

Severance of Lead by Acetylated and Esterified *spent Camellia sinensis* Powder

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Abstract Spent *Camellia sinensis* (black tea) potential to impound lead (II) from waste water was assessed by batch adsorption experiments. Optimize dose of spent tea was explored as 0.05g against 50mg/L of Pb ions solution concentration within 20minutes of agitation time at 100rpm. Percentage removal was only marginally affected by increasing pH in the acidic range while at neutrality 96% of lead sorbed onto biomass. Adsorption equilibrium at variable lead loading was well described by the Temkin equation, with 0.97R² value. Lead removal efficiency was found decreasing for acetylated adsorbent than native suggesting amino group as active binding site. The experimental results suggests spent black tea as fast, economical and environment friendly stand-in for conventional adsorbents.

Keywords Biosorption, Acetylation, Esterification, Equilibrium

1. Introduction

Adsorption is proved to be versatile, readily applicable[1] and promising alternative for effluents treatment, playing an important role in particular to treat dilute heavy metal wastewater[2]. The enormous increase in the use of heavy metals in industrial manufacturing and processing leads to inevitable release in bulk into water bodies[3]. Lead one of the poisoning heavy metals is interfering with the development of nervous system and other body processes[4]. The lowest reported lethal dose (LD₅₀) in human is 1470 µg/Kg[5]. Several factors are responsible for high lead exposure in Pakistani children, including paint, cosmetics, drugs, industrial waste and drinking water[6]. In Pakistan excessively high lead levels in drinking water have been reported in some areas of Karachi[7].

Some agricultural byproducts such as jute and coconut fibers[8], bean husks[9], corn cobs[10], and banana stalk[11] are reported to adsorb heavy metals from aqueous solutions. New and inexpensive adsorbent materials that possess a high capacity for adsorbing heavy metals are developing. Black tea, a mild oxidation product of tea leaves becomes a waste when once the beverage is brewed. Schemes are designed to evaluate its possible use as an energy source[12] or for the removal of pollutants from water like arsenic[13], methylene blue[14], and zinc[15]. However, no description so far been published about Pb adsorption upon surface modified spent

tea. Acetylation and esterification of this food waste was attempted to explore active binding sites for lead fixation from aqueous media.

2. Experimental

2.1. Biosorbent Establishment and Portrayal

Black tea sample, collected from processing plant of Shinkiari Tea Gardens (Mansehra, Pakistan) was prepared as biosorbent by boiling it in distilled water for a known time period (5 minutes). Boiling process removed caffeine, tannin and other dyes. The sample was repeatedly washed with distilled water until no coloration appeared in washing solution. The prepared biosorbent material was oven dried at 50°C for 24 hours followed by grinding and passed through US standard testing (No. 30 and 60) to obtain 600-250 µm particle size range of ground sorbent. Dried biosorbent was stored in desiccators to prevent moisture capture. Surface morphology of untreated and modified sorbent was studied through FTIR spectrums and Boehm's titration procedure [16]. Zero point charge pH (pHpzc) of sorbent was determined following protocol of[17] with slight modification.

To minimize the contamination of used glassware in earlier experiments and to avoid the effects on the present investigations, glassware cleaning steps were followed. Glassware was soaked in detergent water mixture for 24 hours, thoroughly rinsed under tap water and dipped again in 10% nitric acid solution. Glassware was rinsed finally with distilled water; dried in oven and kept in desiccator till use.

2.2. Code of Batch Sorption

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Biosorption protocol was similar to described elsewhere [18], the standard solution (1000 mg/L) of Pb(II) was prepared from lead nitrate (PbNO₃) procured from Merck. The concentration of Pb(II) ions in the sorption medium was determined using Flame Atomic Absorption Spectrophotometer (Varian AA-220, Australia). Cations uptake by spent tea was calculated as percentage removal (%R) of Pb(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. Surface Alteration of Sorbent

The sorbent surface was tailored by adopting procedures reported for esterification[19] and acetylation[20] with slight modifications:

2.3.1. Esterification with Methanol

A known mass of biosorbent was suspended in 633 mL of 99.9% pure methanol and 5.4 mL of concentrated hydrochloric acid, to maintain a final acidic concentration of 0.1mol/L HCl. The mixture was continuously agitated for 48 hours at 60°C.

2.3.2. Acetylation with Acetic Anhydride

Acetylation of amino and hydroxyl groups of the biosorbent was carried out by soaking sorbents in 50mL glacial acetic acid and agitated at 100rpm for 1 h, separated by decanting and soaked in acetic anhydride containing 2 drops of concentrated H₂SO₄ for 2 min.

Chemically treated sorbent was drained to separate the solution and reaction was quenched in deionized water till constant pH. The biomass was filtered, dried in oven at 50°C for 24 hours and stored in desiccator till further analysis.

3. Results and Discussion

3.1. Optimization of Sorption Variables

Optimization practice was carried out by agitating at 100rpm (0.05, 0.1, 0.2g) mass of sorbent into 100-mL Erlenmeyer flasks containing 20mL solution of (15,25,35,50, and 75mg/L) metal ions concentration in separate batches. 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 pH reliance and equilibrium study. Optimize dose of spent tea was explored as 0.05g against 50mg/L of Pb ions solution concentration within 20minutes of agitation time at 100rpm.

Removal efficiency of modified sorbents was explored by contacting 0.1g dose in 25mg/L of initial Pb ions concentration.

3.2. Solution pH Dependence

The effect of pH on the sorption of Pb(II) by spent tea is studied at two values in the acidic (pH3.00 and pH5.00) and the neutral scale. The results are simulated in Figure 1. The general behavior depicted is the ease of removal on shift of pH to neutral end showing highest biosorption efficiency (18.34mg/g). It is notable that a regular decreasing trend with decrease in pH is not followed as biosorption capacity of spent tea for Pb(II) at pH 3.00 and 5.00 is not significantly different. Another contrast is revealed by vice versa relationship owing higher removal (12.29mg/g) at earlier pH and lower (10.58mg/g) at later pH. pH_{max} is used to predict the metal ion species adsorbed and it is determined to be 7.00 for lead ions. It indicates equal-distribution of lead ions as Pb(OH)⁺ and Pb²⁺ and both species contributing to sorption. Our results do not commensurate with the explored data by other researchers using pH4.5 and pH5.0 as pH_{max} for lead and copper sorption, respectively, due to the use of different sorbents like pre-treated arca shell biomass[21] and powdered waste sludge[22]. An attempt to work in the basic pH range for sorption studies was not possible. It lays out that due to precipitation of lead as white visible flocks of lead hydroxide complex[23] do not allow the true solution formation.

The impact of change in pH is selective to the nature of adsorbent and metal ion uptake is affected by difference of binding sites[24]. Spent tea is characterized with high content of ionizable groups such as carboxylic, phenolic, and nitro groups and the ionization constant of carboxyl groups ranges between 4 and 5[25]. At lower initial pH of solution, the carboxyl groups retain their protons therefore the probability of binding to any positively charged cations reduces. Whereas at higher pH values (above 4.0), the attraction of carboxylate ions for positively charged ions increases supporting efficient removal at pH 7.00 in the present study. The development of this behavior proposes that an ion-exchange mechanism is involved due to electrostatic interaction between negatively charged groups on the adsorbent surface and metal cation in solution. Delgado et al.,[26] specified the relationship between the quantity of the negative charges on biomass surface, (depends on the dissociation of functional groups) and solution pH as a cause of variation in the biosorption efficiency.

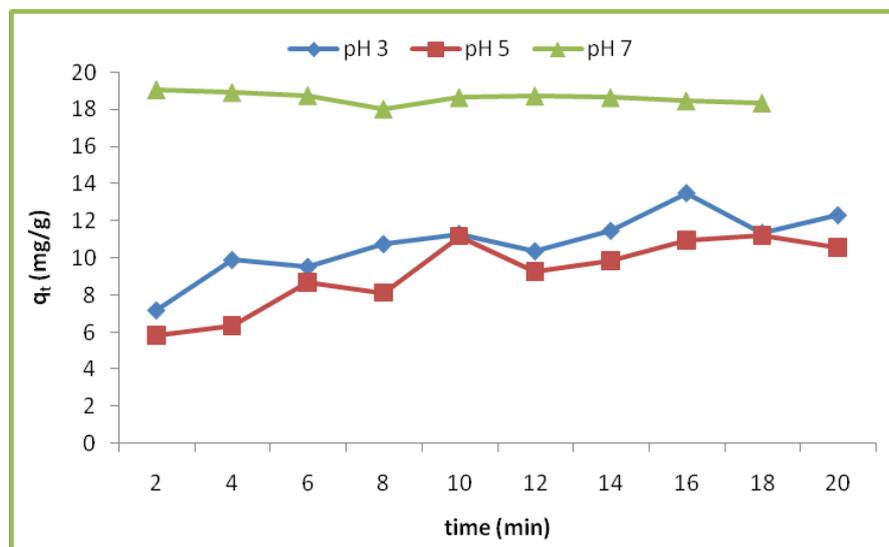


Figure 1. Biosorption capacity of spent tea at different initial Pb solution pH

Increase in Pb(II) removal along the pH increase can also be explained in terms of pH_{pzc} (point of zero charge) of the adsorbent and metal speciation taking place in the solution. The pH_{pzc} of spent tea is found experimentally to be 5.88. At pH above pH_{pzc}, the net negative charge on the biomass promotes the uptake of metal ions. On lowering pH, surface charge on biomass becomes positive inhibiting the positively charge metal cations[27]. The electrostatic force of interaction at pH 3.00 and 5.00 (<pH_{pzc}) is less, resulting in lower sorption capacity.

3.3. Adsorption Equilibrium

For practical design of adsorption, isotherms are considered as indispensable data source for adsorbent and adsorbate relationship. A number of equations are suggested and applied by researchers for analyzing experimental data. Most frequently experienced isotherms are Langmuir, Freundlich; current study incorporates Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms beside the most tested one. These models are applied onto experimental data extracted from batch sorption studies performed at optimized sorbent dose by changing initial metal ion concentration (15,25,35,50, and 75mg/L) at room temperature for optimum contact time.

3.3.1. Langmuir Isotherm

Langmuir isotherm conventional use is to measure and compare efficiency of different biosorbents. It was originally developed to signify physisorption of gas on activated carbon, possesses well-defined adsorption sites having the same adsorption energy[28]. Energetically identical surface binding sites have equal affinity for the sorbate with no interaction among these molecules is main assumption in its formulation[29]. So this model is also called the ideal localized monolayer model. For solid-liquid systems, the Langmuir isotherm is given as:

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

Linear form of the Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where K_L is sorption equilibrium constant (L/mg), q_m is measure of the maximum adsorption capacity (mg/g) in the system; q_e and C_e are sorbed and residual metal ion concentration. A plot of C_e/q_e versus C_e should indicate a straight line of slope ($1/q_m$) and an intercept of ($1/K_L q_m$) from which q_m and K_L can be calculated.

Application of the Langmuir isotherm equation to analyze the equilibrium isotherms of metal ions gives linear plot (Figure 2-A). Langmuir model states that no further adsorption can take place once the site is occupied[30]. Thus the maximum biosorption capacity for Lead is found to be 18.18 mg/g, as against the experimental value of 11.19 mg/g sorbent.

To further quantify the sorption properties the Langmuir isotherm can help to predict whether a sorption system is favorable or unfavorable. For this end K_L the Langmuir constant can be used to find a dimensionless constant separation factor R_L [31] as:

$$R_L = \frac{1}{1 + K_L C_i} \quad (5)$$

Relationship between R_L values and type of sorption can be listed as:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

Calculated separation factor was 0.28, proposing favorable sorption of lead upon spent tea at room temperature.

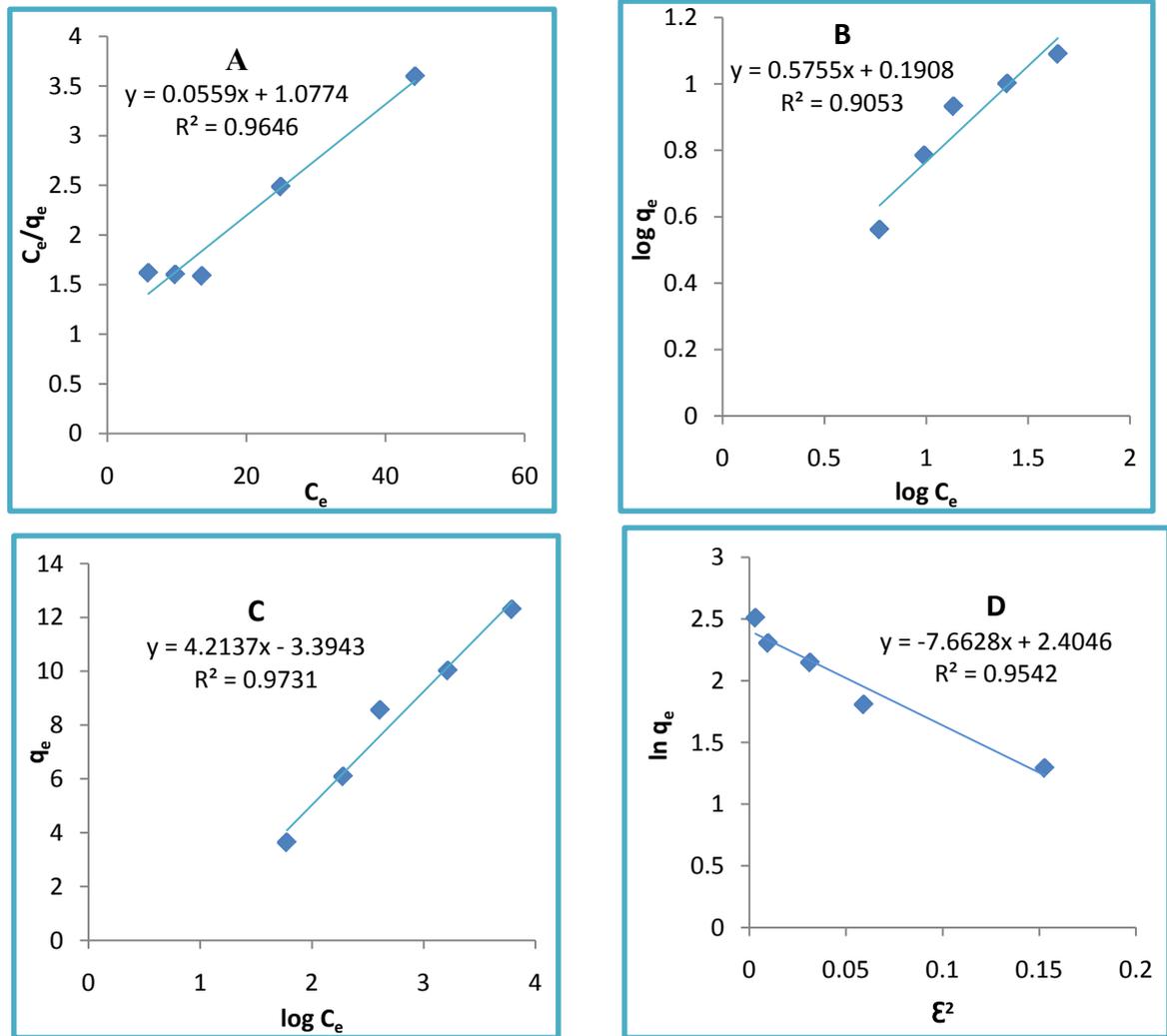


Figure 2. Adsorption isotherms plot (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) D-R

3.3.2. Freundlich Isotherm

The Freundlich adsorption isotherm usually fits the experimental data over a wide range of concentrations[32]. Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). The isotherm derivation is based on the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by:

$$q_e = K_F C_e^n \tag{6}$$

Linear form of the Freundlich isotherm is:

$$\log q_e = \log K_F + 1/n \log C_e \tag{7}$$

where K_F (mg/g) indicates the multilayer adsorption capacity and $1/n$ an empirical parameter related to the intensity of adsorption. A plot of $\log q_e$ against $\log C_e$ yields a straight line, the values of constants ($1/n$) and ($\log K_F$) can be obtained from slope and intercept respectively, from which n and K_F can be calculated.

Straight line plot represented in Figure 2-B for identifying heterogeneity of adsorbent shows 1.55 mg/g multilayer

sorption capacity of Lead onto spent tea. The intensity of adsorption (n) was figured out as 1.74, whereas its value in the range of 2-10 indicates favorable sorption.

3.3.3. Temkin Isotherm

The assumption of Temkin isotherm equation is that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy[33]. The Temkin isotherm is given as:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \tag{8}$$

On linearization the equation becomes:

$$q_e = B \ln K_T + B \ln C_e \tag{9}$$

where $B = RT/b_T$, constant b_T (KJ/mol) is related to the heat of adsorption and K_T (L/g) is the equilibrium binding constant. A plot of q_e versus $\ln C_e$ enables to determine b_T and $\ln K_T$ from the slope and intercept of straight line plot from which B and K_T can be calculated.

Heat of sorption calculated from linear plot of Temkin

isotherm represented in Figure 2-C, indicates weak sorbate-sorbent interaction. Proposing shallow physisorption wells for the spent tea loaded with Lead. Temkin equation represents occupation of more energetic sites first; equilibrium sorption data presents spread of binding constant as 0.45.

3.3.4. Dubinin-Radushkevich Isotherm

The equilibrium data is also tested by the Dubinin-Radushkevich (D-R) isotherm to resolve the nature of biosorption process as physical or chemical. The linear form of this isotherm[34] is:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (10)$$

where K_{DR} is a constant related to the biosorption mean free energy (mol^2/KJ^2), ε is the Polanyi potential and q_m is the maximum biosorption capacity (mg/g). A plot of $\ln q_e$ versus ε^2 is a straight line where K_{DR} and q_m can be obtained from slope and intercept respectively. The Polanyi potential (ε) can be equated as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (11)$$

where R is the gas constant ($0.008314 \text{ KJ/mol K}$), and T is the temperature (K), the mean free energy of adsorption E, is calculated by using the following formula:

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (12)$$

Table 1. Isotherms model constants and their respective coefficients for Pb sorption onto spent tea

Langmuir	q_m (mg/g)	18.18
	k_L (L/mg)	0.05
	R^2	0.96
Freundlich	n	1.74
	K_F (mg/g)	1.55
	R^2	0.91
Temkin	B	0.59
	K_T	0.45
	R^2	0.97
Dubbin-Radushkevich	K_{DR}	-7.66
	q_m	11.07
	R^2	0.95
	E	0.26
Flory Huggins	α_{FH}	-4.75
	K_{FH}	7.55
	R^2	0.89
	ΔG°	-5.04

Calculation of biosorption capacity and mean free energy is made from slope and intercept values of linear plots depicted in Figure 2-D. The maximum biosorption capacity for Lead is found to be 11.07 mg/g, as against the experimental value of 11.19mg/g sorbent. It is confidently reported that calculated and experimental q_m values are close to each other suggesting D–R partiality over Langmuir isotherm. The mean adsorption energy calculation by the

D–R isotherm provides key information about chemical or physical nature of the adsorption process. Involvement of physical electrostatic force in adsorption process is signified by magnitude of E. It has been reported that physisorption processes usually have E values $<40\text{KJ/mol}$ and above this value sorption is of chemisorptions mechanism[35]. The biosorption point toward ion exchange process when E value lies between $8\text{-}16\text{KJ/mol}$, and $<8\text{KJ/mol}$ indicates physisorption process[36]. Calculated E value 0.26KJ/mol suggests physisorption of lead over spent tea, similarly values of the apparent energy of sorption depicted physisorption of Cd(II), Pb(II) and Zn(II) ions on unmodified and EDTA-modified maize husk from waste water[37], and for Cd^{2+} ions on *Moringa stenopetala* and *Moringa oleifera* seed Powders[38]. However chemisorption of divalent metal ions onto agro waste[39] and copper on grafted chitosan[40].

3.3.5. Flory – Huggins Isotherm

The degree of surface coverage of adsorbate on sorbent can be identified by Flory – Huggins model[41]. The linear form of the Flory –Huggins equation is expressed as:

$$\log \left(\frac{\theta}{C_e} \right) = \log K_{FH} + \alpha_{FH} \log(1 - \theta) \quad (13)$$

where θ is the degree of surface coverage, can be computed by:

$$\theta = \frac{1-C_e}{C_i} \quad (14)$$

α_{FH} is the number of metal ions occupying sorption sites and K_{FH} the equilibrium constant of adsorption. The values of K_{FH} and α_{FH} can be obtained from intercept and slope of the plot of $\log(\theta/C_e)$ versus $\log(1-\theta)$ respectively.

Moreover the equilibrium constant K_{FH} can be used to compute the Gibbs free energy for sorption process. The Gibbs free energy is related to equilibrium constant as follow:

$$\Delta G^\circ = -RT \ln K_{FH} \quad (15)$$

A negative correlation is inferred from data of surface coverage (θ) with increase in sorbate concentration, the effect is decreasing from 61% to 41% by increasing lead concentration from 15mg/L to 75mg/L. The negative value of ΔG° shows feasibility and spontaneous nature of the process.

3.3.6. Comparative Best Fit

Design of adsorption systems needs careful consideration of predicted values for isotherm parameters. Fitness of adsorbate adsorbent interaction to theoretical parameters of adsorption isotherm equations is determined by coefficient of correlation (R^2), estimations of this regression analysis is summarized in Table1. Fitness approximation calculates lead fixation onto spent tea equally feasible by all tested models except Flory-Huggins. Highest R^2 value was obtained for Temkin isotherm followed by Langmuir, D-R and Freundlich. Equilibrium dynamics analyses suggest favorable spontaneous multilayer physisorption of lead onto spent tea.

3.4. Chemical Modification

3.4.1. Esterified Biomass

Methanol is used for esterification of spent tea resulting in mass loss (4g) due to chemical interaction. A shift of transmission peaks at 3404 cm^{-1} (O-H) and 1448 cm^{-1} (C=C) wave number appears after decarboxylation of spent tea (Figure 3). Shifts in C-H and C-N peaks from 2962 cm^{-1} to 2926 cm^{-1} and 1026 cm^{-1} to 1033 cm^{-1} indicates modification

with decrease proportion of these sorption sites. Spectra provoke suppression of bands at 1261 cm^{-1} , 1097 cm^{-1} characteristic of carboxyl and alcohol groups. The bonding of carboxyl groups in the IR spectra of methanol esterified biomass provides evidence for successful esterification. This is further supported by decline in carboxylic sites of esterified biomass from 1.23-1.01meq/g and uplift in phenolic sites from 0.38meq/g to 1.03meq/g (see Table 2).

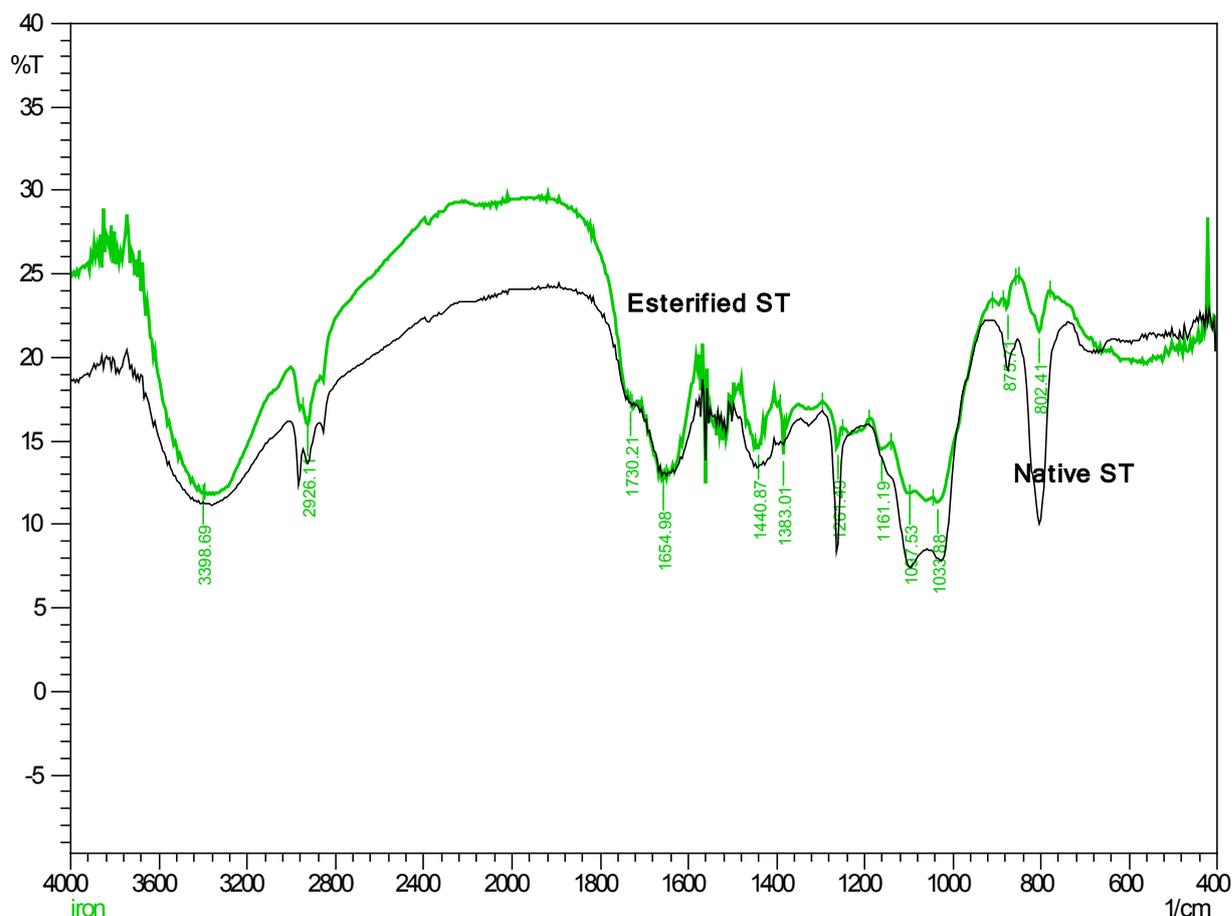


Figure 3. Methanol Esterified spent tea

3.4.2. Acetylated Biomass

Spent tea is acetylated at 27°C with acetic acid and acetic anhydride for 1hour reaction time, spectral analysis (Figure4) of acetylated spent tea shows reduction in transmitted intensity of C-N stretching ($1026\text{--}1233\text{ cm}^{-1}$). The replacement of H^+ of NH_2 by acetyl group is evident from sharp decrease of band at 800 cm^{-1} for N-H bending. In a similar fashion acetylation of amino group is executed using acetic anhydride[42]. Spectra also indicates enrichment of carbonyl stretching absorbance at 1730 cm^{-1} , 1664 cm^{-1} for ester and amide, whereas for nitro group (N-O), it appears at 1383 cm^{-1} . It is interesting to note that no peak is observed from 1840 cm^{-1} to 1760 cm^{-1} and at 1700 cm^{-1} in spectrum of modified sorbent, suggests complete modification and that modified sorbent is free of unreacted acetic anhydride and acetic acid[43].

Table 2 narrates two fold improvements of total acidic sites due to increased phenolic content. In addition, slightly decrease basic sites at the same time are also noted. Comparative lead sorption between native and acetylated spent tea revealed 9% reduction during 40 minutes of contact time, this drop after acetylation proposes involvement of N-H group in metal complexation.

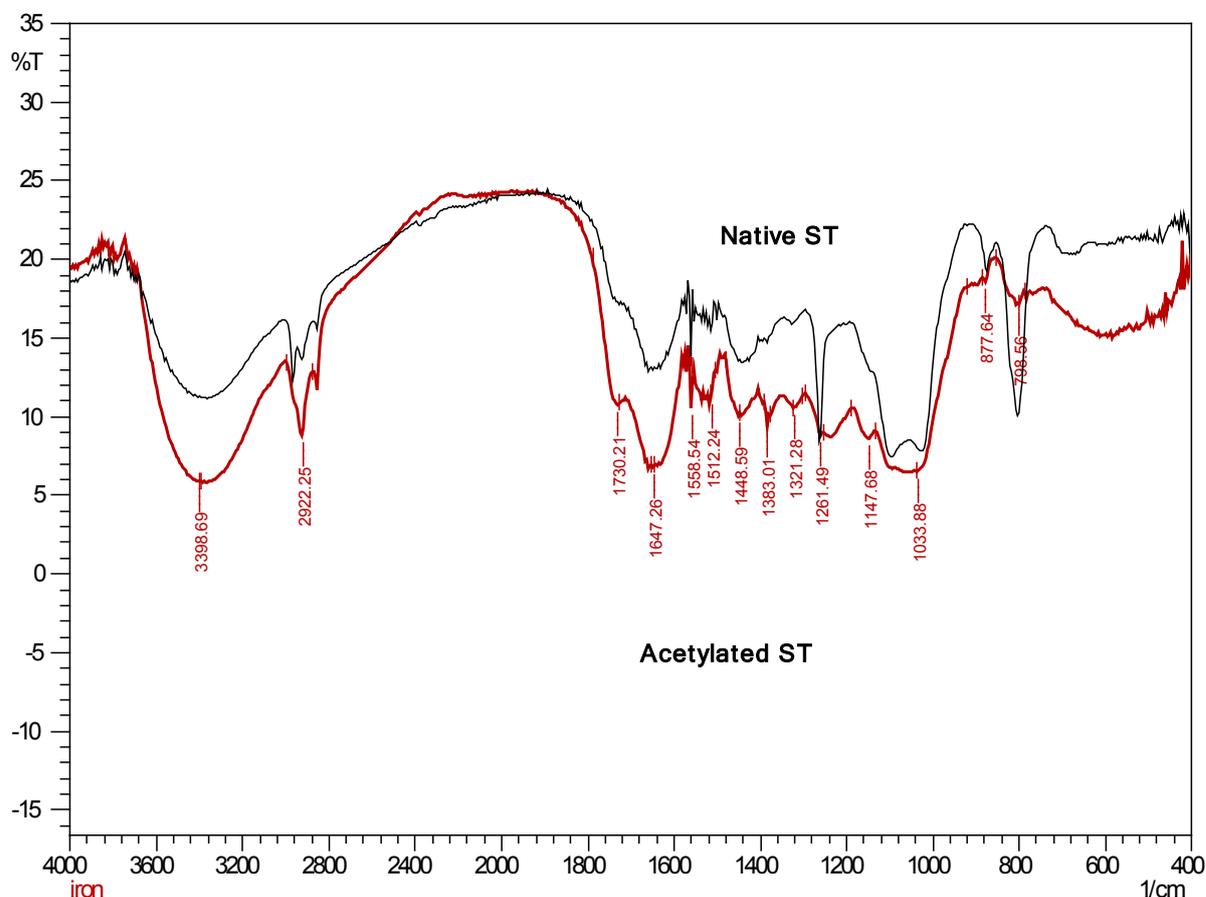


Figure 4. Acetic anhydride acetylated spent tea

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	1.44	-1.51
Esterified	1.03	-0.58	1.01	1.46	-2.20
Acetylated	1.92	-1.03	1.38	2.27	-1.81

4. Conclusions

The study makes public that the sorption of Pb^{2+} ions on to the spent black tea is easy on the pocket. Efficient treatment of heavy metal contaminated wastewater by waste biomass serve as choice to conventional means. Removal was noted to fall within the range of 59-96%, depending on the adsorbent dose, solution composition and pH. Maximum uptake capacity was found at pH 7. Sorption isotherms figured out spontaneous multilayer physiosorption of lead onto spent tea. The tested adsorbent may provide an affordable technology for small and medium scale industries.

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