INVESTIGATION ON THE BIOSORPTION OF MANGANESE USING TEA LEAVES AND TEA FIBERS (*Camellia sinensis*) AS ADSORBENTS

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Abstract. *Heavy metal-containing liquid effluents pose a health and environmental risk due to the rapid industrialization of businesses like mining, petrochemicals, fertilizers, and pesticides. The adsorption of manganese from an aqueous solution utilizing biosorbents such as tea leaves and tea fibers is the subject of this study. The adsorption process was studied by varying the initial concentration, adsorption dosage, time, temperature, and pH of the adsorbents. The FTIR results confirmed the presence of -OH, -NH2, C=O providing binding sites in both tea leaves and fibers. The research uses Langmuir and Freundlich adsorption isotherms, with Freundlich the best fitting for tea fiber and Langmuir for tea leaves. Kinetic studies show second-order kinetics is better for both, confirming an endothermic biosorption process.*

Key words: Biosorption, Manganese removal, tea leaves and tea fibre (Camellia sinensis), Kinetics, thermodynamics, isotherms.

INTRODUCTION

One of the most serious environmental problems in recent times is the pollution of the environments by heavy metals; this is because it is invisible and occurs gradually. This problem may not have acute effects but chronic effects due to the bioaccumulation of the heavy metals in the body system. The presence of heavy metals even traces is toxic to both plants and animals. This is why they have adverse effects on the environments due to the toxicity of the heavy metals involved. With rapid development of many industrials actions and fasts growing industries such as; fertilizers, pesticides, mining, photography, atomic, atomic energy, iron and steel, electroplating, electrolysis, petrochemicals, industries, waste containing these heavy metals are directly or indirectly discharged into the environment causing serious environmental pollutions and threatening human health and life [1].

Heavy metals are the group of contaminants of concern, which comes under the inorganic division. Some strong toxic metal ions such as Hg are very toxic even in lower concentration of 0.0010.1 mg/L. The presence of metal ions in final industrial effluents is extremely undesirable, as they are toxic to both lower and higher organisms. Under certain environmental conditions, metals may accumulate to toxic levels and cause ecological damage [2]. Of the important heavy metals, Mercury, Lead, cadmium, Arsenic and Chromium (Hg, Pb, Cd, As, Cr) are regarded as toxic; whereas, others, such as manganese, copper, nickel, cobalt and zinc are not as toxic, but their extensive usage and increasing levels in the environment are of serious concerns [3].

The Earth's surface comprises of about 70% water, and this is the most valuable natural resource existing on this planet earth. Without these invaluable resources which is water, life on Earth would not exist. Although this fact is widely recognized, pollution of water resources is a common problem in recent times. Heavy metal pollution occurs directly by effluent outfalls from industries, refineries and waste treatment plants and indirectly by the contaminants that enter the water supply from the ground water systems and from the atmosphere through rain water [4]. These environmental problems threaten the aquatic ecosystems mostly. Metal concentration in the aquatic environment has been analyzed using water samples, sediments and aquatic biota taken from study sites. These and other studies have revealed that the concentration of these metals is significantly higher in bottom sediment than in the water columns. Sediments act as a major reservoir of metals and also as a source of contaminants in aquatic environments under favorable conditions [5]. The occurrence of high concentrations of trace metals in sediments found at the bottom of the water column can be a good indicator of artificial or man-induced pollution instead of natural enrichment of the sediment by geological weathering.

Methods Used for the Removal of Metals Ions from Aqueous Phase

Several methods and techniques have been employed for the removal of heavy metal ions from aqueous wastes include; ion exchange, membrane technologies, chemical precipitation, adsorption on activated carbon, electrochemical treatment, reverse osmosis, ultrafiltration, electrodialysis, phytoremediation etc [6]. Each of these methods has its own advantages and disadvantages. Chemical precipitation and electrochemical treatments are ineffective, especially when metal ion concentration in aqueous solution is lower than 50 mg/L. Again, such treatment produces large amounts of sludge to be treated with great difficulties. Ion exchange, membrane technologies and activated carbon adsorption processes are extremely expensive. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [7]. The process description of each method is presented below.

Reverse Osmosis

It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive.

Electrodialysis

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

Ultrafiltration

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge.

Ion-exchange

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions.

Chemical Precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage. Hence the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents.

Biosorption

The search for new cost-effective technologies for the removal of heavy metals from wastewaters has been directed towards biosorption, based on metal binding capacities of various biological materials, which is known for the last few decades. Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure [8]. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [9]. Though using biomass in environmental cleanup has been in practice for a while, scientists and engineers are hoping this phenomenon will provide an economical alternative for removing toxic heavy metals from industrial wastewater and aid in environmental remediation [4]. Algae, bacteria, fungi and yeasts have proved to be potential metal biosorbents, due to metal sequestering properties and can decrease the concentration of heavy metal ions in solution [6]. Bioabsorption is more economical than conventional methods, the use of biomass of plant or animal origin for the biosorption process has been given much attention [10].

Biosorbents are cheap materials often with high affinity and capacity for binding the metal ions. The mechanism of the biosorption process has been explained in terms of the reaction between anionic groups present in the biomasses and the cationic metal ions [11]. Hence, Biosorption is a new technology that can be employ in the removal of metal ions from aqueous solutions, and this serve to replace the old conventional methods such as reduction or oxidation, ion exchange, filtration, electrochemical treatment, membrane technology, evaporation recovery, chemical precipitation, chemical lime coagulation and solvent extraction [12]. This method can be an effective technique for the treatment of heavy metals bearing waste water resulting from humans and industries. Biowaste as absorbent have recently gained importance because their effectiveness. Bye products of soya beans, processing cottonseed hulls, rice straw, sugar cane bagasse, peanut hulls and paper mill sludge have been tested for their usefulness in the removal of heavy metals from aqueous solution [13].

Types of Adsorption

Physisorption: is a type of adsorption in which the interactive forces are relatively weak. It takes place with the formation of multi-layer of adsorbate on adsorbent, and at low temperature below the boiling point of the adsorbate, and as the temperature increases, the process of physisorption decreases. In addition, physisorption involves the attraction of electrical charge difference between the adsorbent and adsorbate.

Chemisorption: In chemisorption, the transfer of electros is significant and equivalent to the formation of chemical bonds between the sorbate and the solid surface. Chemisorption takes place with the formation of unilayer of adsorbate on the adsorbent. It involves a more specific bonding to the adsorbate of the solid. It is a process that is more related to chemical reactions.

Camellia sinensis

Camellia sinensis is a species of evergreen shrub or small tree in the flowering plant family Theaceae. Its leaves and leaf buds are used to produce the popular beverage, tea. White tea, yellow tea, green tea, dark tea and black tea are all harvested from one of two major varieties grown today, *Camellia sinensis* and Var. assamica, but are processed differently to attain varying levels of oxidation with black tea being the most oxidized and green being the least [14]. *Camellia sinensis* is native to East Asia, the Indian Subcontinent, and Southeast Asia, but it is today cultivated all around the world in tropical and subtropical regions. It is an evergreen shrub or small tree that is usually trimmed to below 2 m (6.6 ft) when cultivated for its leaves. It has a strong taproot. The flowers are yellow-white, 2.5–4 cm (0.98–1.57 inch) in diameter, with seven or eight petals. The seeds of *Camellia sinensis* and Camellia oleifera can be pressed to yield tea oil, a sweetish seasoning and cooking oil that should not be confused with tea tree oil, an essential oil that is used for medical and cosmetic purposes and originates from the leaves of a different plant.

Figure 1. Tea Leaves and Tea Fibre (*Camellia sinensis*) plants [14].

This study examines the performance of ***tea leaves (Camellia sinensis) and tea fibers*** biomass as an adsorbent for the removal of manganese from a contaminated aqueous phase solution or industrial effluent. Using natural available adsorbents such as tea leaves **(*Camellia sinensis*) *and tea fibre biomass*** instead of chemicals might give advantages such as low cost of production, less sludge formation, high efficiency, source of income to the government as taxes from sales and source of income to the producer.

METHODOLOGY

Collection and Preparation of Adsorbent

Camellia sinensis (Tea Leaves and Tea Fibres), used for this analysis were obtained from Kakara High Land Tea, Sardauna LGA Taraba state, Nigeria on September, 2022. The Tea leaves (*Camellia sinensis*) obtained was washed with distilled water to removed impurities and then air dried for about 3 weeks (21 days), after which it was pulverized and sieved using a 150 mm sieve size. This sample was stored in an airtight polyethene bag until analysis. The tea fibre which was dried already was pulverized and sieved using 150 mm sieve size. The pulverized dried samples were stored in an airtight polyethene bag until analysis.

Preparation of 0.1 M NaOH Solution

About 2 g of sodium hydroxide (NaOH) crystals was weighed dissolved in 500 cm^3 of distilled water, and then it was shaken to homogeneity and labelled appropriately. This was used throughout the experiments.

Preparation of 0.1M HNO_3 Solution

A volume of 8.60 cm^3 trioxonitrate v acid was measured into 100 cm^3 of water, which was transferred into 1000 cm^3 volumetric flask and filling up to the mark with distilled water, it was shaken to homogenized the solution.

Physicochemical Characterization of Heavy Metal (Manganese)

According to Boonamnuayvitaya *et al.,* [15], the estimation of metals using standard methods shows that the residual concentration of manganese can be determined by the used of atomic absorption spectroscopy at 530 nm. The heavy metal (Manganese) was characterized based on the following parameters:

Preparation of 0.1M Metal Stock Solution:

About 0.1 M of manganese (II) dichloride tetrahydrate $MnCl_2.4H_2O$ of (Mw = 197.92 g/mol), was prepared for use throughout the experimental work. 19.792 g of $MnCl_2.4H_2O$ was weighed using analytical balance and dissolved in 100 mL beaker of distilled water then transfer wholly into a 1000 mL volumetric flask and was shaken. This was kept for serial dilution.

Serial Dilution of Metal Solution

In this study, a total of 5 different concentrations of Mn^{2+} solution was prepared: 20, 30, 40, and 50 mg/L . Subsequently, the manganese solutions with different concentrations and biosorbent materials were required to be put into the orbital shaker (SSL1; Stuart®) at different temperatures (between 40 ºC – 70 ºC). The rotational speed of shaker, in all the experiments, was kept constant at 220 rpm. This experiment was performed in duplicate and the best results were used. Lastly, the solution was filtered to prepare samples for the measurements of the metal ion concentration [11][16].

Adsorption Experiments

Each of the batch biosorption experiments was carried out by contacting the biomass with the metal ions under different conditions for a period of time in a glass tube. Experiments were conducted at 27 ºC to determine the effects of initial metal ion concentration, biosorbent dosage, contact time, temperature and effects of initial solution pH on the biosorption of Mn^{2+} ions. Each experiment was conducted in a thermostated water bath (HaakeWia Model) and the residual metal ion analysed using Atomic Absorption Spectrophotometer (Buck scientific 210 VGP). The amount of metal ions biosorbed from solution was determined by difference and the mean value was calculated for each set of the experiments.

Effect of Initial Concentration

About 50 mL of the metal (Mn) solution, containing different concentrations; 20, 30, 40, and 50 mg/L were measured into different conical flasks. 1 g of the biosorbent was dispersed in each of them, the flasks were corked and the mixture agitated with the aid of a shaker for 1 hour to attain equilibrium, the slurries were then filtered using Whatman filter paper and a plastic funnel, the filtrate was kept in well labelled containers and thereafter the concentrations of the resulting filtrate was determined using Atomic absorption spectrometer [11][17].

Effect of Biosorbent Dosage

A series of 1, 2, 3, and 4 g of the biosorbent were weighed into different conical flasks. 50 mL of each metal solution were measured into each of the conical flasks and labelled appropriately. The flasks were corked and the mixture agitated with the aid of a shaker for 1 hour to attain equilibrium, the slurries were then filtered using Whatman filter paper and a plastic funnel, the filtrate was kept in well labelled containers and thereafter the concentrations of the resulting filtrate was determined using Atomic absorption spectrometer [17][18].

Effect of Time (Time dependence)

Exactly 1g of biosorbent was suspended into different conical flasks containing 50 mL of metal solution. Each beaker was agitated on an electrical shaker/rotatory mixer at 30 rpm with the time difference between each beaker were 10, 20, 30, and 40 minutes. Maintaining this parameter; temperature at 27 ºC, pH of 6, concentration of metal 0.1 M constant. Once the spinning is complete, the solute is extracted and placed into plastic centrifuge tubes after which it was centrifuged for 3 minutes at 6000 rpm. This enabled the separation of the biosorbent from the solution. Then the solution was extracted from the centrifuge tube using a dropper and was placed in clean airtight bottles prior to analysis using atomic adsorption spectrometer (AAS) [17][19].

Effect of Temperature

About 1 g of the adsorbent was weighed and poured in four different conical flasks. 50 ml of 0.1 M stock solution of Mn^{2+} metal was added to each flask on a temperature scale of 40, 50, 60 and 70 ºC. They were placed in the mechanical shaker for 1 hour to attain equilibrium, the slurries were then filtered using Whatman filter paper and a plastic funnel, the filtrate was kept in well labeled containers and thereafter the concentrations of the resulting filtrate was determined using Atomic absorption spectrometer [18].

Effect of pH

The effects of pH on the biosorption of metal ions Mn^{2+} were carried out within the range that would not be influenced by the metal precipitation [20]. Experiments were conducted at 27 ºC to study the effect of initial solution pH on the biosorption of Manganese (Mn) by contacting 1g of the *Camellia sinensis* (tea levaes and tea fibres) biosorbent with 50 mL of the metal ion solution in a glass tube. The pH of each of the solution was adjusted to the desired value with 0.1 M sodium hydroxide and /or 0.1 M nitric acid. The studies were conducted at pH values of 2, 3, 5 and 7. The glass tubes containing the mixture were left in a water bath for 24 hours. The biomass was removed from the solution by decantation and the residual Mn^{2+} concentration in the solution was analyzed. All studies were conducted in triplicates and the mean value was determined for each by the Atomic Adsorption Spectrophotometer (AAS) machine [17].

The metal uptake, qe, was determined using the following equation (Madhavi *et al.,* 2011):

$$q_e = \frac{(Co - Ce)}{m} v$$

Where: q_e = metal ions uptake at equilibrium (mg/g)

C_o = initial concentration of metal ion in solution (mg/L)

C_e = final concentration of metal ion in solution at equilibrium (mg/L)

m= the mass of biosorbent (g)

V = volume of the metal solution used (L)

Estimation of Efficiency of Adsorption %

This is given by the equation:

$$\%\ \text{efficiency} = \frac{\%\ removal}{\mathrm{Cf}} \text{x } 100$$

Where: C_f is the final concentration

Adsorption Isotherms

Freundlich Isotherm

Freundlich isothem demostrate that the adsorption process on a heterogeneous adsorbent surface is multilayered, and the adsorption sites have varrying degree of attraction for the adsorbate. These isotherm model was determined using the following equation below;

$$\log \mathrm{qe} = \log\mathrm{Kf} + \frac{1}{\mathrm{n}} + \log \mathrm{Ce}$$

Where **K** is freundlich isotherm constant (mg/g or dm^3/g) associated with adsorbent adsorption capacity, **n** is the adsorption intensity related to the heterogeneity of the adsorbent surface. A plot of log $\mathbf{q_e}$ against log **Ce** gives a straight line graph of slope $\frac{1}{n}$ and an intercept equal to log $\mathbf{k_f}$, **n** is a constant which depends upon the nature of the adsorbent and the substance at a given temperature.

Langmuir Isotherm

The Langmuir isotherm model which describes the correlation between the amounts (mg/g) of adsorbate adsorbed on the adsorbent and the adsorbate concentration (mg/L) in solution at equilibrium condition was determined using the following equation below;

$$\frac{Ce}{\mathrm{qe}} = \frac{1}{\mathrm{bQo}} + \frac{\mathrm{Ce}}{\mathrm{Qo}}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed on the adsorbent at equilibrium, b is the langmuir isotherm constant (L/mg), Q_o the adsorption capacity of the adsorbents.

Adsorption Kinetics

The adsorption process requires knowledge of diffusion mass transport or kinetics process for different adsorbents. Therefore, models such as pseudo-first order and pseudo-second order were employed to analyze the adsorption kinetics data.

Pseudo-First Order Kinetics Model

The linearized pseudo-first order kinetics is expressed as:

$$\log(qe - qt) = \log qe - \frac{k1}{2.303}t$$

Where: qe is the amount of metal uptake, qt is the amount of metal uptake at time t. If the pseudo-first order is applicable, a plot of log (**qe-qt**) versus **t** should provide a linear relationship. The constant **k_1**and predicted **q_e**, respectively, can be determined from the slope and intercept of the plot.

Pseudo-Second Order Kinetics Model

Integrated rate equation for second order kinetic model is given as:

$$\frac{1}{\mathrm{qe}} = \frac{1}{\mathrm{k_2 q_t^2}} + \frac{1}{\mathrm{qe}}\mathrm{t}$$

Where: qe is the metal uptake**,** qt is the initial concentration**,** t is the initial time**.** The plot of $\mathbf{\frac{1}{qt}}$ against t will give a straight line whose slope is equal to the rate constant **k_2**

Thermodynamics of Adsorption

The nature of an adsorption process is confirmed by the evaluation of its thermodynamic parameters. Thermodynamic parameter like free energy change (ΔG_{ads}), enthalpy change (ΔH_{ads}) and enthropy change (ΔS_{ads}) of adsorption were calculated to evaluate the feasibility and spontaneity of the process. The standard free energy change of adsorption (ΔG^o_{ads}) was calculated using the following equation below;

$$\Delta G^o_{ads} = -2.303RTlog(bQo)$$

Where Q_o is the maximum langmuir adsorption capacity of the adsorbent

b is langmuir isotherm constant**,** R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the thermodynamic temperature. The gibbs fre energy of biosorption can also be calculated (Voudrias *et al.,*2002) as follows;

$$\Delta G^o = -RT \ln K_c$$

Where ΔG^o is the standard Gibb's free energy change for the adsorption (J/mol), R is the universal gas constant (8.314 J/mol/K) while T is the temperature (K). K_c is the distribution coefficient of the adsorbate. A negative Gibbs free energy value indicates the feasibility and spontaneous nature of the adsorption process **[21]**. The plot of $\ln K_c$ versus 1/T gives a straight line with the slope and the intercept giving values of ΔH^o and ΔS^o. The distribution constant K_c can be expressed as **[22].**

$$K_c = C_{ad}/C_e$$

In which C_{ad} (mg/l) and C_e (mg/l) are the concentration of solute adsorbed at equilibrium and the solute concentration in solution at equilibrium, repectively. The relationship of (ΔG^o) to enthalpy change (ΔH^o) and entropy change (ΔS^o) of adsorption is expressed as:

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

The positive value of change in enthalpy (ΔH^o) indicates that the adsorption is an endothermic process, while positive value of change in entropy (ΔS^o) reflects the increased randomness at the solid/ solution interface.

RESULTS AND DISCUSSION

Effect of pH

The pH of the solution is an important factor since it influences the metal chemical speciation, solubility, and the total charge of the biosorbent [23]. At low pH (acidic pH), the hydroxonium ions are closely associated with the active ligands of the biosorbent and therefore, there exists a competition between the protons and metal ions for the binding sites [24]. At higher pH, there exists lower number of H^+ ions, and the number of active sites of the functional groups is free and exposed (negative charge) which results in increased biosorption by attracting positive charged metal ions. At higher pH, the metal might begin to precipitate and form hydroxides and as a consequence hinder the biosorption process [25].

The experimental result on the effect of pH in Figure 2(a, b) shows a steady increase in adsorption from pH 1 through 5 after which equilibrium was attend at pH 5 with an optimum pH for both tea leaves and tea fibre after which there was a decrease in adsorption as the pH increases. The reason for the above trend is that at low pH value (highly acidic), metal ions have to compete with the hydrogen ions present for adsorption but as the pH is increased there is decrease in hydrogen ion and increase in OH- ions. This brought about an increase in percentage removal of the metal ions present in aqueous solution. It can be ascertained that the removal of manganese from aqueous phase is favourable at a pH of 5-7[26] [27].

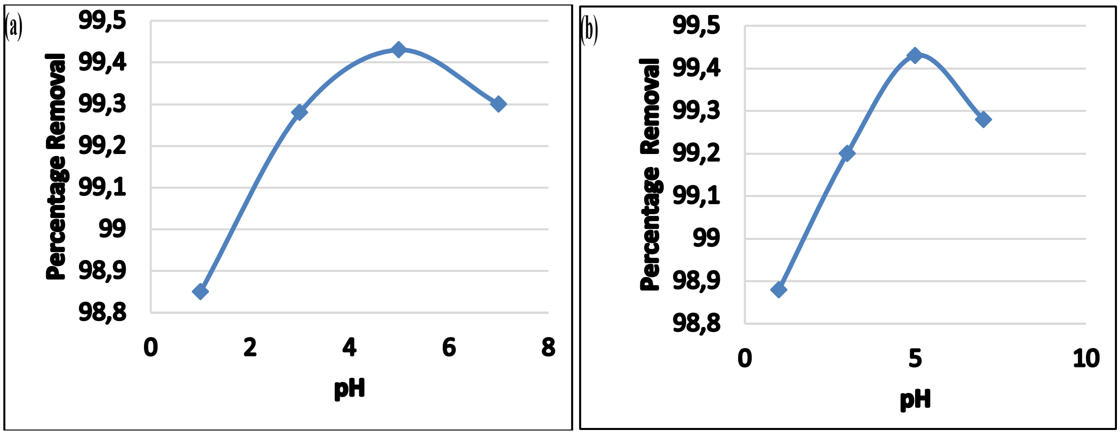


Figure 2: Effect of pH on the removal of manganese from aqueous phase using tea leaves (a) and tea fibre (b).

Effect of Temperature

Temperature deals with the thermodynamics of the process and kinetic energy of the metal ions [23]. The temperature can have a positive or negative effect on biosorption at certain intervals. An increase or decrease in temperature causes a change in the biosorption capacity of the biosorbent. High/increasing temperature enhances the biosorptive removal of biosorbates but it is associated with the limitation of structural damage to the biosorbent [28]. Hence, optimum temperature for efficient biosorption has to be chosen for the maximum binding of metal ions. The effect of temperature on the biosorption of manganese from aqueous phase for both tea leaves and tea fibre is presented in Figure 3(a, b) from experimental work, the result shows that the percentage removal of manganese from aqueous phase increases with an increase in temperature. This is because as temperature increases, the cohesive force between the metal ions become weak hence, adsorption is enhanced with high percentage removal. This confirms to the fact that; High or increasing temperature enhances the biosorptive removal of biosorbates but it is associated with the limitation of structural damage to the biosorbent [28]. Hence, optimum temperature for efficient biosorption has to be chosen for the maximum binding of metal ions.

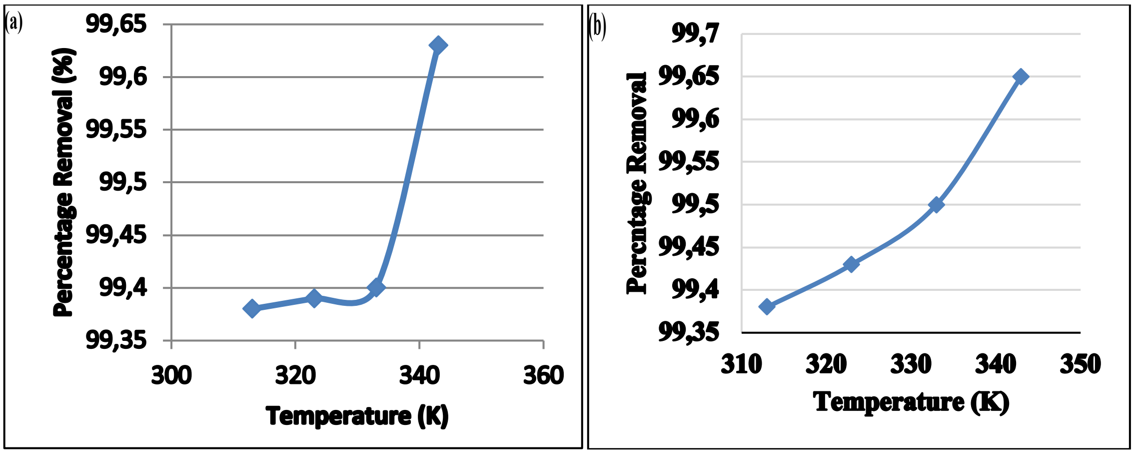


Figure 3: Effect of temperature on the removal of manganese from aqueous phase using tea Leaves (a) and tea fibre (b)

Effect of Initial Metal Concentration

Generally, the mass transfer resistance between the liquid and solid phases can be overcome by the initial concentration of metal ion [27]. The biosorption capacity (quantity of biosorbed metal ions per unit weight of the biosorbent) of the biosorbent increases initially with the increase in metal ion concentration and then reaches a saturation value. However, the biosorption efficiency of the biosorbent decreases with increase in metal ion concentration. The higher biosorption efficiency at low metal concentration is due to the complete interaction of ions with the available binding which sites results in higher rates of efficiency. At higher concentrations, the number of metal ions remaining unbound in the solution is high due to the saturation of available binding sites [27].

In this reseaerch, the result of the effects of initial concentration of manganese in aqueous phase shows a gradual increase in percentage removal with an increase in initial concentration of manganese for both tea leaves and tea fibre as presented in Figure 4 (a, b). This is because at high concentration, the biosorbent active site (tea leaves and tea fibre) will be surrounded by more manganese ions hence, the adsorption process will be carried out sufficiently. The higher biosorption efficiency at high metal concentration is due to the complete interaction of ions with the available binding site result in higher rates of efficiency. So, rise in concentration also result in an increase in adsorption of sorbate on the available sites [27].

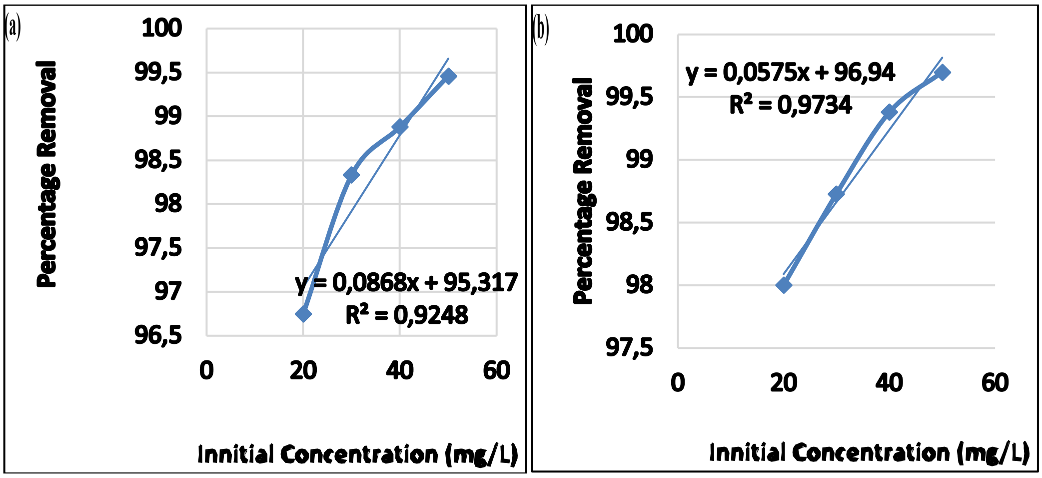


Figure 4: Effect of initial concentration on the removal of manganese from aqueous phase using tea leaves (a) and tea fibre (b).

Effect of Biosorbent Dose

Biosorbents provide the binding sites for metal biosorption, and hence its dosage strongly affects the biosorption process. The increase of the biosorbent dose at a given initial metal concentration increases the biosorption of metal ions due to greater surface area which in turn increases the number of available binding sites [29]. At lower concentrations of the biosorbent, the amount of metal biosorbed per unit weight of the biosorbent is high. Conversely, at high concentration of the biosorbent, the quantity of metal ion biosorbed per unit weight decreases. This is because of lower adsorbate to binding site ratio due to the insufficient amount of solute present for complete distribution onto the available binding sites and possible interaction between binding sites. Figure 5 (a, b) shows a plot of the effect of biosorbent dosage and from the plot, it's observed that, as adsorbent dosage increases keeping all the other parameters constant, percentage efficiency first increases, reaches maximum and then decreases. As adsorbent dosage increases manganese uptake decreases as shown. At lower adsorbent concentration number of active sites is higher. With the increase in adsorbent dosage aggregation of particles take place, as a result efficiency and Mn uptake decreases [30]. This indicate that the adsorption of manganese unto both tea leaves and tea fibre increases and reaches maximum which implies that equilibrium was attend at 2.0 g, then desorption set in and then a sharp rise with efficient removal at 4 g, implying that adsorption of Mn is effective at high dosage because there is active site of the biosorbent to remove the ions present in the solution.

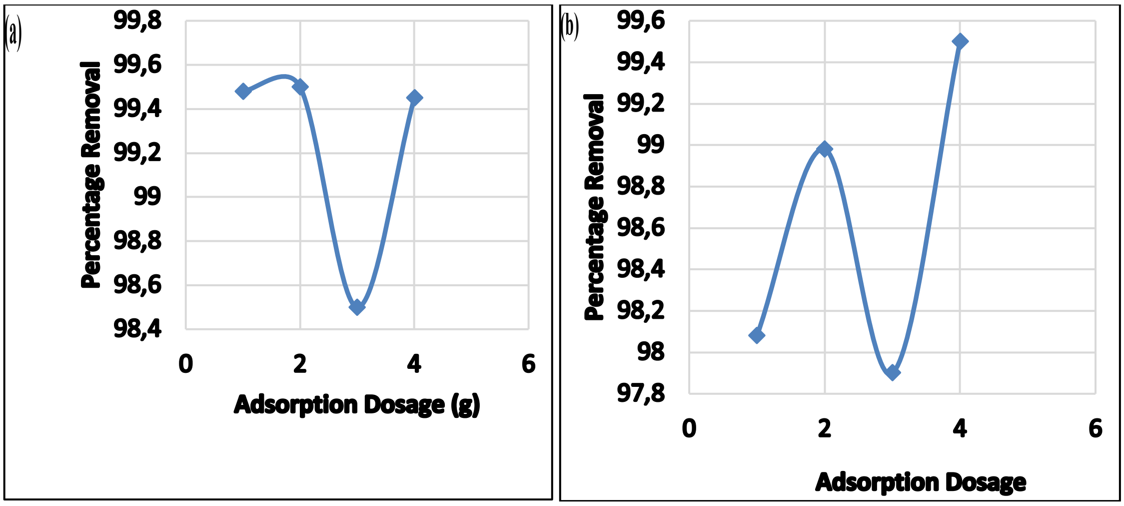


Figure 5: Effect of adsorption dosage on the removal of manganese from aqueous phase using tea fibre

Effect of Contact Time

The time required to attain maximum biosorption depends on the type of biosorbent, metal ion, and their combination. The rate of biosorption is rapid initially (within an hour) with almost 90 % of the metal binding because all the active sites are vacant and available for metal ion biosorption. But with increase in time the rate of biosorption decreases due to increase in percentage saturation by metal ions remaining in the solution similar to the work of Abdel-Ghani *et al.,* [31]. The effect of contact time for both tea leaves and tea fibre as presented in Figure 6(a, b) shows that adsorption increases with increase in time. The adsorption process was found to be very rapid and hence high percentage removal of manganese from aqueous phase. From research, the biosorption process increases initially (within an hour) with high percentage removal because all the active sites are vacant and available and so the adsorbate ion easily becomes bonded to the sites. The effect of time on the adsorption of manganese has been confirmed with the result of the adsorption of Zn and Pb using the same adsorbent tea leaves and tea fibre as reported by Etim *et al.,* [11].

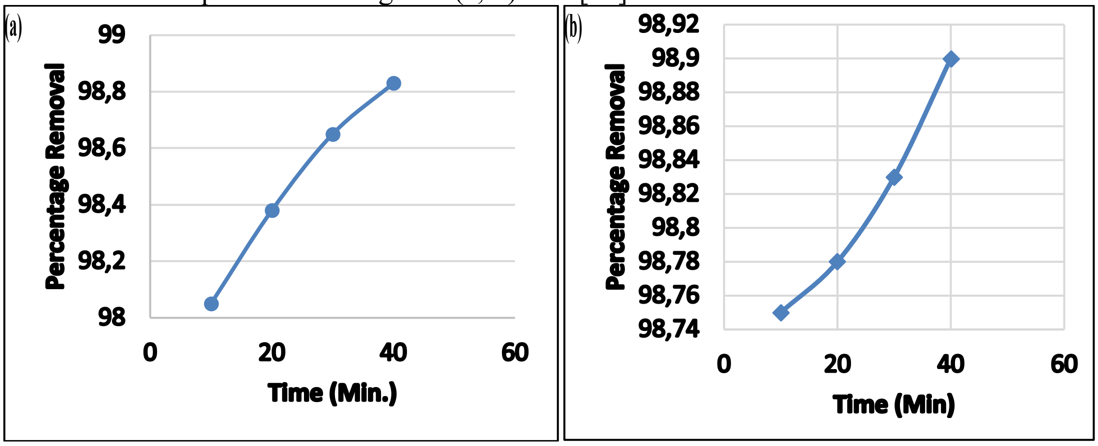


Figure 6: Effect of contact time on the removal of manganese from aqueous phase using tea leaves (a) and tea fibre (b)

Adsorption Isotherms

The process of adsorption is usually studied using graphs known as adsorption isotherms as shown in Figure 7 (a-d). Adsorption isotherm is a graph that shows the relationship between the amount of the adsorbates on an adsorbent as a function of its pressure (if gas) or concentration at constant temperature. Or a graph that represents the variation in the amount of adsorbate (x) adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature. Upon application of excess pressure on the system, the equilibrium shifts in the direction where the number of molecules decreases so that the pressure in the system decreases. Both the Langmuir and Freundlich adsorption isotherm are obtained from the data presented in Table 1.

Table 1: Parameters for plotting Langmuir and Freundlich adsorption isotherm of Mn^{2+} ions by tea leaves and tea fibre (*Camellia sinensis*)

Adsorbent	Co (mg/l)	Ce (mg/L)	$\frac{1}{Ce}$	Log Ce	Qe (mg/g)	$\frac{1}{Qe}$	Log Qe	$\frac{Ce}{Qe}$	% Removal
	20	0.650	1.54	-1.19	0.9675	1.30	-0.01	0.67	96.75
Tea leave	30	0.500	2.00	-0.30	1.4750	0.68	0.17	0.34	98.33
	40	0.450	2.22	-0.35	1.9775	0.51	0.30	0.23	98.88
	50	0.270	3.70	-0.57	2.4865	0.40	0.40	0.11	99.40
	20	0.400	2.50	-0.40	0.9800	1.02	-0.01	0.41	98.00
Tea fibre	30	0.380	2.63	-0.42	1.4810	0.68	0.17	0.26	98.73
	40	0.250	4.00	-0.60	1.9870	0.50	0.30	0.30	99.38
	50	0.170	5.88	-0.77	2.4915	0.40	0.40	0.40	99.67

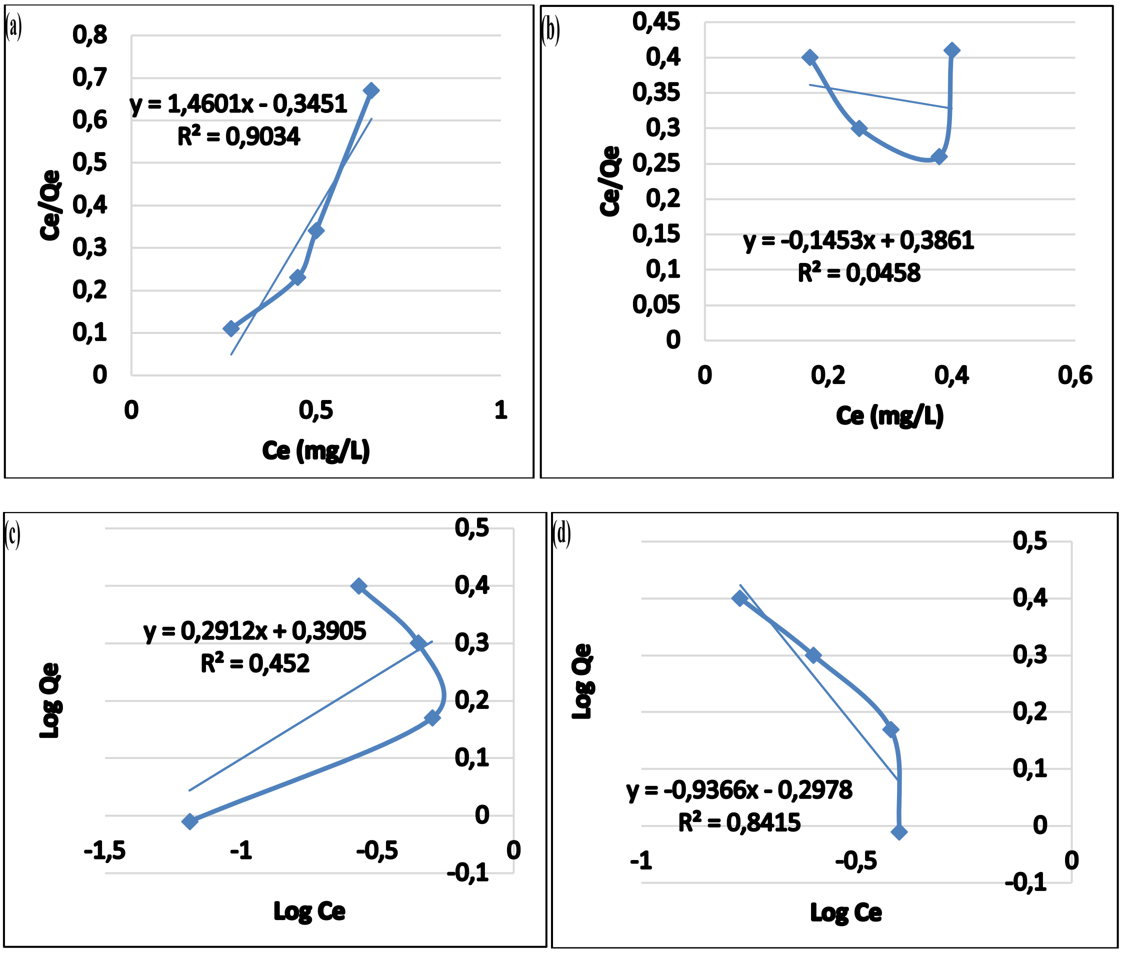


Figure 7: Langmuir (a, b) and Freundlich (c, d) adsorption isotherm plot for tea leaves (a, c) and tea fibers (b, d).

Adsorption isotherms are graphs that show the relationship between the adsorbate concentration in the bulk and the adsorbed amount at the interface, it assumes that every adsorption site is equivalent [32]. The Langmuir and Freundlich Isotherm model were employed for the purpose of this research. The biosorption isotherms for the uptake of Mn^{2+} ion was studied using initial concentration between 20 – 50 mg/L. The regression correlation coefficient (R^2) for both tea levees and tea fibre was found to be; 0.9034 and 0.0458 respectively for Langmuir and for that of Freundlich was 0.452 and 0.841 respectively shown in Table 2. This implies that the experimental equilibrium data for tea leave with R^2 value of 0.903 fit best for Langmuir isotherm which assume that a monolayer is found and the uniform energies of adsorption onto the tea leaves and no transmigration of manganese ions on the adjacent binding sites [33]. While the data for tea fibre applies well for Freundlich isotherm model with R^2 value of 0.841 which assumes that an adsorbate behaves as an ideal gas and that dynamic equilibrium exceed between the adsorbed and free gaseous molecules.

Table 2: Langmuir, Freundlich adsorption isotherm of Mn^{2+} ions unto tea leaves and teach fibre (*Camellia sinensis*)

Metal Ion	Langmuir Isotherm				Freundlich Isotherm			
Mn^{2+}	**Q_o (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**	$\frac{1}{n}$	**n**	**K_f (mg/g)**	**R^2**
Tea Leaves	1.4601	-0.3451	0.0633	0.9034	0.2912	3.434	0.3905	0.4520
Tea Fibre	-0.1453	0.3861	0.0573	0.0458	-0.9366	1.068	-0.298	0.8415

Kinetic Studies

The first order kinetic model considers the rate of change that occurs in the uptake of adsorbate at a particular reaction time to be directly proportional to the difference in the concentration and rate at which the adsorbate is removed with time. The model is also known as Largergren model. The pseudo–second-order kinetic model is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on concentration of adsorbate **[34]**. One major advantage of this model over Lagergren first order is that the equilibrium adsorption capacity can be calculated from the model; therefore, there is theoretically no need to evaluate adsorption equilibrium capacity from experiment.

For kinetic studies, first and second order kinetics were employed and experimental values for the effect of time were used for the kinetic studies. It can be seen from the kinetic plots as presented in Figure 8(a, b, c, d), that the adsorption kinetics follows both the first order and second order kinetic for both the tea leaves and tea fibre but the most fitted adsorption kinetics for the sorption of manganese using tea leaves and tea fibre is the second order kinetic with R^2 value of 1.00 as compared to the first order kinetic with R^2 value of 0.973 and 0.889 respectively for both tea leaves and tea fibre. This suggests that the adsorption of manganese on tea leaves and tea fibre, there were chemisorption due to the sharing of electrons between the adsorbent and the adsorbate.

Table 3: Parameters for the plotting of kinetic studies of Mn^{2+}ion using tea leaves and tea fibre (*Camellia sinensis*)

Adsorbent	Time(mins)	Ce(mg/L)	Qe(mg/L)	% removal	Log (Qe –Ce)	$\frac{t}{Qe}$
	10	0.750	1.9610	98.05	0.072	5.00

Tea Leaves	20	0.650	1.9675	98.38	0.120	10.00
	30	0.540	1.9730	98.65	0.156	15.00
	40	0.470	1.9765	98.83	0.178	20.00
	10	0.500	1.9750	98.75	0.169	5.00
Tea Fibre	20	0.490	1.9755	98.78	0.172	10.00
	30	0.470	1.9765	98.83	0.178	15.00
	40	0.420	1.9790	98.95	0.193	20.00

On application of first order kinetics equation $K_1 = \frac{2.303}{t} \log \frac{a}{a-x}$ for tea leaves and tea fibre, table 4 was generated to present the first order constant K_1.

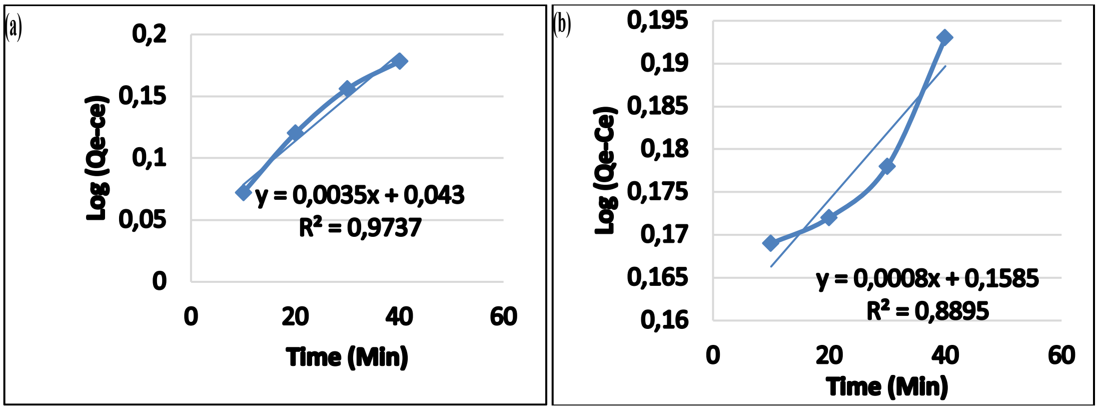
Table 4: first order kinetic for both tea leaves and tea fibre (a = 40).

Adsorbent					
Tea leaves					**Tea fibre**
Time(min)	**a-x**	**K_1**	**Time(min)**	**a-x**	**K_1**
10	38.0390	0.000503	10	38.0250	0.000506
20	38.0325	0.000504	20	38.0245	0.000253
30	38.0270	0.000169	30	38.0235	0.000169
40	38.0235	0.000127	40	38.0210	0.000127

Applying the second order kinetic equation ($K_2 = \frac{1}{at} x \frac{x}{a-x}$) to Table 3, Table 5 can be generated to present the second order constant K_2. The infinitesimal change in K_2 compared to K1 for all conditions suggested that the kinetics followed the second order route which has already been deduced by the correlation coefficient R^2.

Table 5: second order kinetics for both tea leaves and tea fibre

Adsorbent							
Tea leaves							**TeaFibre**
Time(min)	**a – x**	**X**	**K_2**	**Time(min)**	**a-x**	**X**	**K_2**
10	38.0390	1.9610	0.000129	10	38.0250	1.9750	0.000130
20	38.0325	1.9675	0.000065	20	38.0245	1.9755	0.000065
30	38.0270	1,9730	0.000043	30	38.0235	1.9765	0.000043
40	38.0235	1.9765	0.000033	40	38.0210	1.9790	0.000033



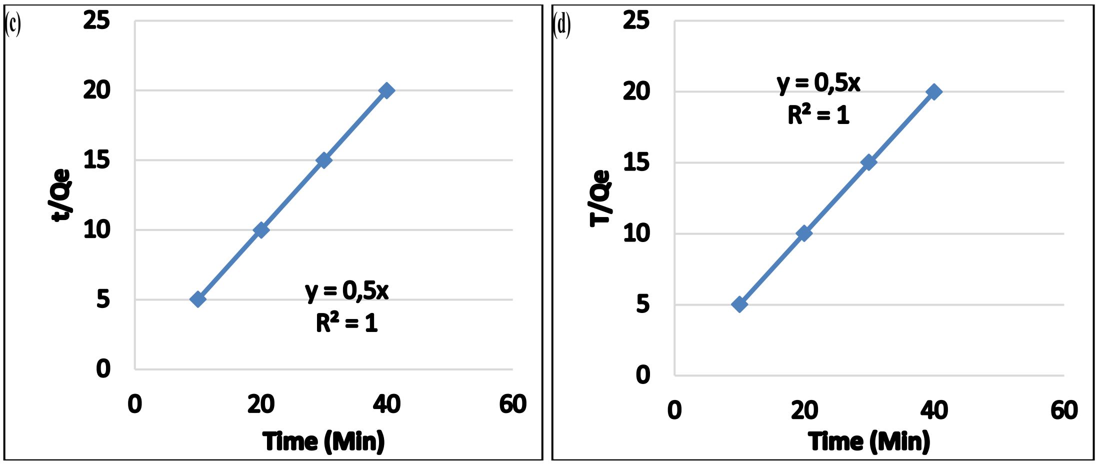


Figure 8: First order (a, b) and Second order (c, d) kinetics studies plot for tea leaves (a, c) and tea fibre (b, d).

Thermodynamics Studies

The nature of an adsorption process is confirmed by the evaluation of its thermodynamic parameters in Table 6. Thermodynamic parameters like free energy change (ΔG_{ads}), enthalpy change (ΔH_{ads}) and entropy change (ΔS_{ads}) of adsorption are calculated to evaluate the feasibility and spontaneity of the process. The thermodynamic studies of the biosorption of Mn^{2+} ions on the biomass can be fully explain by calculating the thermodynamic parameters which includes; enthalpy and entropy from the slope and intercept of ln K versus 1/T as shown in Figure 9 (a, b) for the tea leaves and tea fibre respectively. The thermodynamic parameters for the biosorption of manganese ions on both tea leaves and tea fibre revealed that the positive value of enthalpy change ΔH^o indicate that the biosorption process is endothermic and the positive value of entropy change ΔS^o implies an increase in the randomness at solid/solution interface during the bisorption process. The Gibbs free energy change ΔG^o is an indication of spontaneity of chemical reaction and therefore is an important criterion for feasibility. The negative value of Gibbs free energy change as shown in Table 7, confirms the feasibility and spontaneous nature of the biosorption process.

Table 6: Thermodynamic parameter

Adsorbent	Temperature (k)	$\frac{1}{T}$x10^{-3}	Ce(mglL)	Qe(mglg)	Kc (g/L)	ln Kc	% Removal
	313	3.20	0.250	1.9875	7.95	2.07	99.38
Tea leaves	323	3.10	0.245	1.9878	8.11	2.09	99.39
	333	3.00	0.240	1.0880	8.28	2.11	99.40
	343	2.90	0.150	1.9925	13.28	2.59	99.63
	313	3.20	0.250	1.9875	7.95	2.07	99.38
Tea fibre	323	3.10	0.230	1.9885	8.65	2.16	99.43
	333	3.00	0.200	1.9900	9.95	2.30	99.50
	343	2.90	0.140	1.9930	14.25	2.66	99.65

Table 7: Thermodynamic results for both tea leaves and tea fibre (*Camellia sinensis*)

		Adsorbent			
Tea leaves			**Tea fibre**		
Parameter	**Temperature**	**ΔG^0(kJ/mol)**	**parameter**	**Temperature**	**ΔG^0(kJ/mol)**
	(k)			(k)	
	313	-3781.642		313	-4452.499

	323	-3851.982		323	-4533.729
	333	-3922.322		333	-4614.959
	343	-3992.662		343	-4696.189
ΔH^0(kJ/mol)	**-1580**		**ΔH^0(kJ/mol)**	**-1910**	
ΔS^0(kJ/mol)	**7.034**		**ΔS^0(kJ/mol)**	**8.123**	

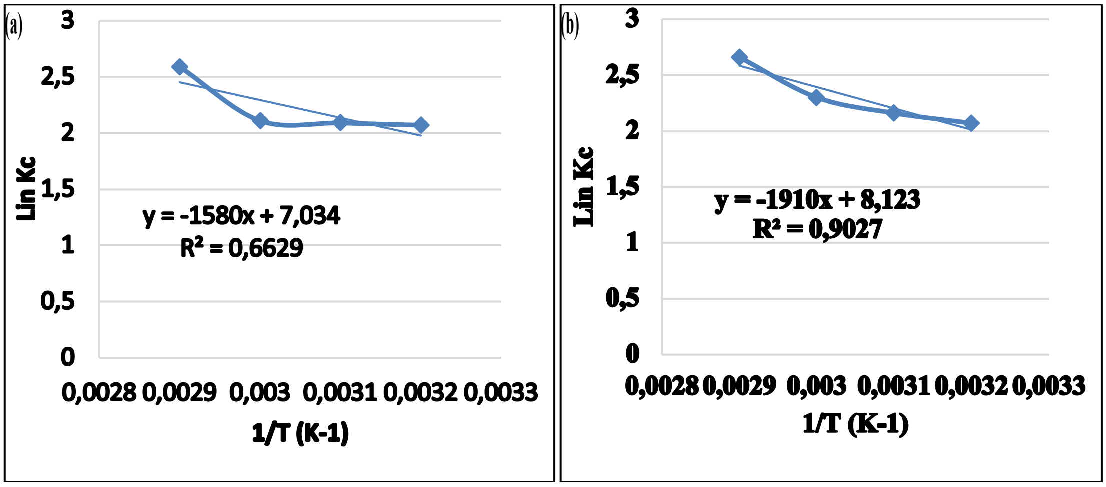


Figure 9: Thermodynamic studies plot for tea leaves (a) and tea fibre (b).

CONCLUSION

In this research, tea leaves and tea fibre were investigated as biosorbent for the adsorption of manganese from aqueous phase and were found to be very effective for the removal of manganese from solution which can be applied in the treatment of effluent containing manganese as a heavy metal. The FTIR result of the adsorbent shows the presence of some functional groups in the adsorbent and confirmed the adsorption onto the tea leaves and tea fibre. Different parameters were tried to cross check their effect on the adsorption process these include; initial concentration, adsorbent dosage, time, temperature and pH. From the research tea leaves has been confirmed as a better adsorbent when compared to tea fibre with a high percentage removal of 99.67 %. Two adsorption Isotherms were tried; Langmuir and Freundlich. Using the initial concentration result, it was observed that the Langmuir isotherm is best fitted for tea leaves with an R^2 value of 0.9034 as compared to 0.0458 for tea fibre, consequently the Freundlich isotherm is best applied for tea fibre with an R^2 value of 0.8415 as compared 0.4520 for tea leaves. In general, the Langmuir isotherm is more suitable for the adsorption of manganese because of the higher R^2 value of 0.903. Furthermore, kinetic studies were done exploring first and second order kinetics and experimental values for the effect of time were used for the kinetic studies of which the second order was well fitted for both tea leaves and tea fibre. Thermodynamics studies confirm the feasibility and spontaneous nature of the biosorption process implying that it's an endothermic process. This research therefore, presents tea leaves and tea fibre as effective, cheap and readily available biosorbent for the removal of manganese from aqueous waste water or effluents.

Funding

Not applicable

Conflict of interest

The authors declare that there are no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval

Not applicable

Informed consent

Not applicable

Data Availability Statement
No datasets were generated or analyzed during the current study.

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