Asian Journal of Environmental Research

Research Article

Vol. 1 (1), 2024

Page: 24-38

Eco-Friendly Remediation: Tea Leaves and Fibres as Adsorbents for High Cobalt Concentrations; Thermodynamics, Isotherms and Kinetic Studies

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Abstract

Increasing industrialization has produced huge amounts of liquid effluents, which are a key source of ecological unrest in diverse ecosystems. The high toxicity level of cobalt in surface water has drawn a lot ofattention; hence,a low-cost adsorbent made from leaves and fibres of Camellia sinensis has been developed to remove cobalt from wastewater. The kinetics of the pseudo-first and second-order sorption interaction, as well as the physicochemical parameters of the precursor adsorbent, was investigated. There was a linear relationship between Cobalt uptake and biosorbent dosage under ideal conditions; the optimum dosage was 4 g. Between 10 to 40 minutes of contact time, clearance of cobalt was greater than 90 per cent. The Gibb's free energy (ΔGo) at various temperatures ranges from -9980 to -1020, indicating a spontaneous system, viable for both parts of the precursor adsorbent. The entropy change (ΔSo) was found to be +31.05 and +35.12 for tea leaves and fibre respectively, implying a highly disordered biosorption interface. The enthalpy (ΔHo) was found to be-8.58 and -10.03 for tea leaves and fibres hence, an exothermic system was suggested by the enthalpy with a second order kinetics. Therefore, Camellia sinensis is a suitable adsorbent for the effective removal of high cobalt concentrations in wastewater.

Keywords: *Biosorption, cobalt removal, kinetics, thermodynamics, isotherms*

1. Introduction

The globe today views industrialization as one of the positive indicators of progress, an agent of civilizationbut yet accompanied by various environmental issues posing significant health risks. Before now, a lot of water bodies were considered fit for domestic activities until heavy metals being a key part of most industrial effluents were discharged.Contaminated water bodies carrying toxic metals are channeled to surface water, endangering aquatic life and other living organisms and posing a severe riskto food security.Variousagents of civilization such as petrochemical refining, prolonged mining, and electroplating activities in the steel industrial are at the forefront (Akhtar et al., 2004) and hence, scientists from all over the world are concerned about how to address this problem, therefore, the emergence oftechniques such as ion exchange, chemical precipitation, complexometric techniques, Usage of chelating agents, membrane filtration, reverse osmosis, solvent extraction,etc. however, these strategies have proven ineffective in many circumstances due to low removal efficiency or high operating costs, particularly in less metal concentrated wastewater and high energy demand.Biosorption hasrecently been proposed as a way of removing harmful metallic ions from wastewater (Iqbal and Saeed, 2007; King et al., 2007). This technique is simple and economical hence, it isused in several most water treatment processes (Barros et al., 2007).

In recent cases, the removal of Polycyclic aromatic hydrocarbons (PHCs) contamination in wastewater by biosorption has been proposed and proven effective (Christensen and Rorrer 2009; Olivella et al. 2013). Rawat*et al.,* (2014) have reported the biosorption of multiple heavy metals (Cu^{2+}, Zn^{2+}, and Cr^{6+}) in the leaves of J. *curcas* which is a well-known plant for its biodiesel component in which the plant shows excellent adsorption capacity on the heavy metals. In several other research, it has been reported that plants likepaper mulberry, Ficus religiosa,Alyssum discolor, neem etc., can eliminate heavy metals (Nagpal *et al.,* 2011; Qaiser *et al.,* 2009; Al-Masri *et al.,* 2009; Bayramoglu*et al.,* 2012; Serencam*et al.*, 2013; Arshad *et al.,* 2008).The interaction between the metallic cations and the anions contained in the biomass has been proposed as the mechanism of the biosorption process (Pradhan *et al.,* 2007). Following several assumptions, the sorption process involving the interaction between the adsorbate and the adsorbent can be expressed in one or two models called adsorption isotherms such as the Langmuir and Freundlich isotherm (Mann, 2014). The thermodynamic consequence of this process is also of utmost importance, it illustratesthe exothermic and endothermic aspects of the biosorption process in this way.Biosorbents are low-cost materials that have a high tendencyto bind metals (Con-rad and Hansen, 2007) therefore, the usage of biosorbents from plants or animalshas received a lot of consideration.

Camellia sinensis is an angiosperm dicot plant whose leaves and budsare used to make tea. It is a member of the genus *Camellia*and belongs to the family Theaceae. Its nativity was traced back to China and Asia (Dupler, 2001)although grown all over the globe in both tropic and sub-tropic locations. The strong tap-rooted shrub is evergreen andis usually cut to less than 2 meters when cultivated for its leaves.Thediameter of the flowers isapproximately 4 cm, and the petals are either seven or eight with yellowcoloration. C. sinensis seedscan be hard-pressed (Xia et al., 2017) toyield tea oil. The fresh leaves which contain about 4 % caffeine are 4-15 cm long and 2-5 cmbroad. (Xia et al., 2017).

Figure 1. *Camellia sinensis* plants.

Food companies' processing of *C. sinensis* for Tea productionhas sparked a lot ofinterest in the plant, with little regard for its sorption properties.In as much as the extract from the leaves is essential for tea, the leaves themselves can also be of great use for biosorption of heavy metals to cop the pollution of the environment, hencethis research aims to remove heavy metals in an aqueous solution using tea leaves and tea fibres (***camellia sinensis***) as absorbent. This will be of great importance as it intends to assess the potency of ***camellia sinensis*** biomass as an adsorbent for the elimination of cobalt from aqueous phase contaminated solution or industrial effluent and thus, can be employed in various sectors especially industries that require safe water treatment techniques.

2. Experimental

2.1. Collection and Preparation of Biomass

The tea leaves and fibreswere collected from the Sardauna local Government area of Taraba State, using the method according to Etim *et al.*, (2022) for sample collection and preparation. They were washed, rinsed, sun-dried for seven days, pulverized, filtered via a150mm sieve, and finally stored in an airtight container.

2.2. Preparation of Metal Stock Solution

Exactly 0.1M of $CoCl_2.6H_2O$ (with MW=237.95g/mol) was prepared in advance for use in the experiments by dissolving23.8g of $CoCl_2.6H_2O$ salt in 500 cm^3 of distilled water.Serial dilutions of 0.02, 0.04, 0.06, 0.08 were prepared from the 0.1 M stock solution already prepared providing a total of four distinct concentrations of Co solutions.

2.3. Adsorption Experiments

Adsorption experiments were conductedfor various concentrations of Co solutions, pH values, contact time and absorbent dosage, in a capped glass tube. A constant 50 cm^3 of the metal solution in a conical flask was used in all cases. The flask was introduced into an orbital shaker whose temperatures were variedbetween 30ºc-60ºc and rotating at a constant speed of 220 rpm throughout the process and centrifuged afterwards. For each case, the process was repeated twice for reproducibility. For each batch of biosorption experiment carried out in a glass tube, the biomass is kept in constant contact with the metal ions for some time. The effects of initial solution pH, contact time, biosorbent dosage, temperature and initial metal ion concentration on the biosorption of Co (ii) ions were investigated at 27^0C. Each experiment was carried outin a thermostatic water bath (Haake Wia Model), and an AAS machine (ICE 3000 SERIES) was then used to analyze theremains of metal ion concentration in solution. For each set of trials, the number of metal ions adsorbed by the biomass from the solution was assessed by difference, and the mean value was derived.

2.4. Effect of Initial Concentration

The method according to Etim *et al.*, (2019) was used to investigate the effect of initial concentration of the metal ions on the boisorbent. In this case, 50 cm^3 of each metal solution, at concentrations ranging from 20 mg/L to 50 mg/L were each dispersed with 1 g of the biosorbentand kept on stand for 1 hour to attain equilibriumafter which the slurries were filtered using a funnel and Whatman filter paper. The filtrates were then examined for the metal ion concentrations using Atomic absorption spectrometer.

2.5. Effect of Biosorbent Dosage

Measurement of the effect of biosirbent dosage on metal ion concentrations was ascertained using a modified method according to Etim *et al.*, (2019).In this method, various weight of the biosorbent (1 g, 2 g, 3 g and 4 g)were each taken into distinct conical flasks containing 50 cm^3 of the metal solution. The flasks were corked and properly agitated using a shaker for 1 hour until equilibrium was attained.After the filtration of the slurries by using Whatman filter paper and a plastic funnel, the filtrates werethereafter measured for the concentrations of metal ions using Atomic absorption spectrometer.

2.6. Effect of Time on the Sorption Potentials of the Biosorbent

The method according to Etim *et al.*, (2022) was used to investigate the effect of time on the sorption potential of the biosrobent. In this experiment,1 g of biosorbent was introduced into four distinct conical flasks containing 50 cm^3 of metal solution, it was then agitated at 30 rpm, and they were allowed to stand.The time difference between each beaker were 10 min, 20 minutes, 30 min and 40 minutes at costant conditions of 25^oc, pH of 6 and 0.1M metal concentration. On completion of the spinning, the extracted solutes were placed in a plastic centrifuge tube and were centrifuged for 3minutes at 6000rpm to allow for the partition of the biosorbent from the solution and subsequently, the solution portion was extracted from the tubes using dropper and analyzed using atomic adsorption spectrometer.

2.7. Effect of pH

The method according to Etim *et al.*, (2022) was used to investigate the effect of pH on the biosorption of metal ions, and also pavasant*et al*., (2006) provides the methods to avert metal precipitation as used in this investigation hence, the specification of the pH range 3.0 – 9.0 as the most suitable for Co (ii) ion since their sorption is pH influenced. In this case,50 cm^3Co (ii) solutionswere dispersed with 1 g of the biosorbent at 25 °C in a glass tube. 0.1 M each of NaOH and M HCl were used to regulate the pH of each of the solutions.The investigations were carried out at pH values of 3.0; 5.0; 7.0; and 9.0 with each glass tube containing the mixture allowed to stand in a water bath for 24 h. On decanting, the biomass was removed from the solution followed by the analysis of the residual Co (ii) concentration using AAS after shaking for 1 hour. This was done thrice with the mean values being considered.

2.8. Effect of Temperature

The method according to Reddad*et al*., (2002)was used for this experiment. In this procedure, 1 g of the adsorbent was introducedinto four distinct conical flasks containing 50 cm^3 of 0.1 Msolution of Co^{2+} metal. Theywere agitated in a shaker for 1 hour to get to equilibrium and the temperature variations were 20, 30, 40, and 50 °C.The slurries' filtrates were analysed using AAS after the mixtures were filtered using Whatman filter paper and a plastic funnel.

The equilibrium metal uptake q_e and the adsorption efficiency in percentage of the biomass were thus calculated as follows (Madhavi *et al.*,2021).

$$\boldsymbol{q_e = \frac{(Co-Ce)}{m} v}, \quad \textbf{and \% efficiency} = \frac{(Co-Ce)}{Co} X\ 100$$

Where q_e is the metal ions uptake at equilibrium (mg/g),V is the volume of the metal solution used (L),C_o is the initial concentration of metal ion in solution (mg/L),C_e is the final concentration of metal ion in solution at equilibrium (mg/L), and m is the mass of biosorbent (g).

2.9. Adsorption Kinetics

For diverse adsorbents, understanding of diffusion mass transport or kinetics is required for the adsorption process. To examine the adsorption kinetics data, models such as pseudo first and second order, intraparticle diffusion, and Elovick kinetics were used.

Pseudo-first order Kinetics Model

The expression of the linearized form of the pseudo-first order kinetics is given thus:

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

Where qe is the amount of metal uptake at equilibrium (mg/g)**,** qt is the amount of metal uptake at time t.A plot of log (qe-qt) versus t should yield a linear connection if the pseudo-first-order is applicable.The slope and intercept of the curve can be used to derive the constant k_1 and projectedq_e, respectively.

Pseudo-second order Kinetics Model

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

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

where k_2 (mg/g.minute) is the rate constant of the second-order equation, q_t (mg/g) is the metal adsorbed at time t (min), and qe is the metal adsorbed at equilibrium (mg/g). The plot of $\frac{\mathbf{1}}{\mathbf{qt}}$ against t will give a linear curve whose slope is equal to the rate constant $k_{2.}$

Adsorption Isotherms

Langmuir Isotherm

The Langmuir isotherm model was determined using the equation below, which depicts the relationship between the quantities (mg/g) of adsorbate adsorbed on the adsorbent and the adsorbate concentration (mg/L) in solution at equilibrium condition.

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

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)andQ_o the adsorption capacity of the adsorbents.

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;

$$\log qe = logK_f + \frac{1}{n}logCe$$

Where K_F 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 q_e against log C_e gives a straight-line of slope $\frac{1}{n}$ and an intercept eqaul to log K_F

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;

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

The maximal langmuir adsorption capacity is Q_o and the langmuir isotherm constant is b.

T is the thermodynamic temperature and R is the gas constant (8.314 J mol^{-1} K^{-1}).

The gibbs fre energy of biosorption can be computed (Voudrias *et al.*,2002) as follows;

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

Where ΔG^orepresents the standard Gibb's free energy change for the adsorption (J/mol), R represent the universal gas constant (8.314 J/mol/K) and T represent the temperature (K). Theadsorbate's distribution coefficient is K_c. A negative Gibbs free energy value suggest that the adsorption process is feasible and spontaneous (Din *et al.*, 2014).The plot of ln K_c versus 1/T yields a straight line with values forΔH^o and ΔS^o as the slop and intercept.K_c is the distribution constant and can be writtren as (Salman *et al.*, 2015)

$$K_c = \boldsymbol{C}_{ad}/\boldsymbol{C}_e$$

C_{ad} (mg/l) and C_e (mg/l), respectively, are the concentration of solute adsorbed at equilibrium and the concentration of solute in solution at equilibrium.

The following is the relationship between (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) of adsorption:

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

Positive change in enthalpy (ΔH^o) implies that the adsorption is an endothermic process, but positive change in entropy (ΔS^o) reflects enhanced randomness at the solid/ solution interface.

3. Results and Discussion

The effect of the initial concentration of the metallic cobalt solution on the biosorption of both the leaves and fibres of C. senensis is presented in **Figure 1**. As the initial concentration of cobalt in the aqueous solution increases, the per cent elimination increases rapidly for both tea leaves and tea fibre but reaches a plateau (equilibrium concentration) at about 40 mg/Lconcentration of cobalt solution and then decreases rapidly as shown in **Figure 1(a)**.This behaviourhasbeen reported by Rawat*et al.*, (2014); in a case of J. *curcas* used as a biosorbent for the elimination of Cu^{2+}, Zn^{2+}, and Cr^{6+} in which above 40 mg/L of the metallic solution, desorption of already absorbed metal set in.The plateau value obtained is an indication of the saturation of the biosorbent by the cobalt metals, a point at which desorption of the metal occurs. As the metal/biomass ratio grows above the point of equilibrium concentration, the biosorption efficiency decreasesbecause ofthe desorption of already adsorbed cobalt metal. This can be attributable to the biomass's accessible binding sites becoming saturated. This means that as the quantity of metal ions vying for available reacting sites on the biosorbentgrows the number of metals complexed with the biomass decreases. As a result, the higher the initial cobalt concentration above 40 mg/L, the more Co (ii) ions remained in solution. There is a linear relationship between the metal ion uptake and the initial concentration of the cobalt metal as shown in **Figure 1(b)**. This is true for both the leaves and fibre of C. *senensis* as a biosorbent.

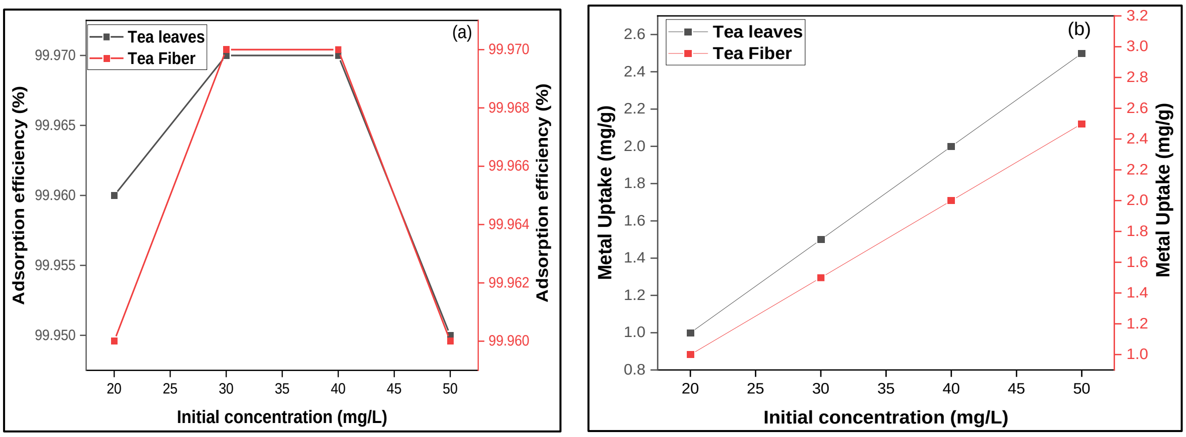

Figure 1. Effect of concentration on the biosorption of the leaves and fibres of C. sinensis (a) adsorption efficiency (b) metal uptake.

The effect of the biosorbent dosage of tea leaves and fibre between the range of 1-4g on the sorption of Co (ii) ionswas examined. The adsorption efficiency shows a parabolic increase with the increase in biomass dosage as presented in **Figure 2(a)**. The findings reveal that biosorption performance is largely reliant on biomass dose. The proportion of Co (ii) ion removed rose as the biosorbent dose was raised in both the tea leave and tea fibre with no sign of decline. This means that increasing the amount of biosorbent could elevate the quantity of adsorbed biosorbate triggering higher efficiency. This is true becausethe exterior portion of the biosorbent grows, providing more accessible binding sites(Esposito *et al.*, 2001). Under these conditions, 4g and 2g tea leaves eliminated 99.97 per cent and 99.89 per cent, respectively, while 99.99 per cent and 99.89 per centwere removed by 4g and 2g of tea fibre. The metallic ion intake or adsorption capacity on the other hand decreases with increasing amount of biosorbent dosage (**Figure 2(b)**), which is consistent with the result of Rawat*et al.*, (2014).

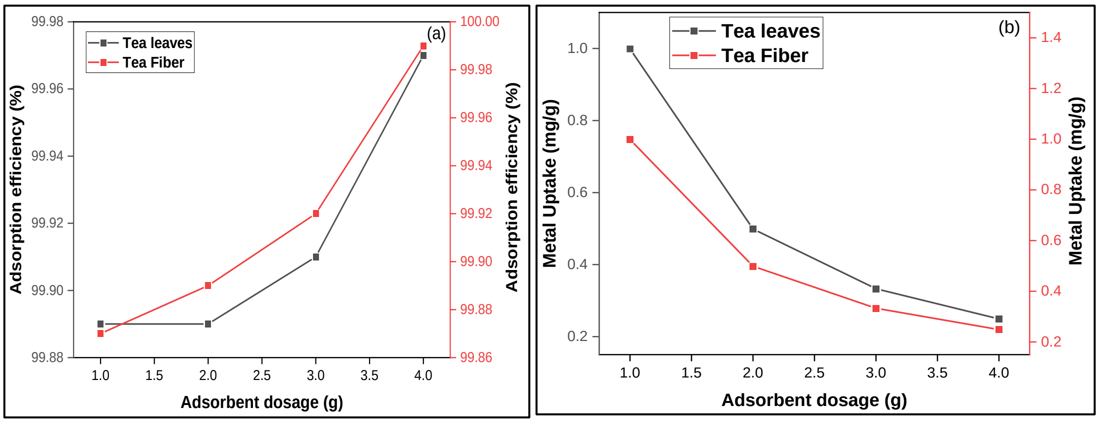

Figure 2. Effect biosorbent dosage on the biosorption of cobalt. (a) adsorption efficiency (b) metal uptake

Time is a significant parameter in adsorption studies cause it gives an idea of the period within which the biosorbent can be proven effective before reaching equilibrium condition. The research looked at the effect of contact time on Co (ii) ion biosorption. The result of the effect is shown in **Figure 3**, which shows that the amount of cobalt adsorbed by the sorbent increases as time goes on. Using tea leaves and tea fibres, the influence of contact time can be used to characterize the kinetics of cobalt sorption. The adsorption efficiency by tea fibre shows a steep increase between 20 and 30 minutes before reaching equilibrium condition at 30 minutes and thereafter slows down (**Figure 3(a)**). This increase at the initial stage of the sorption process can be attributed to the wide level of concentration gradient between the active biding sides on the biosorbent and the metal concentration while above 30 minutes the reaction slows down due to the exhaustion of the active binding side. whereas that of the leaves present a steep increase up to 40 minutes of the process with no sign of decline in the biosroption. This behavior is seen replicated in the adsorption capacity shown in **Figure 3(b)**.

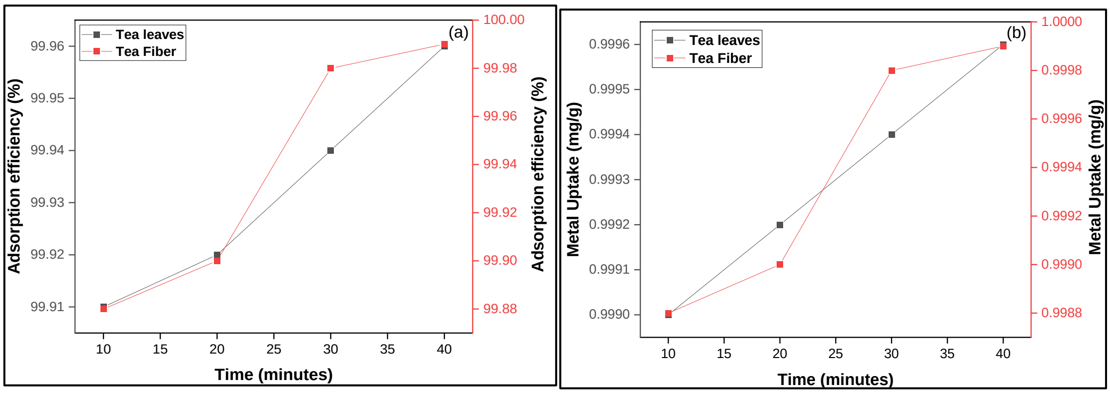

Figure 3. Effect of time on the biosorption of the leaves and fibres of C. sinensis (a) adsorption efficiency (b) metal uptake

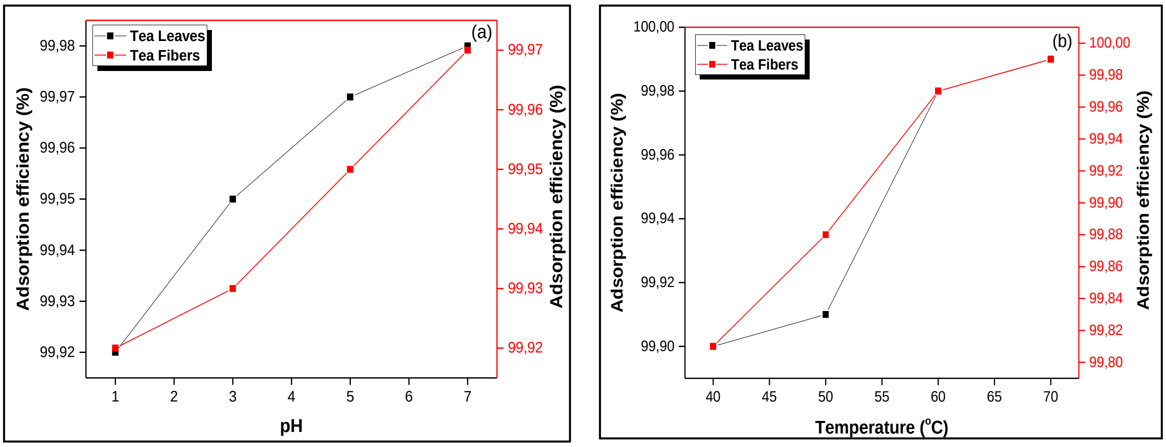

Figure 4. Effect of pH (a), and temperature (b) on the biosorption of the leaves and fibers of C. sinensis

The pH of the metal solution has a great deal in influencing the extent to which the biosorbent can get to maximum adsorption capacity. Negative charge magnitudes are the most influenced in the initial pH conditions which greatly impact on the surface functionality and adsorption efficiency. The proportion of Co(ii) ion elimination increases as the pH increases from 1 to 5 and thus reaches equilibrium at a pH of 5 for the tea leaves after which it suffers a decline in the adsorption efficiency, whereas for tea fibers, the efficiency is flatten between the pH of 1 and 3 after which a steep increase in the efficiency is observed as is the case in figs 4(a). These findings suggest that a weak acidic pH promotes Co(ii) ion biosorption on both the tea leaf and tea fibre. Many H^+ ions in the solution compete with Co(ii) ion and are more preferentially bonded to the negatively charged active sites on the adsorbent, making this site less available for Co(ii) cation at low pH values. On the other hand, metal hydroxides are generated at high pH, and both species are adsorbed at the surface of the adsorbent via an ion change mechanism or hydrogen bonding. As a result, there is competition at the active sites. In general, the biosorption capacity increases with increasing pH for tea leaves and fibers and this have been reported by a good number of researches for various biomass adsorption capacities (Arshad *et al*. 2008; Qaiser *et al.* 2009).

Temperature is a significant parameter for thermodynamic studies of biosorption, this is because temperature is a state function and can be related to the Gibbs free energy, entropy and even enthalpy of the biosorption process, hence the studies on the effect of temperature is highly significant. The effects of temperature on the biosorption of Co (ii) ion from aqueous solution of tea leaves and tea fibres was investigated in the temperature range of 40 – 70^{o}c as presented in Fig 4(b). The result shows that biosorption efficiency is highly dependent on temperature. The percentage Co (ii) ion removal increased with increase in temperature in both the tea leaves and tea fibre from 40 – 70 ℃. For tea fibers, it increases steeply between 40 up to 60 ℃ and then attained an equilibrium condition at about 60 ℃ before declining. The case of tea leaves is some worth different, in that it remains flattened between 40 and 50 ℃ before increasing sharply up to the equilibrium temperature at about 60 ℃ (**Figure 4(b)**).

3.1. Kinetic Studies

The phenomenology and data modeling of the kinetics of sorption is crucial as it provide tremendous insight on the pattern and comparative capabilities of various biorsorbent used in a commercial scale in industries and other water treatment companies. This could be of help in parameter optimization and enhanced efficiency in prediction of suitable biosorbent for pollutant removal. **Table 1** and **2** present the calculated data which represent this kinetics, for pseudo – first and second order kinetics for the biosorption of cobalt by tea leaves and fibers. **Figure 5(a)** shows the plot of Log (qe-qt) against time in minutes for the biosorption of cobalt by the leaves and fibers of C. *sinensis* which corresponds to the pseudo-first order kinetics. The R^2 values for both tea leaves and tea fibers were 0.937 and 0.900 respectively. **Figure 5(b)** shows the plot of 1/qe against time in minutes for the biosorption of tea leaves and fibers corresponding to the pseudo-second order kinetics. The R^2 values obtained from this plot for tea leaves and fibers are 1 and 0.906 respectively.

Table 1. Pseudo first and Second order kinetic for cobalt using tea leave

Time (min)	Qt (L/min)	Qe (m/g)	1/qe	Log (qe-qt)
10	0.017	0.9990	1.0010	-0.0079
20	0.016	0.9992	1.0008	-0.0074
30	0.012	0.9994	1.0006	-0.0055
40	0.007	0.9996	1.0004	-0.0032

Table 2. Pseudo first and Second order kinetic for cobalt using tea fibre

Time (min)	Qt (m/l)	Qe (m/g)	1/qe	Log (qe-qt)
10	0.025	0.9988	1.0012	-0.0115
20	0.020	0.9990	1.0010	-0.0092
30	0.004	0.9998	1.0002	-0.0018
40	0.003	0.9999	1.0001	-0.0013

From the observed R^2 values for each kinetic studies, it can be seen that the most fitted adsorption kinetics is of the second order for the sorption of cobalt using tea leaves and tea fibres with R^2 values of 1 and 0.906 respectively although the kinetics can be argued to follow both pseudo- first order and pseudo- second order kinetic for both the tea leaves and tea fibres. The first and second order rate constant k_1 and k_2 for the biosorption of cobalt by tea leaves and tea fibers rewe obtained from the slope of the plot of **Figure 5 (a,b)** respectively whereas their intercept were used to obtain thir corresponding qe.

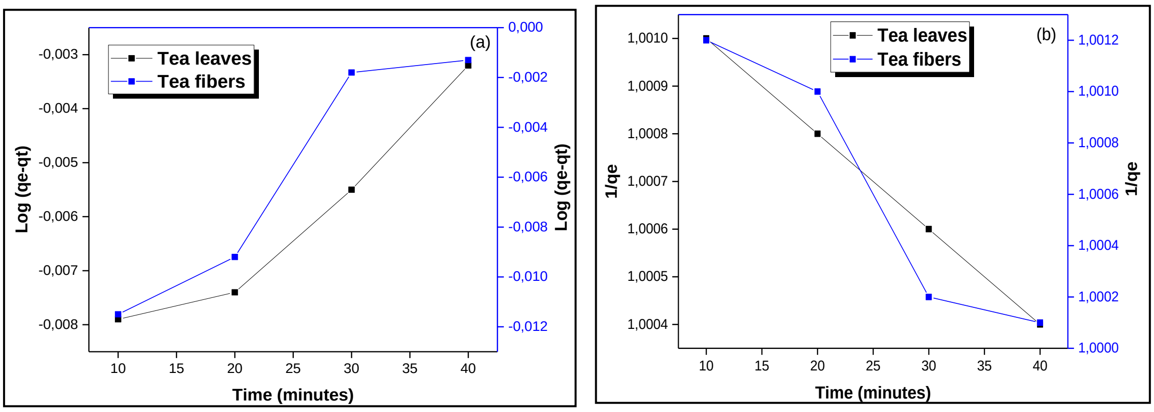

Figure 5. First (a) and second (b) order kinetics for tea leaves and fibers.

3.2. Thermodynamic Studies

Thermodynamic studies for biosorption are crucial because it entails or provide insight on the possible energy consumed or released during the biosorption process (enthalpy), the degree of randomness of the biosorption process (entropy), and if at all the biosorption process is feasibility (Gibbs free energy). **Figure 5** is a plot of the logarithm of the activity constant K against the inverse temperature which help to accertein the thermodynamic evidence for the biosorption of Co (ii) by tea leave and tea. The thermodynamic behavior of the biosorption of Co (ii) ion on the biomass was described using thermodynamic parameters such as enthalpy and entropy computed from the slope and intercept of Ink versus 1/T. The R^2 values of this plot for both tea leaves and fibers were obtained to be 0.911 and 0.964 respectively.

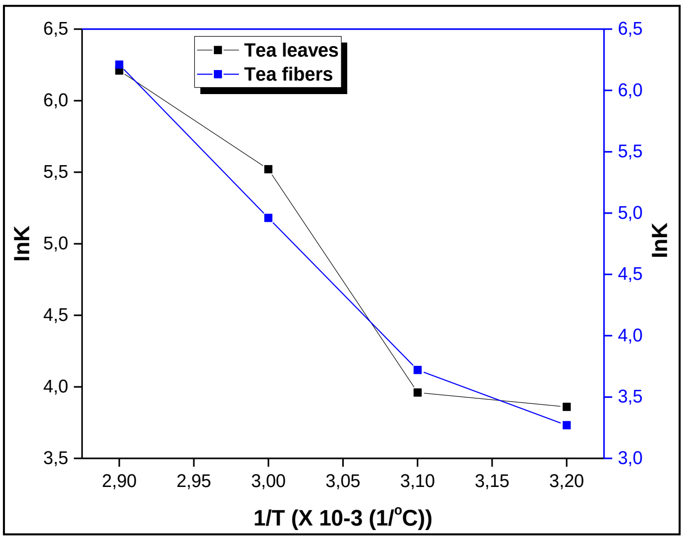

Figure 5. Plot of Ink against inverse temperature for the biosorption of both tea leaves and fiber

Table 3. Thermodynamic parameter for the biosorption of cobalt on tea leave and tea fibre

Adsorbent	**R^2**	**ΔH^o ($kJmol^{-1}$)**	**ΔS^o ($kJmol^{-1}$)**	**ΔG^o at T= 313k**	**ΔG^o at T=323k**	**ΔG^o at T=333k**	**ΔG^o at T=343k**
Tea leave	0.911	-8.58	31.05	-9980	-1020	-1060	-1091
Tea fiber	0.964	-10.03	35.12	-1134	-1034	-1204	-1239

The summery of the thermodynamic parameters obtained from the investigation of the plot of **Figure 5** is presented in **Table 3**. The biosorption of cobalt by both tea leaves and fiber shows negative enthalpies. The negative values of enthalpy (ΔH^o) are an indication that the process is exothermic. The entropy change of the processes are both positive values which is a clear evident of high degree of disorderliness at the phase between solid and solution throughout the biosorption process for both the tea leaves and tea fibers. The Gibb's free energy (ΔG^o), provide an evidence for spontaneity and feasibility of the chemical interaction. The negative values of (ΔG^o) Gibb's free energy outlined in **Table 3** confirmed the feasibility and hence, the spontaneous nature of the biosorption process in both tea leaves and tea fibers.

3.3. Absorption Isotherm

Adsorption isotherms are being used to understand the nature of adsorption layer as well as the nature of homogeneity of adsorption sides. Langmuir isotherms provide exhaustive information about monolayer adsorption on a homogeneous side whereas Frueunndlich isotherm is known for their application in the studies of multilayer adsorption on a heterogeneous site. **Table 4** present the various experimental and calculated data obtained from the biosorption for the purpose of studying the nature of adsorption whether it follows the Langmuir or Frueundlich isortherm.

Table 4. Langmuir and frueundlich isotherm parameters for tea leave and tea fibre

Adsorbent	**Final Conc.(c_e) (Mg/L)**	**1/c_e**	**Log c_e**	**q_e**	**1/qe**	**Logq_e**	**c_e/q_e**	**% Removal**
Tea leave	0.009	111.11	-2.05	0.99955	1.00	-0.0002	0.009	99.96
	0.010	100	-2.00	1.4995	0.70	0.1759	0.007	99.97
	0.014	71.43	-1.85	1.9993	0.50	0.3008	0.007	99.97
	0.025	40	-1.60	2.4988	0.40	0.3977	0.010	99.95
Tea fibre	0.007	142.86	-2.15	0.99985	1.00	-0.00007	0.007	99.96
	0.009	111.11	-2.04	1.49955	0.70	0.1759	0.006	99.97
	0.013	76.92	-1.89	1.99935	0.50	0.3008	0.007	99.97
	0.022	45.45	-1.66	2.4989	0.40	0.3977	0.009	99.96

Figure 6 (a,b) present the plot of Ce/qe and Log qe against final concentration Ce from which the slope and interface provides significant information about the respective isotherm parameters necessary for the biosorption of cobalt by both tea leaves and tea fiber biosorbents. These parameters are presented in **Table 5** for both Langmuir and Frueundlich isotherms respectively.

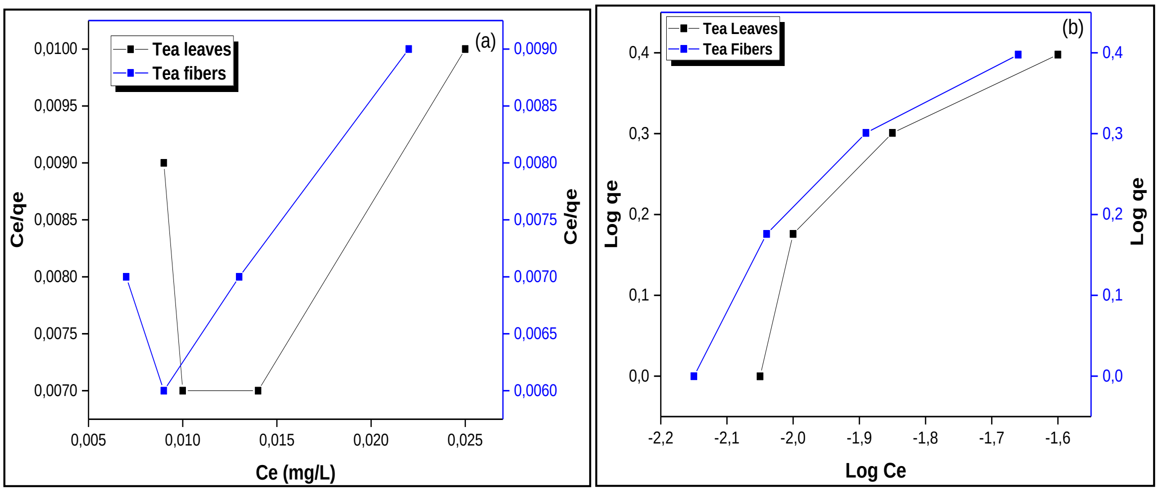

Figure 6. A plot of Ce/qe against Ce (a) and Log qe against Log Ce (b) for both tea leaves and fibers

Table 5. Frueundlich and Langmuir parameter for biosorption of cobalt using tea leave and tea fibre

Adsorbent	**k_f**	**1/n**	**R^2**	**Q_o**	**b**	**R_L**
Tea leave	1.671	0.774	0.831	0.12	0.006	0.89
Tea fibre	1.716	0.774	0.914	0.167	0.005	0.9

The frueundlich isotherm parameters; 1/n, k_f as presented in **Table 5** presents the slope (1/n) = 0.774 and the intercept (k_f) = 1.671 for the tea leaveand that for the tea fibre to be slope (1/n) = 0.774 and the intercept (k_f) = 1.716. the Langmuir isotherm as presented in **Table 5** shows that the slope Q_o = 0.12 and the intercept b = 0.006 for the tea leaves while for the tea fibres, Q_o = 0.167 and b = 0.005. The separation factor R_L which is an indication of the nature of adsorption was obtained to be 0.89 for the tea leaves and 0.9 for the tea fibres implying that the adsorption is favourable since ($0 < R_L < 1$) in both the tea leaves and tea fibres. Therefore, both Frueundlich and Langmuir isotherm models was successfully applied but the most fitted adsorption isotherm in this biosorption process is the Frueundlich isotherm models with (R^2 = 0.831 for tea leaves and 0.914 for the tea fibres) while for the Langmuir isotherm models (R^2 = 0.385 for the tea leaves and 0.7885 for the tea fibres).

3.5. FTIR Analysis

Certain functional groups present on the surface of the biomass are highly involved in the biosorption process. Some of these functional groups including O-H, -C=O and –C-C- groups have been reported by Bhattacharya *et al.*, (2014) to have been active functional group or active sites in algae for the biosorption of Pb metal in waste water. **Table 6** present the active FTIR information of the various functional groups present in both tea leaves and fibers, showcasing the presence of both O-H and –C=O functional groups suspected to have contributed to the biosorption of cobalt by the biosorbents in the current studies.

Table 6. FTIR analysis for tea leaves

FTIR analysis for tea leaves			**FTIR Analysis for tea fibre**		
Peak wavelength	**Bond type**	**Functional group**	**Peak wavelength**	**Bond type**	**Functional group**
3697.5	N-H	Primary amine	3276.2	O-H	Carbohydrate; protein; phenol
3615.6	O-H	Carbohydrate; protein;	2918.5	C-H	Alkane
2918.5	C-H	Alcohol	1625.1	-C=O	Amide band I
2322.1	P-	Alkane	1513.1	-C=O	Carboxylic acid
1729.5	C=O	Phosphine	1315.8	C-N	Amide band III
1606.5	N-H	Aromatic ketone	1144.2	C-O	Secondary alcohol
1461.1	-C=O	Primary amine	1017.6	C-O	Ether
1364.2	C-N	Inorganic carbonate			

1233.7	C-O	Aromatic amine
1010.1	C-O	Carboxylic acid Primary alcohol

Conclusion

This study investigates the biosorption of cobalt by tea leaves and tea fibers of *Camellia sinensis* which were shown to be very effective adsorbent for removing the metal ion from a specific water sample or from industrial effluent. The tea fiber showed a greater percentage of adsorption capacity of 99.99 percent. The pseudo first and second order kinetic adsorption model were both relevant, however the pseudo second-order kinetic model with R^2 values of 1 for tea leaves and 0.906 for tea fibre was the best fit. The feasibility of the biosorption process in both plant parts was proven by the negatives gives energy whose enthalpy suggested an exothermic condition with a highly disordered adsorption process. The tested isotherm suggested that the sorption follows the Frueundlich adsorption isotherm indicative of a multilayer adsorption in a heterogeneous surface. In summary, both the leaves and fibers of C. *sinensis* show excellent biosorption capacity on the uptake of cobalt ion and can be recommended for industrial waste water treatment.

Acknowledgments

I would like to express my sincere thanks for the support from the Department of Chemical Sciences, Federal University Wukari.

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