



Adsorptive Removal of Lead and Zinc Ions From Aqueous Solution using Thiolated Tea (*Camellia sinensis*) Seed Shell

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A B S T R A C T

This study aims at investigating the adsorption of Zinc and lead ions onto thiolated tea (*Camellia sinensis*) seed shell (TTSS) in batch process. Equilibrium data were fitted into Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The equilibrium data favored the Langmuir adsorption isotherm with maximum adsorption monolayer coverage of 397.6 and 475 mg/g for Pb (II) and Zn (II), respectively. In order to fit the kinetic data, three kinetic models; Lagergren first-order, pseudo-second-order and intraparticle diffusion models were used. The adsorption behavior was best described by pseudo-second-order with q_e value of 76.61 and 97.19 mg/g for Pb (II) and Zn (II), respectively. Thermodynamic parameters such as changes in Gibbs free energy ΔG° , enthalpy ΔH° , and entropy ΔS° were calculated. Adsorption process was found to be feasible, endothermic, and spontaneous. The energy of adsorption values of the metal ions (0.717 and 0.759 kJ/mol) and the large negative value of ΔG° confirm the physiosorption nature of the adsorption of Pb (II) and Zn (II) onto TTSS.

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INTRODUCTION

The generation and subsequent introduction of heavy metal from natural or industrial points into the environment has become a worrisome scenario today. This worry is borne out of the associated health implications of the discharge of these metal ions. Heavy metals constitutes a major conservative pollutants that defies breakdown by either bacteria or other degradation process, hence they find their way and accumulate in the environment.

Contamination of water for example by heavy metals contributes to majority of the known health hazards. Cadmium for example on exposure is responsible for impairment of the kidney as well as osteomalacia [1]. Lead interferes with enzymatic functions and the formation of red blood cell and can affect the nerves and brain at minimal concentration [2]. Excessive intake of copper ions by humans can lead to severe mucosal irritation; wide spread capillary damage,

gastrointestinal irritation, and irritation of the central nervous system followed by depression [3].

Different methods exist for the treatment of metal ions from aqueous solutions and this include chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation, electrochemical coagulation chelation etc [4-6]. However, these techniques have their own drawbacks such as less efficiency, sensitive operating conditions, and production of secondary sludge requiring further costly disposal [7]. These setback, coupled with the need for more economical and efficient methods for recovery of heavy metals from wastewater have resulted in the development of alternative separation technologies. Activated carbon adsorption remain the most powerful technology that is available for the removal of heavy metal ions from wastewaters and industrial effluents but its applications is limited due to high cost. However, low cost adsorbents from agricultural residues have been reported to be of economic importance. Avalanche of low cost adsorbents have been prepared from agricultural biomass for the adsorption of heavy metal ions including rice and wheat

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bran [8]; fly ash [9]; wood saw dust[10]; corn and corn cob [11]; cassava tuber bark waste [12]; walnut shell, hazelnut shell and almond shell [13] etc.

In this work, *Camellia* seed shell was modified by thiolation with glycolic acid to produce thiolated tea seed shell. Tea (*Camellia sinensis*) is an evergreen tree plant, which belongs to the *camellia* genus in Theaceae family. The fruit is a capsule with a loculicidal dehiscence, 10-15mm high and 2-3cm in diameter with one, two and three or even four loculi each containing one or two seeds. The seed is spherical to hemispherical, brown when it is matured. The leaf contains a number of bioactive molecules responsible for health promoting properties of tea such as flavonoids. The tea industry generates large volume of shell, which has not been adequately tapped in tea plantations. This agricultural biomass is renewable and abundantly available at little or no cost.

The present study reports the removal hazardous heavy metals, Pb (II) and Zn (II) from aqueous solution by thiolated tea (*Camellia sinensis*) seed shell.

MATERIALS AND METHODS

Preparation of Biomass

Tea (*Camellia sinensis*) seed shells (TSS) was obtained from the Mambilla substation of the Cocoa Research Institute of Nigeria, Ibadan. The seeds were broken and the content removed. The shells were washed to remove dirt, sun-dried until constant weight was obtained and chopped into small particle size. The dried sample was ground then sieved through a sieve of different mesh size and retained until ready for use. The lead and zinc salt used for this study were analytical grade of Pb (NO₃)₂ and Zn(NO₃)₂.6H₂O supplied by BHD chemicals Ltd., Poole, England.

Activation of Biomass

The screened portion of the biomass retained on the 250 μm mesh was then steeped in dilute nitric acid solution (2% v/v) for 24 hours. After 24 hours duration, the meal was filtered using a Whatman No. 41 filter paper and then washed with deionized water, dried at 105°C for 12 hours and then stored in desiccators.

Thiolation of tea (*Camellia sinensis*) seed shell

Thiolation of tea seed shell was carried out according to the procedure described in literature[14]. In a typical experiment, 30 g of the screened tea seed shell was hydrolyzed with 15 times its weight of 7% (v/v) aqueous solution of sulphuric acid for 90 minutes. The mixture was filtered and the residue was washed with deionised water and dried at 50°C. A 25 g of the hydrolyzed TSS was treated with 0.3dm³ of 1M

thioglycolic acid solution in a well-ventilated hood. The mixture was filtered and the TSS was washed copiously first with deionized water, followed with methanol and then finally with distilled water and then air-dried. The resultant product is the thiolated tea seed shell. The degree of thiolation was determined titrimetrically by reaction of the thiolated TSS with iodine and back-titration of the unreacted iodine with sodium thiosulphate solution.

Preparation of Adsorbent

All reagents used for this study were of analytical reagent grade and were used without further purification. Doubly distilled and deionized water was used in the preparation of all sample solution. Stock solution of Pb²⁺ and Zn²⁺ metal ion of 1000 mg/L concentration were prepared using lead nitrate (Pb(NO₃)₂) and Zn(NO₃)₂.6H₂O, respectively. From the stock solution, aliquot of 100 mL (initial concentration) of metal ions were prepared by serial dilution with deionized water

Adsorption Experiments.

The batch adsorption experiments were carried out on the removal of Pb (II) and Zn (II) ions from aqueous solution to study the kinetics, mechanisms, and thermodynamics properties. In the kinetic experiments, the batch adsorption studies was carried out by shaking 0.5 g of the thiolated tea seed shell with 25 mL of different concentrations (10 – 100 mg/L) at varying pH (1-8) containing the metal ions for various contact times (10 -180 min) over a range of temperature. The influence of pH on the sorption behavior of the metal ions was carried out within the range that would not be influenced by metal precipitated. The initial pH of each solution was thus adjusted to the desired pH by drop wise addition of 0.1M HNO₃ and/or 0.1M NaOH solution. At the end of each contact time, the mixture was filtered and the residual concentration was determined using Atomic spectrophotometer, AAS (Buck scientific model 210 VGP). The amount of Pb (II) and Zn (II) removed from solution by TTSS was taken as the difference between initial and residual concentrations of the metal ion. All the experiments were carried out in triplicates and the mean value taken. Percentage removal of the metal ions was estimated using the following equation:

$$\text{Removal \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where,

C_i : Concentration of heavy metal ions before adsorption
C_f : Concentration of heavy metal ions after adsorption
The amount of metal ion adsorbed at time t (q_t) was calculated using the formula [15]:

$$q_t = \frac{(C_i - C_f)v}{m} \quad (2)$$

where,

v : volume of aqueous solution used for adsorption

m : mass of adsorbent used

RESULTS AND DISCUSSION

Effect of contact time on sorption capacity

The effect of contact time on the sorption capacity of Pb (II) and Zn (II) on thiolated TSS is shown in Figure 1. The initial rate of adsorption for Zn (II) was rapid and the major part in the Zn (II) uptake was observed at 40 minutes. The improved level of adsorption of Zn (II) by TTSS could be as result of the relative ease of exchanging hydrogen atoms of the thiol group of the thioglycolic acid with the metal ions. Previous workers [16, 17] have reported similar observations. However, there was a reduction in the adsorption of Pb (II) on the modified seed shell. The observed trend may be due to the low affinity of Pb (II) for the thiol groups (S-H). The differences in the level of metal ions uptake can be attributed to the difference in ionic size of the two metal ions, the nature and distribution of functional groups on the adsorbent as well as mode of interaction between the metal ions and adsorbent.

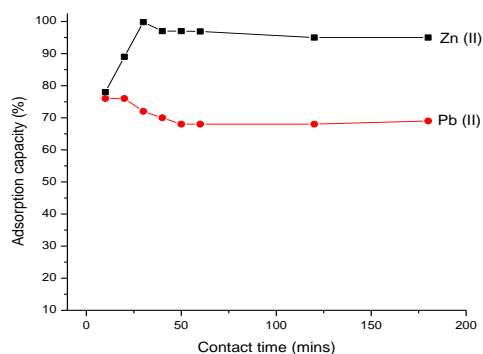


Figure 1. Effect of contact time on the adsorption of Pb (II) and Zn (II) on TTSS

Adsorption isotherms

Adsorption isotherm models are often used to describe adsorption and investigate its mechanisms. The adsorption isotherm shows how the adsorbed molecules distribute themselves between the liquid phase and the solid phase until equilibrium state is reached for the adsorption process. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models were used to fit Pb (II) and Zn (II) adsorption isotherm data for thiolated TSS.

Langmuir isotherm model

This assumes monolayer adsorption into a surface containing a finite number of adsorption sites, which are uniform for adsorption with no transmigration of adsorbate in the plane of surface [18]. The equation is stated as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where q_e is the metal ions adsorbed (mg/g) C_e are the equilibrium concentration (mg/L), q_{max} is monolayer adsorption capacity (mg/g), K_L is Langmuir adsorption constant.

As data presented in Figure 2, the Langmuir isotherm showed good relationship for the adsorption of Pb (II) and Zn (II) on TTSS with R^2 0.999 and 0.998 respectively. The R_L values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The lower R_L value, which represents adsorption intensity for this study, further suggests that the interaction of these metal ions with the modified adsorbent was favorable. The values of q_m and K_L were calculated from the slopes ($1/q_m$) and intercepts of the linear plots of $1/q_e$ or $1/r$ versus $1/C_e$ (Table 1.) The R^2 value of Langmuir isotherm, when compared with Freundlich isotherm indicates that the adsorption of Pb (II) and Zn (II) on TTSS fits the Langmuir isotherm. This also compared with the results of other workers [19-21].

Freundlich isotherm model:

The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir varies as a function of the surface coverage. The equation in the linearized form is shown below:

$$\log q_e = \frac{1}{n \log C_e} + \log K_F \quad (4)$$

where q_e is the metal ions adsorbed (mg/g) at equilibrium, C_e are the equilibrium concentration (mg/L) k is Freundlich constant with multilayer adsorption, n is adsorption intensity. Plots of $\log q_e$ versus $\log C_e$ gave linear graphs (Figure 3) with lower values of R^2 Compared to Langmuir model. This indicates that the adsorption data does not fit the Freundlich isotherm model. The Freundlich constants, K_F and n from the plots are shown in Table 1. The adsorption intensity, n obtained were 1.016 and 1.458 for Pb (II) and Zn (II) respectively (Table 1) which is greater than 1 also corroborates the fact that the model is not suitable.

Dubinin-Radushkevich model (D-R)

Dubinin-Radushkevich model is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant adsorption potential.

This is applied to distinguish between the physical and chemical adsorption.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where q_e is the number of metal ions adsorbed per unit weight of adsorbent (mg/g), q_m is the maximum adsorption capacity, β is a constant related to the mean free energy of adsorption per mole of adsorbate (kJ^2/mol^2) and ε is the Polanyi potential which is related to the equilibrium concentration C_e by the following expression:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

TABLE 1. Parameters of Langmuir, Freundlich and D –R adsorption isotherm constants for adsorption of Pb (II) and Zn (II) on thiolated tea seed shell

Isotherm	Constants	Pb (II)	Zn (II)
Langmuir	q_m (mg/g)	397.6	475
	K_L (L/mg)	0.0089	0.015
	R^2	0.999	0.998
	R_L	0.313-0.744	0.107- 0.577
Freundlich	n	1.016	1.458
	R^2	0.8564	0.974
	q_m (mg/g)	16.3	22.8
	β (kJ^2/mol^2)	3.76×10^{-5}	5.33×10^{-5}
Dubinin Radushkevich (D-R)	E (kJ/mol)	0.717	0.759
	R^2	0.8686	0.7791

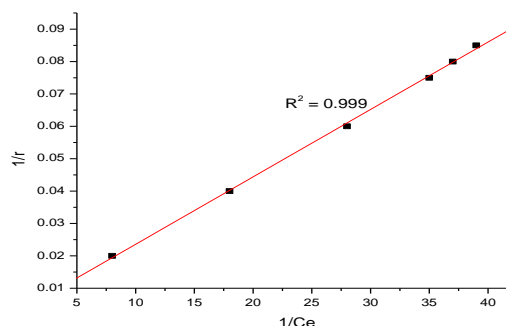
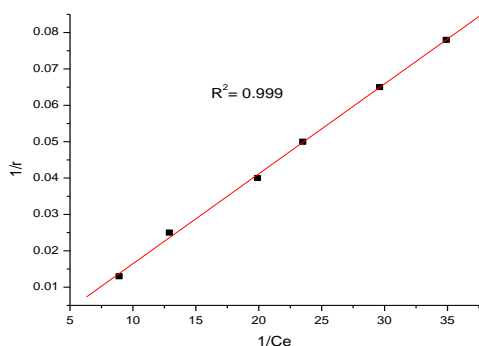


Figure 2. Langmuir isotherm plots for adsorption of (A) Pb (II) and (B) Zn (II) on TTSS

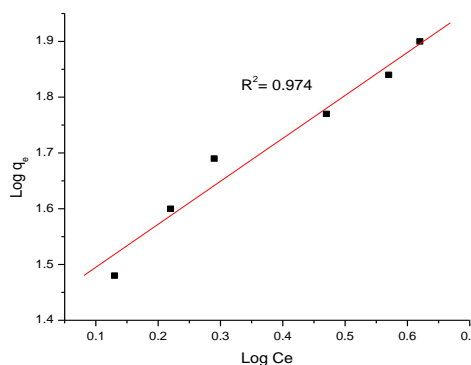
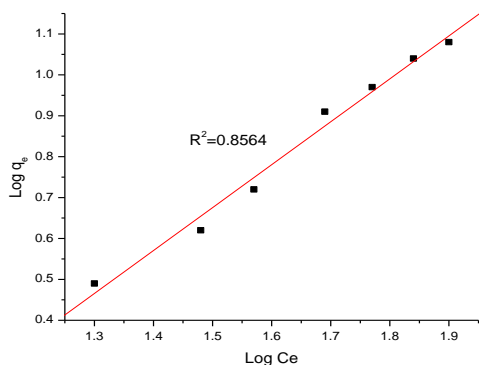


Figure 3. Freundlich isotherm plots for adsorption of (A) Pb (II) and (B) Zn (II) on TTSS

where R is the gas constant ($\text{J}/\text{mol}\cdot\text{K}$) and T is the absolute temperature. The slope of the plot (not shown) of $\ln q_e$ versus ε^2 gives β (mol^2/J^2) and the intercept yields the sorption capacity. The energy of adsorption can be calculated as follows:

$$E = \frac{1}{(-2\beta)^2} \quad (7)$$

The sorption energy gives information about the about the sorption mechanism, either chemisorption or

physiosorption. The D-R parameters calculated from the plots are also presented in Table 1. The E values for TTSS on Pb (II) and Zn (II) were found to be between 0.717 - 0.759 kJ/mol over the range of temperatures used in the study. Since $E < 8\text{kJ}/\text{mol}$, it suggests that the adsorption mechanism is physical in nature [22-24].

Kinetic modeling

The kinetics of Pb (II) and Zn (II) adsorption on thiolated tea seed shell were subjected to three models:

the Lagergren first-order according to Lagergren described in literature [25], pseudo-second-order [26], and intraparticle diffusion models. The explored models were followed according to the equations stated as follows:

Lagergren first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.03} \times t \quad (8)$$

Where: q_e and q_t are adsorption capacity at equilibrium and time t , respectively (mg/g). K_1 is the rate constant of Pseudo first-order (min^{-1}). The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot. Values of k_1 and q_e calculated for this study are presented in Table 2 (figure not shown). The result shows that R^2 values are low (< 0.999), therefore the adsorption of these metal ions onto TTSS do not follow the pseudo first order kinetics.

Pseudo second-order equation:

The pseudo second order equation expressed in literature [25] according to the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where: k_2 = rate constant of the Pseudo second-order (g/mg.min). The plot of (t/q_t) and t should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively [27]. From the study, plot (figure not shown) of (t/q_t) versus t gave linear graph from which q_e and k_2 were estimated from the slope and intercept (Table1) for temperatures between 294-310K. The correlation coefficients for the metal ions were high and close to unity and the q_e (cal.) values agree with experimental values. The results suggest that the pseudo second order model describes the adsorption kinetics of the present study.

TABLE 2.: kinetic models constants for the adsorption of Pb (II) and Zn (II) on thiolated tea seed shell

Model	Pb (II)	Zn (II)
Pseudo- first order		
k_1 (min^{-1})	0.0319	0.062
q_e (mg/g)	14.7	29.4
Correlation coefficient R^2	0.6441	0.6751
Pseudo-second order		
K_2 (g/mg min)	0.166	0.125
q_e (mg/g)	76.61	97.19
h_0 (mg/g min)	112	163
Correlation coefficient R^2	0.9998	0.9999
Intraparticle diffusion		
n	0.0053	0.0013
K_{id} (min^{-1})	91.661	96.943
Correlation coefficient (R^2)	0.9776	0.8768

Intraparticle diffusion

To understand the mechanisms and rate controlling steps affecting the kinetics of adsorption, intraparticle diffusion plays a vital role in the extent of adsorption and can be expressed according to [28] as:

$$R = K_{id} t^n \quad (10)$$

A linearized form of the equation is:

$$R = \log K_{id} + n \log t \quad (11)$$

where,

R = percent metal ion adsorbed

t = contact time

n = gradient of linear plots

K_{id} = intraparticle rate constant (min^{-1})

A plot of $\log R$ versus $\log t$ gives a straight line. The value of n depicts the adsorption mechanism and K_{id} may be taken as a rate factor [29]. For the present system, plot (figure not shown) of $\log R$ versus $\log t$ showed linearity with n and K_{id} representing the slope and intercept respectively. The value of K_{id} increases in the order: Pb (II) > Zn (II). This illustrates an enhancement in the rate of adsorption of the metal ions onto TTSS. Large n value also implies better adsorption mechanism and this is brought about by improved interaction between the adsorbent particles and the metal ions. With the relative large value of n obtained (0.0053 and 0.0013), it suggests that the sorption process is particle diffusion controlled [12, 29].

Temperature and thermodynamics of adsorption

In an attempt to study the thermodynamics of adsorption studies were carried out at 294, 296, 298, 300, 302, 305 and 310K. Thermodynamic parameters such as Gibbs free energy, standard enthalpy change, standard entropy change affect the feasibility, heat change, and spontaneity of the adsorption process. These parameters are obtained using the equation below:

$$K_c = \frac{C_{ad}}{C_e} \quad (12)$$

Change in Gibbs free energy of adsorption process is stated as follows:

$$\Delta G^\circ = -RT \ln K_c \quad (13)$$

Where ΔG° = standard Gibbs free energy change of adsorption

R = universal gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$)

T = temperature (K)

From thermodynamics,

$$\Delta G^\circ = \Delta H - T\Delta S \quad (14)$$

A plot of ΔG° against T gives a straight line with slope - ΔS and intercept of ΔH .

For the present study, a plot of ΔG° against T is shown in Figure 4. From the plot, a slope of -19.63 J/mol.K was obtained and an intercept value of 53.91 kJ/mol for Pb (II) while Zn (II) had a slope and intercept of -76.25 kJ/mol and 43.37 kJ/mol , respectively. The implication of this is that while Pb (II) had entropy of 19.63 J/mol.K and enthalpy of 53.91 kJ/mol , Zn (II) had entropy and enthalpy of -76.25 kJ/mol and 43.37 kJ/mol , respectively. It could be seen that the values of free energy decrease with increase in temperature for the removal of Pb and Zn ions. The implication of this is that the adsorption of these ions on thiolated TSS is endothermic in nature. The negative value of ΔG° is an indication of the spontaneity of the adsorption process. The positive value of standard entropy change, ΔS° , shows increased randomness at the solid/solution interface occurring in the adsorption process reflecting the affinity of modified TSS toward the metal ions. It has been reported that the change of standard free energy for physisorption process is in the range of -20 to 0 kJ/mol while chemisorptions process varies from -80 to -400 kJ/mol [30, 31]. For the present study, the overall Gibbs free energy change obtained for the adsorption of Pb and Zn ions onto modified TSS is -6.938 kJ/mol and -7.001 kJ/mol for Pb (II) and Zn (II) respectively at 310 K . This corroborates the energy of adsorption values obtained and the large negative values further confirmed the fact that the adsorption of these metal ions on thiolated TSS is physisorption in nature.

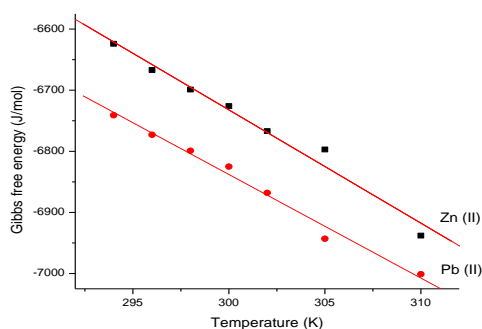


Figure 4. Gibbs free energy change in the adsorption of Pb (II) and Zn (II) on TTSS

CONCLUSION

The potential of Thiolated *Camellia sinensis* seed shell conducted in this study suggested that it can serve as an effective adsorbent for the removal of Pb (II) and Zn (II) from aqueous solutions. The adsorption process was best described by the Langmuir adsorption isotherm with maximum adsorption monolayer coverage of 397.6 and 475 mg/g for Pb (II) and Zn (II) respectively. There is therefore indication that thiolated tea seed shell

can serve as effective adsorbent in removing heavy metal ions from aqueous solutions.

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Persian Abstract

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چکیده

پژوهش حاضر با هدف بررسی جذب روی و یون های سرب بر روی عصاره چای سیاه و سبز فرآوری شده در فرآیند ناپیوسته است. اطلاعات تعادل با مدل های لانگمر، فروندلیچ و دوینین را پردازش می شود. داده تعادل مورد علاقه ایزوترم جذب لانگمر با حداکثر پوشش تک لایه جذب ۳۹۷/۶ و ۴۷۵ میلی گرم/گرم سرب (II) و روی (II) بود. به منظور پردازش داده، سه مدل سینتیک، لاگرتن مرتبه اول، شبه مرتبه دوم و مدل های نفوذ درون ذره ای مورد استفاده قرار گرفت. رفتار جذب به بهترین شکل با مدل شبه مرتبه دوم با ارزش q_e از ۷۶/۶۱ میلی گرم/گرم و ۹۷/۱۹ میلی گرم/گرم سرب (II) و روی توصیف (II) شد. پارامترهای ترمودینامیکی از قبیل تغییر در انرژی آزاد گیبس ΔG° ، آنتالپی ΔH° ، و انتروپی ΔS° محاسبه شد. فرآیند جذب امکان پذیر، گرماگیر و خود به خودی شد. انرژی جذب مقدار یونهای فلزی ۰/۷۱۷ و ۰/۷۵۹ (کیلوژول بر مول) و مقدارهای بزرگ منفی ΔG° ماهیت جذب فیزیکی از جذب سرب (II) و روی (II) بر روی عصاره چای سیاه و سبز فرآوری شده را تایید می کند.
