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ORIGINAL RESEARCH ARTICLE

Kinetics, Thermodynamics, and Isotherm Properties of Lead & Silver Metal Ions Removal from Aqueous Solution Using Tea Leaves and Tea Fibers (*Camellia sinensis*)

Emmanuel Edet Etim*, Haruna Anas, Shedrach Yakubu, Liberty Joshua Moses and Humphrey Sam Samuel
Department of Chemical Sciences, Federal University Wukari, Taraba State, Nigeria

ABSTRACT

The growing human population and industrial demands increase heavy metal contamination, posing health risks. This research explores sustainable methods for removing heavy metal using *Camellia sinensis*, commonly known as tea leaves and tea fibers, examining adsorption capacity and effects of temperature, chemical dosage, time, and initial metal concentrations. Adsorption isotherms were employed to analyze the research data to show the thermodynamics and kinetics studies of the sorption process. FTIR spectroscopy confirmed active functional groups like C-O, N-H, and C-N in the Tea leaves and fibers. The Langmuir adsorption isotherm shows the correlation coefficient (R^2) of 0.3791 and 0.0092 for investigating the biosorption of silver and 0.0379 and 0.1708 for the biosorption of lead by tea leaves and tea fibers respectively. On silver, the Freundlich isotherm shows R^2 values for tea leaves and tea fibers as 0.5218 and 0.1392, respectively, and on lead, it yields R^2 values of 0.0308 and 0.1771, respectively. The kinetic results utilized first and second-order kinetics, with the second-order fitting well for experimental results of the sorption process of tea leaves and tea fibers sanctum on silver and lead. Thermodynamic studies suggest a spontaneous, endothermic, and practical adsorption process. This study indicated that Tea leaves is a more appropriate cost-effective Lead Pb(II) and Silver (Ag) removal of industrial effluent and wastewater.

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INTRODUCTION

Heavy metal contamination in water sources remains a critical environmental problem, especially in regions where industrial wastewater discharge is often poorly regulated. Conventional remediation methods can be cost-prohibitive and not readily accessible. The significance of this study lies in its potential to provide an effective, low-cost, and sustainable solution for heavy metal removal from aqueous solutions. Given the exponential growth of the human population and the continuously expanding demands of the industrial sector, the amount of pollution emission into the ecosystem is increasing. Heavy metals can build over time and are not biodegradable; they pose a significant effect on human health (Tumampos *et al.,* 2021; Etim *et al.,* 2019; Etim *et al.,* 2023; Zhang *et al.,* 2019; Adekola *et al.,* 2014). With an atomic density higher than 4g/cm^3, heavy metals are poisonous. Large-scale industrial effluent releases into water bodies are a major source of heavy metal pollution, endangering aquatic and terrestrial life. Manganese, lead, zinc, antimony, and silver are examples of heavy metals. Lead can damage the body's metabolic processes and build up in the kidneys, muscles, brain, bones, and brain. Studies by the World Health Organization show that the standard threshold of lead in drinking water is 0.1 – 0.05mgL$^{-1,}$ and zinc is 5.0 mgL^{-1}(Samuel *et al.,* 2023; Samuel *et al.,* 2023). Zinc is also released into industrial effluents through wastewater treatment plants, galvanizing factories, and mine drainage. Manganese poisoning can cause a wide range of symptoms, including muscle weakness, loss of balance, and difficulty walking. Brain injury that cannot be reversed may occur in severe circumstances. Furthermore, continuous exposure to manganese dust can cause a lung disorder called manganism, which has symptoms akin to Parkinson's disease. Although manganese may be toxic, there is also some evidence that it may be carcinogenic (Verma *et al.,* 2017; Etim *et al.,* 2023, 2024; Mohsen *et al.,* 2023).

Many methods, including ion exchange, filtration, membrane technology, evaporation technology,

Correspondence: Emmanuel Edet Etim. Department of Chemical Sciences, Federal University Wukari, Taraba State, Nigeria.
✉ emmaetim@gmail.com.

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precipitation, solvent extraction, etc., have been employed to treat water from industrial effluent. Adsorption is an environmentally friendly and efficient way of removing metal ions from aqueous solutions by means of the reaction between cationic metal ions and the anionic groups contained in the adsorbent (Tripathi and Ranjan, 2015; Singh *et al.,* 2007; Kuan *et al.,* 2018). Adsorption is a surface phenomenon that occurs when an adsorbent absorbs a solution containing the adsorbate. Adhesion of an adsorbent to the surface of an adsorbate is known as physical adsorption because of van der Waals forces and the independent nature of the material, in contrast to chemisorption, which is the formation of strong, attractive forces due to chemical reactions on the adsorbent surface that result in the formation of covalent and electrovalent bonds. A reversible process known as physical adsorption is less selective than chemisorption, which is an irreversible process (Asuquo *et al.,* 2017; Malandrino *et al.,* 2006; Etim *et al.,* 2022; Adelagun *et al.,* 2021). Many biological elements have been utilized extensively to extract heavy metals from industries (Demirbas *et al.,* 2002; Emmanuel *et al.,* 2019).

Common adsorbents frequently used in water treatment to remove metal ions include activated carbon, clays, flash ash, activated sludge, cellulose, chitosan, inorganic-organic nanocomposites, and chelating fibers. However, the water treatment field has paid close attention to bio-absorbents due to their low cost, high removal efficacy, biodegradability, and environmental friendliness (Etim *et al.,* 2019). The common biosorbents are by-products of processing soybeans, cottonseed hulls, sugarcane bagasse, rice straw, peanut hulls, and paper mill sludge. Adopting a naturally occurring, plentiful, and cost-effective metal adsorption system has significant promise because of the increasing focus on sustainability, upcycling, and environmental protection (Inyang *et al.,* 2018). A study on the kinetics and thermodynamics of copper ion adsorption using tea leaves and tea fibers as adsorbents was analyzed by Shyam *et al.* 2005; Asuqwo *et al.* 2007; Etim *et al.* 2017. Comparison of the several theoretical models for the adsorption process was done. The research revealed tea leaves and tea fibers to be effective copper ion adsorbents. Moreover, the large amounts of tea leaves produced in cafeterias as a waste by-product could be used to extract heavy metals from aqueous solutions. The research aims to study the kinetics, thermodynamics, and isotherm properties of lead & silver metal ions removal from aqueous solution using tea leaves and tea fibers. Many previous studies have examined the removal of single heavy metals using either tea fibers or tea leaves but this research uniquely addresses the simultaneous removal of two metal ions Lead (Pb) and Silver (Ag) from aqueous solutions. This study comprehensively analyzes the adsorption process by evaluating kinetics, thermodynamics, and isotherm models. The research offers a comparative analysis of the effectiveness of tea leaves and tea fibres in removing both metal ions from wastewater. While prior research may have looked at these biosorbents independently or with other materials, this study directly compares their performance under identical conditions with binary metal ions.

MATERIALS AND METHODS

Sample Collection, Preparation, and Analysis

The *Camellia sinensis* used in this study was sourced from Sardauna L.G.A in Kakara High Land Tea in Taraba State, Nigeria. They were gathered in the morning, thoroughly cleaned to get rid of any moisture and debris, and then rinsed with purified water. After being adequately dried at room temperature, he sample was ground up and sieved using a 150 mm micron sieve.

The stock solutions of 0.1 M of Lead (II) nitrate, 0.1M Silver, and 0.1 M sodium hydroxide were prepared according to the method described by Etim et al. (2017) with no modification. The solutions were prepared for use throughout the experimental work. Measure 20 cm^3, 30 cm^3, 40 cm^3, and 50cm^3, respectively, of the stock metal solution into a 100 mL volumetric flask; four distinct metal concentrations were created by serial dilution from the metal solution: 20 mg/L, 30 mg/L, 40 mg/L, and 50mg/L and shaken to determine homogeneity and initial ion concentration (Asuquo *et al.,* 2012; Asuquo *et al.,* 2017)

Atomic absorption spectroscopy (AAS) was used to analyze lead (Pb) and silver (Ag). This involves placing a sample solution containing the metal ions into a flame, which excites the metal ions and causes them to emit light at particular wavelengths indicative of the binary metal ions present. The amount of lead and zinc in the solution is then determined by measuring the intensity of the released light. AAS is a very accurate and sensitive technique frequently used to analyze a variety of metal ions in solution. The Atomic Absorption Spectrometer was initially calibrated using standard solutions of known concentrations for each metal ion being studied (e.g., lead, silver). These standards were prepared at various concentrations to cover the samples' expected range of metal ion concentrations. The calibration curves for each metal ion were generated by measuring the absorbance of each standard solution at the specific wavelength corresponding to that metal. he specific AAS model used was the PerkinElmer PinAAcle™ 900T, and the precision determined using the standard solution. (Asuquo, *et al.,* 2012).

Batch Adsorption Experiment

The rates of adsorption and equilibrium values were obtained using batch adsorption studies. The adsorbent materials were first prepared by drying *tea* leaves and *Tea fibers* at 60°C until a constant weight was achieved. The dried leaves were then ground into a fine powder using a mechanical grinder and sieved to obtain a uniform particle size. Standard solutions of Pb (II) and Ag ions were prepared by dissolving appropriate salts ($Pb(NO_3)_2$ for lead and $AgNO_3$ for silver) in deionized water. A range of initial metal ion concentrations was prepared, typically from 10 to 100 mg/L, to study the adsorption kinetics and equilibrium. The effects of concentration, dosage, time, pH, and temperature were all varied during this process.

Effect of Biosorbent dosage

1g, 2g, 3g, 4g, and 5g were weighed into various conical flasks of Ag and Pb, and 50mL was shaken for an hour to reach equilibrium after the flasks were corked, and the metal solution was measured into each conical flask and labeled. The slurries were then filtered using plastic funnels and Whatman filter paper, and the filtrate was stored in containers with clear labels. The filtrate concentrations were then measured using an atomic absorption spectrophotometer (Tan *et al.,* 2012).

Effect of time

50mL of the Ag and Pb metal solution was suspended in about 1g of Biosorbent in various conical flasks. Ten, twenty, thirty, and forty minutes were the intervals between each beaker's agitations on an electrical shaker/rotatory mixer set at 30 rpm. Maintaining a constant pH of 6, 25 °C, and 0.1 M of metal concentration. Upon completion of spinning, the solutes were extracted and transferred into centrifuge tubes made of polypropylene. After that, they were centrifuged at 4000 rpm for three minutes. The biosorbent was able to separate from the mixture as a result (Asuquo *et al.,* 2012).

Effect of Initial Concentration

Ag and Pb solutions, each of about 50 cm^3 and prepared in four different concentrations 20, 30, 40, and 50 mg/L), were measured and added to separate conical flasks. Each flask received 1 g of the biosorbent, and the mixture was shaken for an hour to reach equilibrium. The filtrate was stored and labelled easily readable after the slurries were filtered using a Whatman filter paper and plastic funnel. An atomic adsorption spectrometer was then used to measure the concentration of the heavy metal that was produced (Asuquo *et al.,* 2012).

Effect of pH

To examine the effect of beginning solution pH on silver (Ag) and lead (Pb) biosorption, 10g of tea leaves and *Tea* fibers were inserted in a 50 cm^3 of Ag solution in a conical flask. The experiments were conducted at 25°C. Using either 0.1 M sodium hydroxide or 0.1 M nitric acid, the pH of each solution was brought to the appropriate level. The tests were conducted at various pH values of 1.0; 3.0; 5.0; and 7.0. Analyses were conducted on the residual Ag concentration in the solutions after the biomass was extracted from them using decantation. A mechanical shaker was used to shake them all for one hour. The AAS machine calculated the mean value for each sample, which was all carried out in triplicate [32].

Effect of temperature

Four distinct conical flasks were filled with approximately 50 cm^3 of the Ag and Pb metal solution at a concentration of 40 mg/L. The weighing procedure was followed by adding 0.1 g of the adsorbent to each flask. The slurries were filtered with a plastic funnel and Whatman filter paper on the mechanical shaker after one hour to achieve equilibrium. The AAS was then used to determine the filtrate's concentration, which was then stored in a container with a label (Etim *et al.,* 2023).

Kinetics of the Adsorption Process

Using the pseudo-first-order kinetic model, the rate of reaction was ascertained. The pseudo-first-order and pseudo-second order rate equations were applied to the kinetic analysis, as shown in the equations below.

$$Log(q_i - q_t) = log q_e \frac{k_1}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

The amounts of metal ions adsorbed (mg g^{-1}) at equilibrium, and at time t are denoted by qi and qt, respectively; the pseudo-second-order rate constant (gmg^{-1} min^{-1}) is represented by k_2, and the Lagergren rate constant of the biosorption is represented by k_1.

Thermodynamics studies

The adsorption of Ag and Pb is reversible and, as such, can be represented by

$$k_c = \frac{C_{ad}}{C_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Since $\boldsymbol{kc}$ is temperature-dependent, it is used to estimate the thermodynamic parameters. Equation (4) also connects it to a change in free energy, while equation (5) connects the latter to thermodynamic parameters (Etim *et al.,* 2023).

$$\Delta G^o = -RTInK_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

R = universal gas constant (8.314 J mol^{-1}K^{-1}),

G° = standard Gibbs free energy (kJ mol^{-1}),

T = temperature (K)., ΔG^o = entropy change

ΔH^o = change in enthalpy.

Instrumental Characterization

The FTIR machine model Cary 630 by Agilent Technologies, USA, was used, and the spectrometer crystal was cleaned with Ethanol.

RESULTS AND DISCUSSION

FTIR Results

Tea fibers and tea leaves functional groups were examined using infrared Fourier transform spectroscopy, as shown in Figures 1 and 2. Tables 1 and 2 show the differences in functional categories for Tea fibers and tea leaves. The FTIR data of Tea leaves reveal the presence of alkane at the C-H band at 2918.5 cm^{-1}, alcohol, carbohydrates, proteins, and phenols at the O-H band at 3615.6 cm^{-1}, phosphine and C=O signaling an aromatic ketone at P-band at 2322.1 cm^{-1}, and primary amine at N-H at 3697.5 cm^{-1}. The band provides complete confirmation of the presence of the primary amine at 1606.6 cm^{-1}. The band shows the presence of an aromatic amine at 1364.2 cm^{-1}. The band indicated the presence of the carboxylic acid at 1233.7 cm^{-1}.

Tea fibers shows O-H stretch band at 3276.3 cm^{-1} corresponding to alcohol, carbohydrates, proteins, and phenols; C-H band at 2918.5 cm^{-1} indicating an Alkane; a –C=O band at 1625.1 cm^{-1} indicating the amide; C-O band at 1144.2 cm^{-1} corresponding to secondary alcohol; and C-O band at 1017.6 cm^{-1} indicating an ether or/and primary alcohol. The spectrum shows what caused certain peaks to shift or disappear while others grew. This suggests that chemical adsorption is taking place, as this change shows the involvement of these functional groups in the adsorption process.

Table 1 FTIR analysis for Tea leaves

Peak wavelength (cm^{-1})	Bond Type	Functional Group
3697.5	N-H	Primary amine
3615.6	O-H	Carbohydrate; Protein; Alcohol
2918.5	C-H	Alkane
2322.1	P-	Phosphine
1729.5	C=O	Aromatic ketone
1606.5	N-H	Primary amine
1461.1	-C=0	Inorganic carbonate
1364.2	C-N	Aromatic amine
1233.7	R-COOH	Carboxylic acid
1010.1	C-O	Primary alcohol

Table 2. FTIR for Tea Fibers

Peak wavenumber (cm^{-1})	Bond type	Functional group
3276.2	O-H	Carbohydrate; Protein; Phenol
2918.5	C-H	Alkane
1625.1	-C=O	Amide band I
1513.1	-C=O	Carboxylic acid
1513.8	C-N	Amide band III
1144.2	C-O	Secondary alcohol
1017.6	R-O-R	Ether

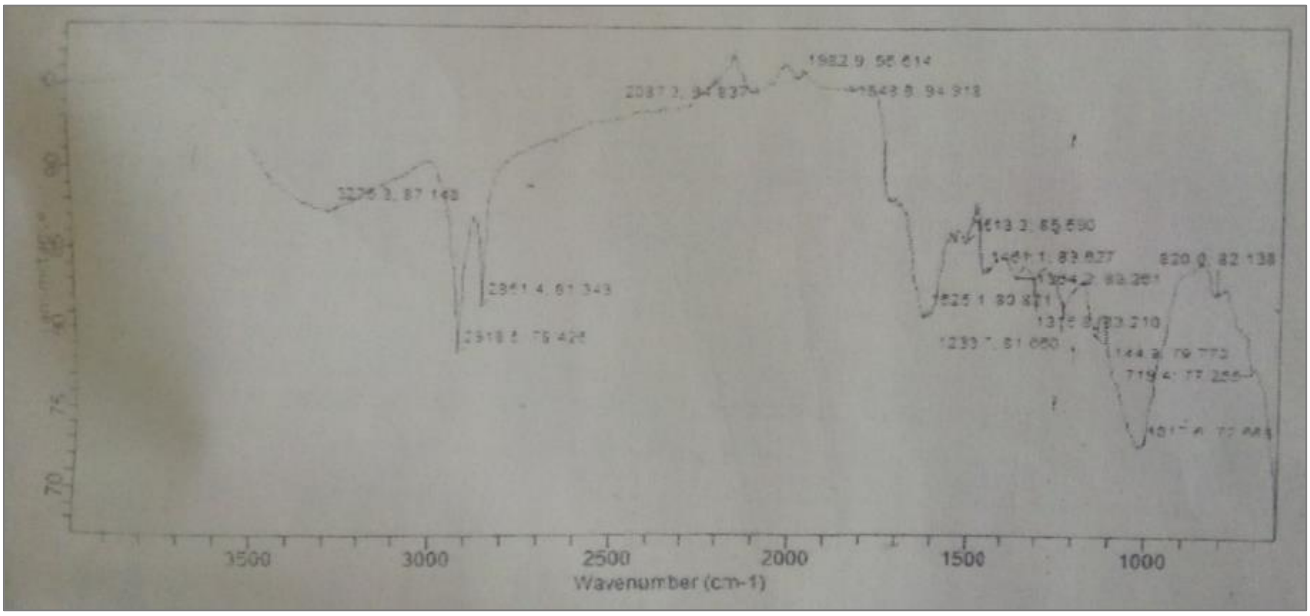

Figure 1. FTIR spectra of tea fiber

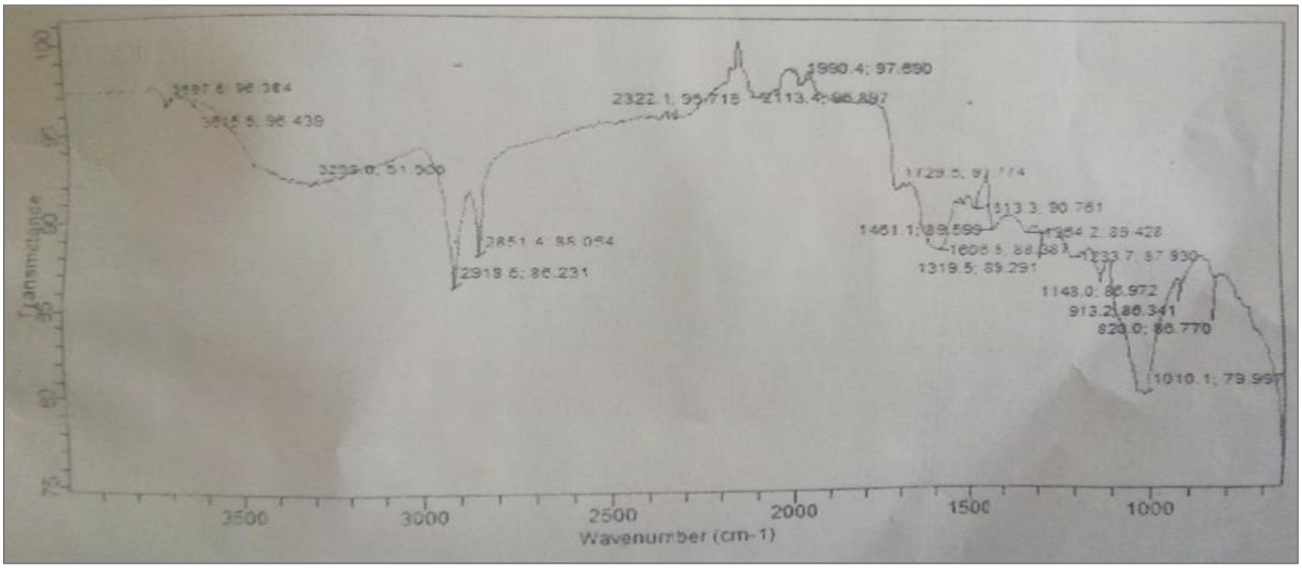

Figure 2. FTIR Spectra of tea leaves

Scanning Electron Microscopy (SEM) of Adsorbent

The surface morphology of the adsorbent was evaluated with a scanning electron microscope. The SEM data indicate the growth of pores and adsorbate occupation. The *Tea leaves* and *Tea fibers*microscopy are displayed on the plates. The *Tea leaves* have a homogeneous size, a honey-like appearance, and a porous structure, as seen from the results in Plate 1.

Adsorption study

The batch adsorption method was used to carry out the adsorption study. pH, adsorbent dosage, temperature, initial concentration, and time were varied to determine the ideal conditions for removing Pb and Ag from aqueous media using Tea fibers and tea leaves as adsorbents.

Effect of pH

Figure 3 gives plots of pH on Silver and Lead. Based on the graph, it was noted that adsorption decreases as pH dropped from a value of 1-5 where Tea fibers adsorption of Pb (II) decreases as the pH increases. The pH of the initial solution was adjusted with NaOH and HCl to pH ranging from 2, 5, 7, and 9. These graphs show that the amount of Silver and Lead absorbed using Tea fibers is higher than that of tea leaves. It can then be concluded from the result that an acidic pH favors the adsorption of both Silver and Lead using tea leaves and Tea fibers with the exception of Pb (II) adsorption by Tea fibers. Since H^+ ions are more abundant at low pH values, metals must compete with them for adsorption on the sorbent surface. Nevertheless, a considerable increase in adsorption was observed when the pH value was raised because of the attraction that arose between positively charged metal ions and negatively charged sorbent surfaces due to –OH groups.

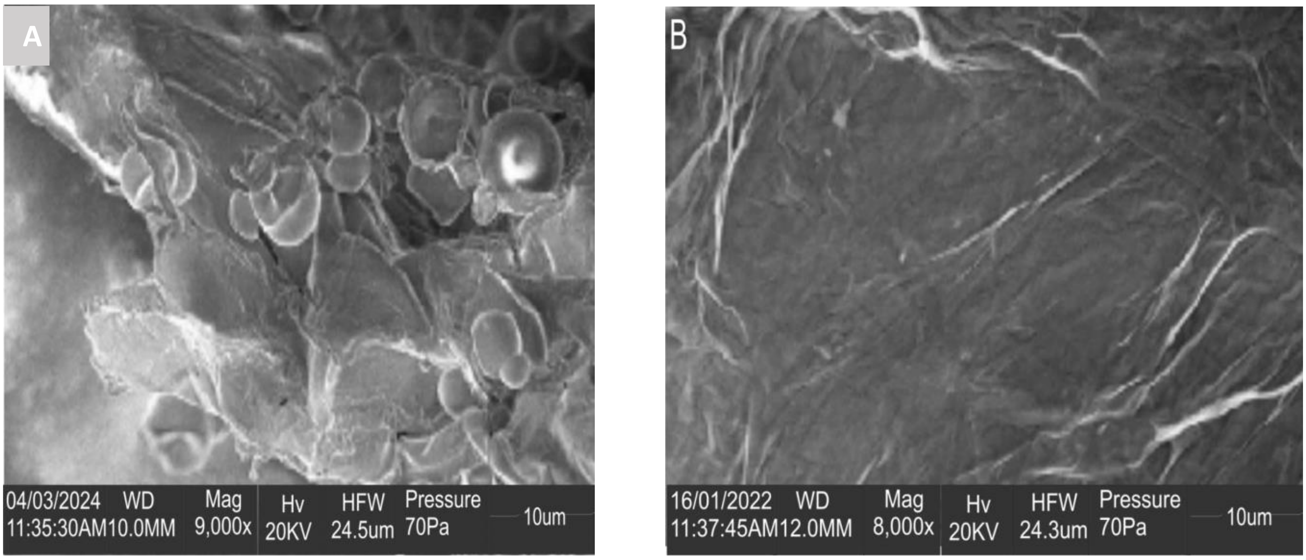

Plate 1: SEM Micrograph for tea leaves and tea fibers *(Camellia sinensis)*

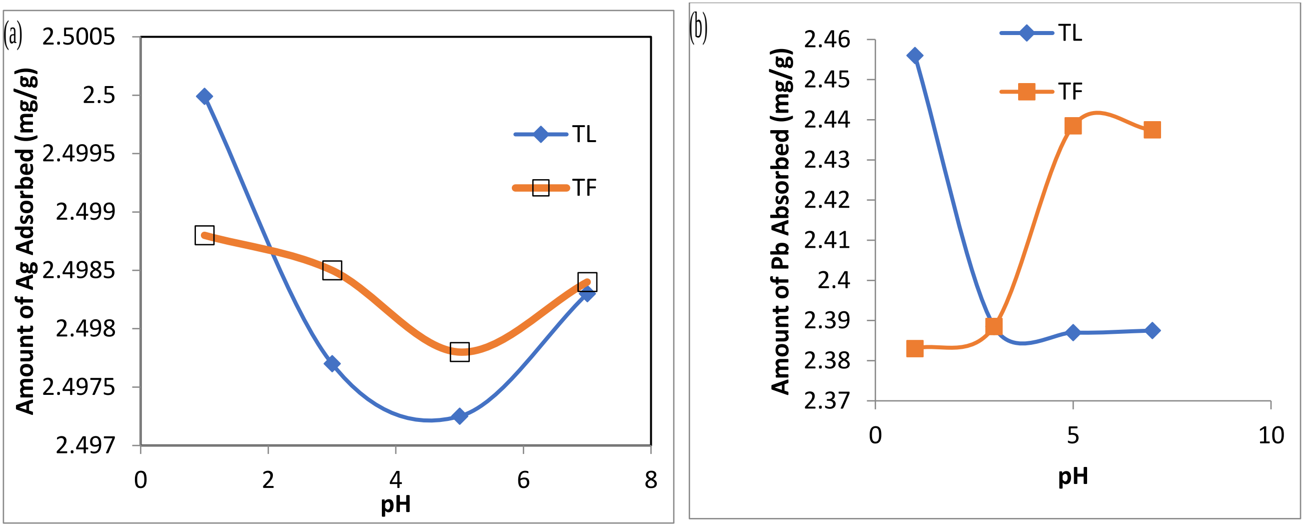

Figure 3 Effect of pH on (a) Silver and (b) Lead adsorption onto Tea leaves and Tea fibers *(Camellia sinensis)*

Effect of Adsorbent Dosage on Adsorption of Lead and Silver

Figure 4 illustrates the experiment's influence on adsorbent dosage respectively; show that equilibrium was reached for the adsorption of lead and silver on Tea leaves and Tea fibers at adsorbent doses of 2g and 3g grams. The results displayed in Figure 4 indicate that the adsorption capacity of both lead and silver rises as the adsorbent dose increases, with the exception of Pb removal by Tea fibers, which shows a consistent reduction in adsorption capacity with increasing adsorbent dosage. Different amounts of the adsorbent, ranging from 1g to 4g, were added to the solution with an initial concentration of 50 mg/L. It was found that when adsorbent dosage is increased for Silver and Lead adsorption using Tea leaves, the percentage removal of Silver and Lead decreases when utilizing Tea fibers. For the purpose of adopting Tea leaves for silver and lead, 4g of the adsorbent dosage on the solution has the highest adsorption capacity (Qe), whereas 1g of the adsorbent dosage on the solution has the highest adsorption capacity (Qe) for the binary metal employing Tea fibers.

Effect of Solution Initial Concentration on Adsorption of Silver and Lead

The results displayed in Figure 5 indicate that adsorption capacity rises as concentration does. When the initial solution concentration is changed from 20, 30, 40, and 50%, the percentage removal of lead and silver using Tea leaves and Tea fibers reveals that the percentage removal for both metals is about identical with little variations.

Effect of Temperature on Adsorption of Silver and Lead

Figure 6 results demonstrate how adsorption capacity drops as temperature rises. Compared to the temperature of the Tea leaves at 323K, the temperature of 313K promotes the adsorption of silver and lead utilizing Tea fibers. When exposed to temperature treatment, *Tea* fibers adsorbs the adsorbate more than Tea leaves, as seen by the higher percentage of silver and lead removed when employing Tea fibers. We may deduce that at 30°C, higher rates of metals were removed and that this percentage decreased as the temperature rose to 50°C. As the temperature rises, Temperature increases are known to accelerate the adsorbate molecules' rate of diffusion within pores and change the adsorbent's equilibrium capacity for a particular adsorbate. Above 20°C to 30°C, this is primarily because of the decreasing surface activity.

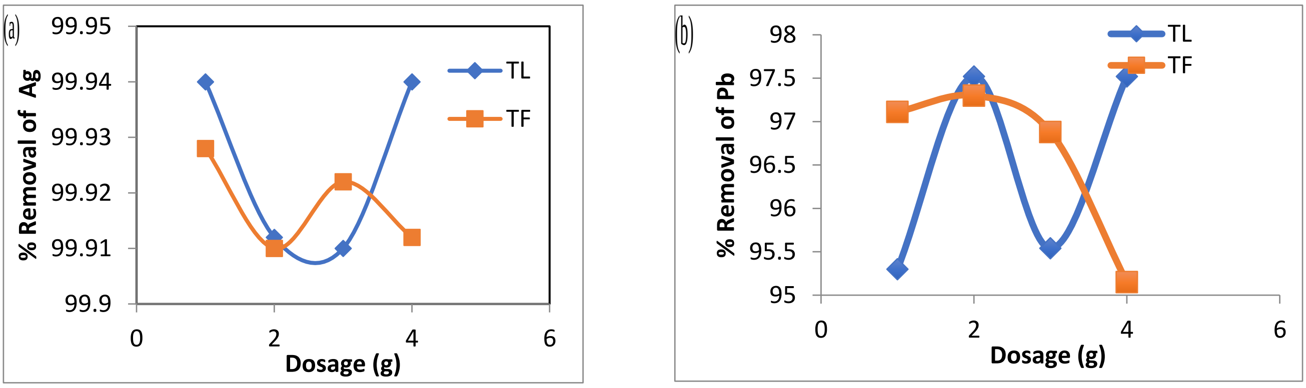

Figure 4. Effect of adsorbent dosage on Silver (a) and Lead (b) adsorption onto Tea leaves and Tea fibers *(Camellia sinensis)*

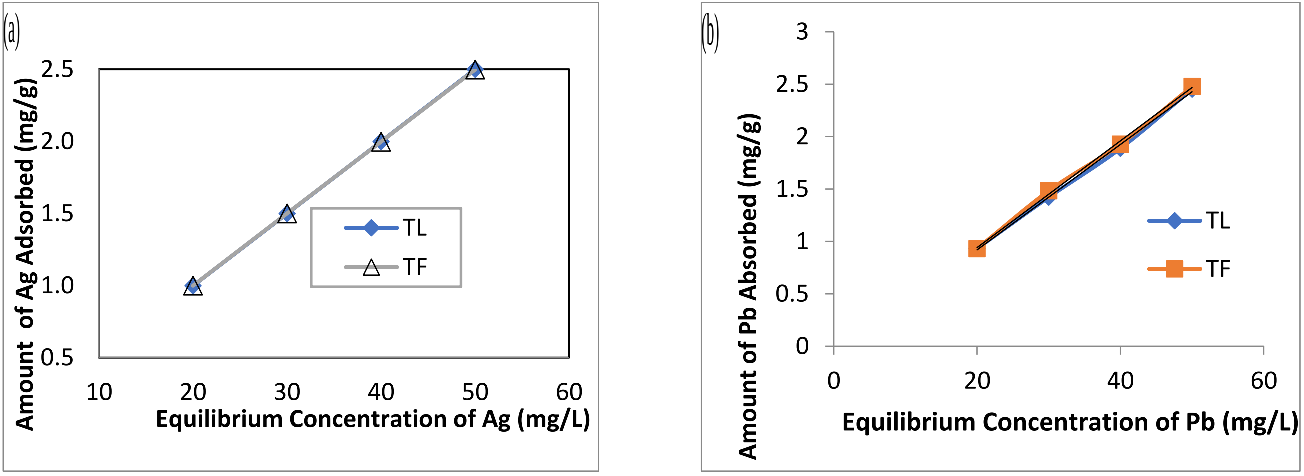

Figure 5. **Effect of initial concentration on Silver (a) Lead (b) adsorption onto Tea leaves and Tea fibers *(Camellia sinensis)***

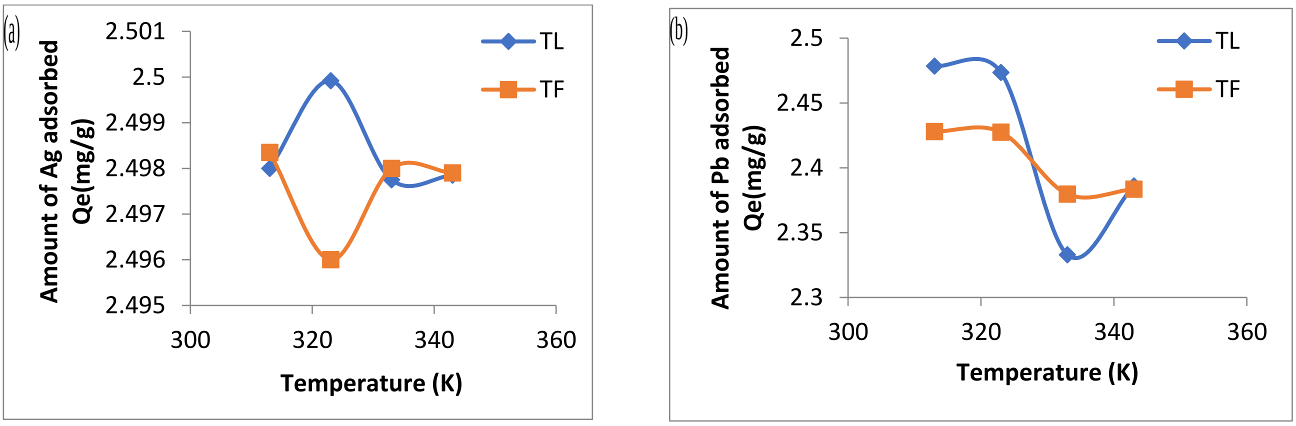

Figure 6. **Effect of temperature on Silver (a) Lead (b) adsorption onto Tea leaves and Tea fibers *(Camellia sinensis)***

Effect of Contact Time on Adsorption of Silver and Lead

Figure 7 shows the rise in adsorption capacity for Ag adsorption using both Tea leaves and *Tea* fibers and illustrates the reduction in lead adsorption capacity using both Tea leaves and Tea fibers with increased contact time. With a Qe value of 2.4987 and 2.4990, respectively, the percentage of silver removed using Tea fibers is somewhat greater than the percentage of silver removed using Tea leaves, and the difference in contact time ranges from 10, 20, 30, and 40 minutes. The percentage removal of lead using Tea fibers was at equilibrium from time 10 – 30 minutes and increased from 30-40 minutes with Qe value of 2.463; on using Tea leaves, the percentage removal of lead increased rapidly with time ranging from 10-40 minutes with Qe value of 2.4785. Obviously, adsorption capacity increased with increasing contact time (*Q*t). It can be concluded that Tea leaves, with the highest value of Qe is more effective for removing silver and lead from aqueous solution than Tea fibers.

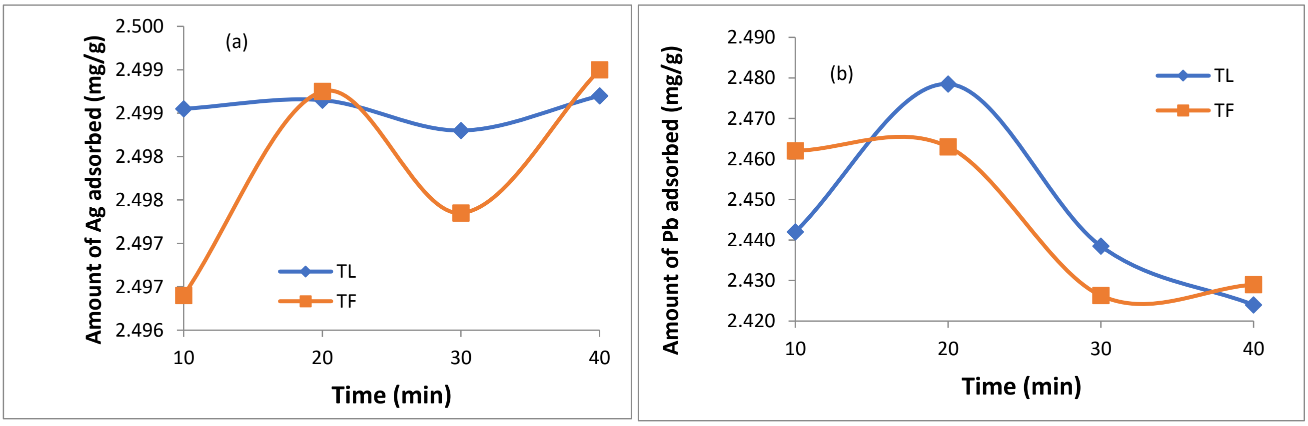

Figure 7. **Effect of time on Silver (a) Lead (b) adsorption onto Tea leaves and Tea fibers**

Adsorption Isotherm

Adsorption isotherms represent the amount adsorbed at the interface and the adsorbate concentration in the bulk. It is assumed that each adsorption site is equal, and the occupancy of neighbouring sites has no bearing on a particle's ability to bond there. In this study, the process simulation employed Freundlich and Langmuir isotherm models to better understand the lead and silver adsorption isotherm. According to the Langmuir model, the regression correlation coefficient (R_2) for lead and silver was found to be 0.0379 and 0.1708 for lead and 0.3791 and 0.0092 for silver, respectively, and for silver it was found to be 0.5218 and 0.1392 for both Tea leaves and Tea fibers and for lead 0.0308 and 0.1771 for Tea leaves and Tea fibers respectively as shown in Table 3. This implies that the equilibrium data agrees with Freundlich better than Langmuir theorem, as shown in Figure 8, 9, and 10.

Table 3 Adsorption isotherm studies result for Silver and Antimony onto Tea leaves and Tea fibers *(Camellia sinensis)*

Adsorbate	Adsorption studies	Tea leaves	Tea fibers
Silver	Langmuir		
	Slope =1/bQm	0.001	0.001
	b(L/mg)	12.12	0.003
	Qm(mg/g)	9.090	3.012
	Intercept=1/Qm	0.110	0.332
	R^2	0.980	0.987
Lead			
	Slope =1/bQm	0.2290	0.2280
	b(L/mg)	0.7598	0.6799
	Qm(mg/g)	5.7470	6.4516
	Intercept=1/Qm	0.1740	0.1550
	R^2	0.9860	0.8640
Silver	Frendlich		
	Slope=1/nf	0.7790	0.4670
	intercept=log(kf)	2.7600	1.4520
	Kf(mg/g)	575.40	28.314
	Nf	1.2837	2.1413
	R^2	0.9590	0.9850
Lead			
	Slope=1/nf	0.7410	0.6980
	intercept=log(kf)	0.4120	0.4180
	Kf(mg/g)	2.5823	2.6061
	Nf	1.3495	1.4327
	R^2	0.9870	0.8930

According to Langmuir, the occupancy of adjacent adsorption sites has no bearing on a particle's ability to bond there because all adsorption sites are equal.

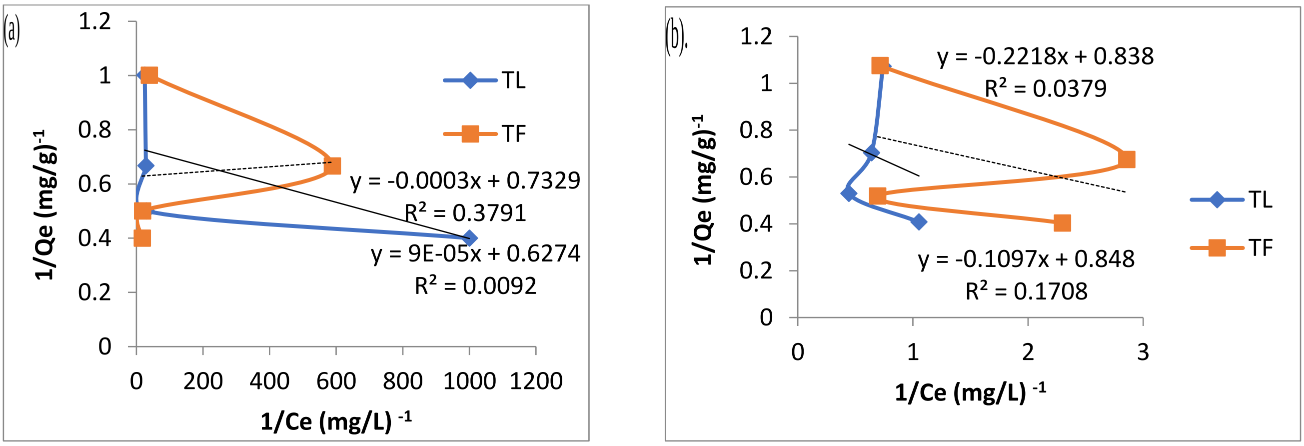

Figure 8. Langmiur adsorption Isotherm plot for Tea leaves and Tea fibers onto Ag (II) ion (a) and Pb (II) ion (b).

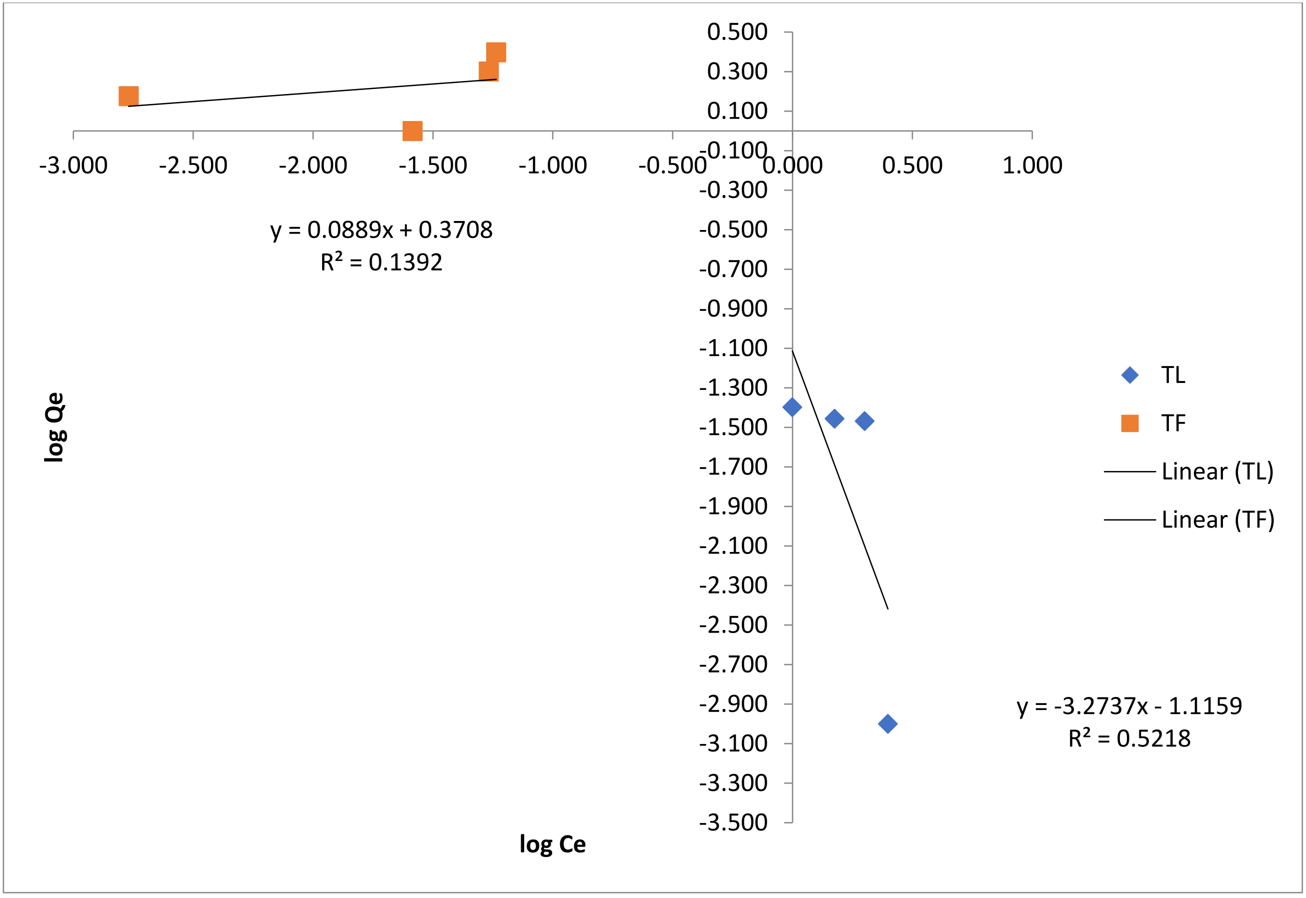

Figure 9. Freundlich adsorption Isotherm plot for Tea leaves and Tea fibers onto Ag (II) ion

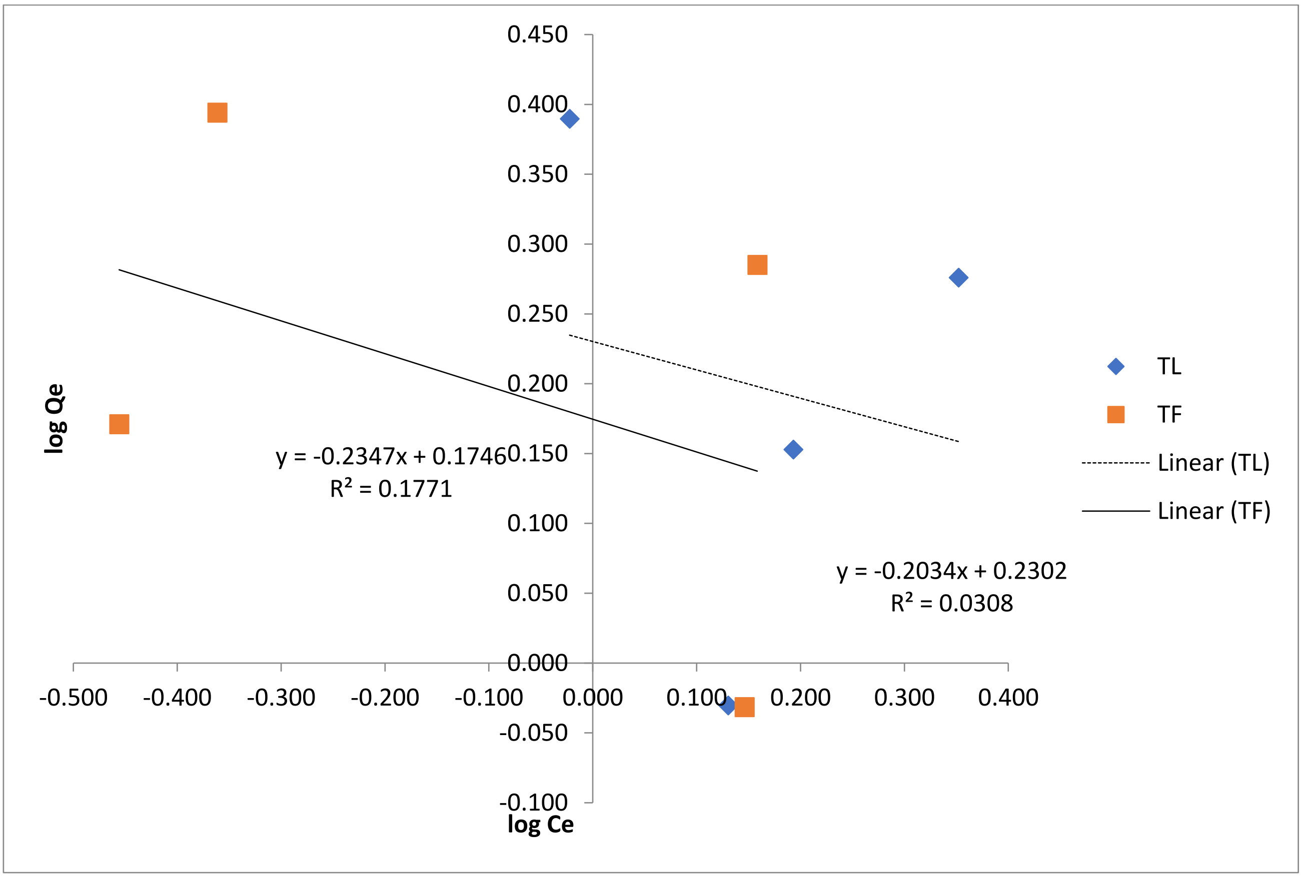

Figure 10. Freundlich adsorption Isotherm plot for Tea leaves and Tea fibers onto Pb (II) ion

Kinetic Studies

Table 4: Application of pseudo first and second order kinetics for Tea leaves and Tea fibers *(Camellia sinensis)*

Adsorbate	Model	Adsorbent	Adsorbent
Lead	First Order	Tea leaves	Tea fibers
	$K_1(Lmin^{-1})$	9.212×10^{-3}	0.0115
	Qe(mg/g)	4.85×10^{-3}	0.0190
	R^2	0.482	0.7420
Lead	Second order		
	$K_2(Lmin^{-1})$	4.1356	272.1
	Qe(mg/g)	2.49	2.475
	R^2	1	1
	$h(g.mg/m^{-1}$	25.64	1666.8
Silver	First Order		
	$K_1(Lmin^{-1})$	-0.2142	0.0829
	Qe(mg/g)	7.7627×10^{-6}	5.382×10^{-4}
	R^2	0.416	0.987
Silver	Second order		
	$K_2(Lmin^{-1})$	160	160
	Qe(mg/g)	2.5	2.5
	R^2	1	1
	$h(g.mg/m^{-1}$	360	360

The experimental data for the adsorption of lead and silver onto Tea leaves and Tea fibers were described by two kinetic models, as shown in Figures 11 and 12. For the first order, the correlation coefficients (R_2) for lead were 0.7594 and 0.4888 for Tea leaves and Tea fibers, respectively, while for silver, they were 0.6196 and 0.4328 for Tea leaves and Tea fibers. Conversely, the experiment data is in good agreement with the value of R_2 for silver for the second order, which was 1.00 for Tea leaves and Tea fibers, respectively, and 0.9998 and 0.9999 for the lead for the same. Nonetheless, the increased R_2 value suggests that the kinetic adsorption process is best described by the second-order kinetics model.

Thermodynamic Studies

One crucial factor influencing the spontaneity of the adsorption process is thermodynamics [15]. Table 5 shows the calculated values for Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy (ΔS). These were calculated from the plot of log (qe/Ce) versus 1/T, which gives a straight line graph where –(ΔH0/2.303R) is the slope and (ΔS0/2.303R) is the intercept. The Gibbs free energy change was measured using the equation (ΔG)=(ΔH) – TΔS as plotted in Figure 13 Silver and lead, respectively. The thermodynamic parameters for the lead and silver biosorption on Tea leaves and Tea fibers showed that the potential enthalpy change value suggests an exothermic biosorption process. The positive entropy change value for silver indicates a rise in randomness at the solid/solution contact during the biosorption process, whereas the lead's negative entropy change value suggests a decrease in randomness at this same interface. One crucial need for viability is the Gibbs free energy change, which signifies the spontaneous nature of a chemical reaction.

Table 5 shows that the biosorption process is both feasible and spontaneous due to the negative values of the Gibbs free energy change for Silver for both Tea leaves and Tea fibers. Table 5 indicates that the biosorption process is not spontaneous due to the positive value of Gibbs free energy change for lead in both Tea leaves and Tea fibers.

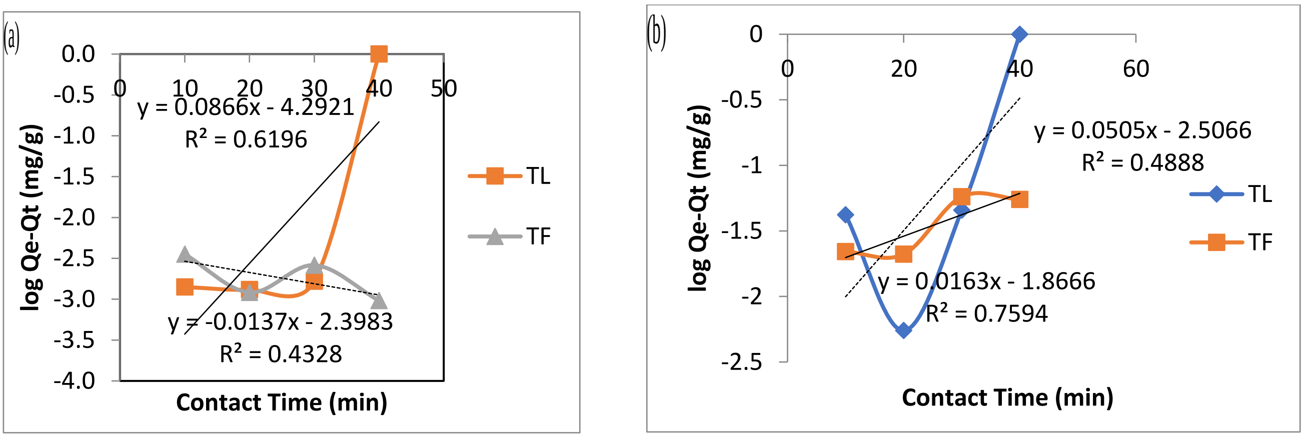

Figure 11. First order kinetics studies for Tea leaves and Tea fibers onto Silver (a) and Lead (b)

Table 5 Thermodynamics results for both Tea leaves and Tea fibers onto Silver and Lead

Adsorbate	Adsorbent	ΔH (KJ/mol.1000)	ΔS (J/molK)	R^2	ΔG (KJ/mol.1000)
Silver	Tea leaves	-1.1878	30.597	0.997	-32.475
	Tea fibers	-1.1333	27.570	0.978	-28.71
Lead	Tea leaves	-1.5807	-27.74	0.952	26.16
	Tea fibers	-4.0030	-91.54	0.924	87.54

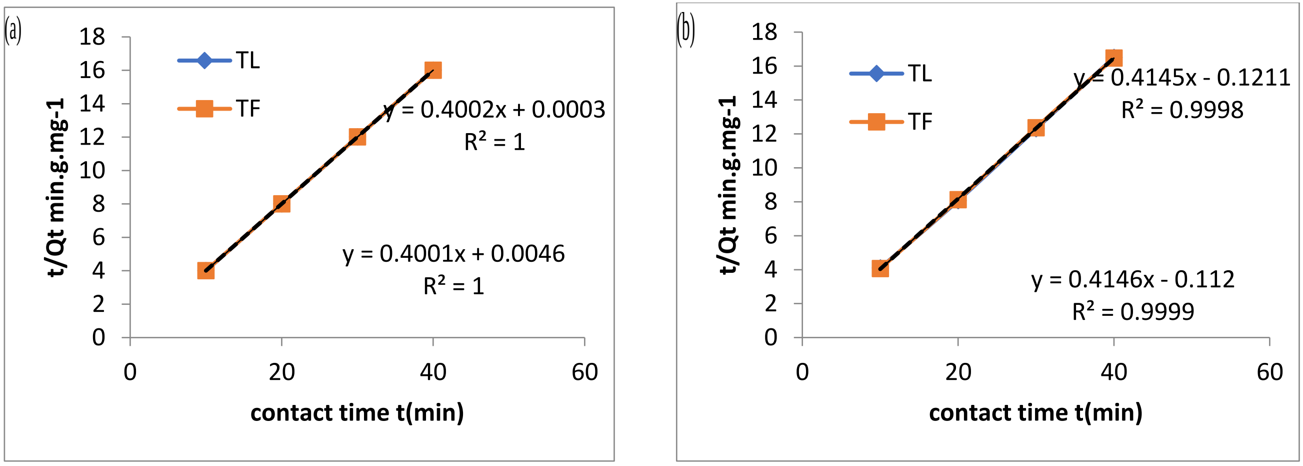

Figure 12. **Second-order kinetics studies for Tea leaves and Tea fibers onto Silver (a) and Lead (b)**

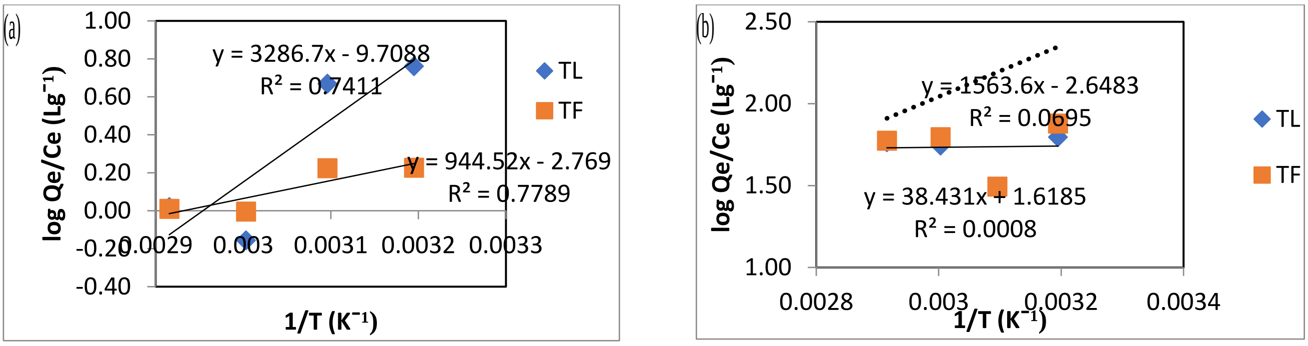

Figure 13. **Thermodynamic studies for Tea leaves and Tea fiber onto Silver (a) and Lead (b)**

CONCLUSION

Tea leaves and Tea fibers have shown to be an excellent biosorbent for the removal of lead and silver (II) ions from wastewater. The result indicates that adsorption decreases as pH drops from a value of 1-5, where Tea fibers adsorption of Pb (II) decreases as the pH increases and adsorbent dosage is increased for Silver and Lead adsorption using Tea leaves, the percentage removal of Silver and Lead decreases when utilizing Tea fibers. The result shows that at 30°C, a higher percentage of metals were removed and that the percentage decreased as the temperature rose to 50°C. The FTIR spectrum changes, analyzed using the Langmuir and Freund adsorption isotherms, demonstrate the adsorption onto the Tea leaves and Tea fibers. The Langmuir isotherm yields the correlation coefficient R2 values of 0.0379 and 0.1708 for Tea leaves and Tea fibers onto lead and R2 values of 0.3791 and 0.0092 for Tea leaves and Tea fibers onto silver. The Freundlich isotherm produces values for Tea leaves and Tea fiberson lead of 0.0308 and 0.1771, respectively, and values on silver of 0.5218 and 0.1392, respectively. The first and second-order kinetics were used in the kinetic analysis, with the second-order fitting the experiment results for Tea leaves and Tea fibers on both silver and lead quite well. Thermodynamic studies demonstrated the adsorption process to be spontaneous, endothermic, and practical. As a result, the study offers Tea leaves and Tea fibers, which are widely available and inexpensive by-products of processing Tea leaves and Tea fibers, as efficient biosorbents for removing lead and silver from wastewater. Future research should include other commonly found heavy metals, such as cadmium, chromium, or mercury, which could help to better understand the versatility of these natural adsorbent. Future research should focus on scaling up the process for potential industrial or municipal water treatment applications.

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