak of cadmium confirms the presence and appropriate filling of the surface with metal ions. The role of metal ions in adsorption process through ion replacement is also envisaged from EDX. The disappearance of K in Cd loaded spent tea gives the probability of metal replacement.

CONCLUSIONS

Factors influencing sorbent selectivity at industrial level include, low-cost, availability, profitability, ease of operation, and above all environment friendly. Underutilized biomass, spent tea not only possesses all these characteristics, but additionally noticed having huge appetite for cadmium. Benefit of using spent tea is also favorable due to no additional processing steps like crushing, homogenization, coning, quartering, and pulverization, needed for other adsorbents. Spent tea is accessible in powder or granular form round the year throughout the world. The total cost for the preparation of spent tea as adsorbent is connected to its collection and minor processing steps like washing with water, drying in air feasible to maintain porous surface, because high temperature drying alter surface porosity.

Cadmium sorption was found to be dependent on experimental conditions, dosage, initial solution concentration of Cd²⁺ ions and

temperature. Activation energies indicate exothermic sorption of cadmium on spent tea with increasing temperature. FTIR spectrum shows that principal functional groups taking part in the sorption process included carboxyl and amine.

Performance assessment of materials is followed by its cost, collection of tested sorbents comprises labor and transportation cost. High biosorption capacity of sorbent reduces labor and operational cost. The proposed adsorbent spent tea is found to be promising candidate for the removal of metal cations, representing an economical, effective and environmentally clean utilization of waste matter.

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