IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 4 Ver. II (Apr. 2015), PP 20-26
www.iosrjournals.org

Kinetics and Thermodynamics of Pb (II) and Zn (II) ions uptake from aqueous phase by Tea (Camellia sinensis) seed shell

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Abstract: *The use of Tea (Camellia sinensis) Seed Shell (TSS) for the removal of Pb (II) and Zn (II) ions from aqueous solution was studied. The effect of contact time, pH, and adsorbent dose were evaluated and the results indicate that optimum adsorption occurred at pH 4 and 5 for Zn (II) and Pb (II) respectively. Kinetic, mechanisms, and thermodynamic parameters have been estimated. Result shows that Pseudo- second order favored the adsorption process with R^2 values of 0.999 and 0.9997 for Pb (II) and Zn (II) ions respectively. Weber and Morris Intraparticle model gave a better fit with intraparticle rate constant, K_{id} of 94.47 and 89.65 min^{-1} for Pb (II) and Zn (II) ions respectively. Gibbs free energy, ΔG^o, enthalpy change, ΔH^o and entropy change, ΔS^o values shows that the adsorption process of these metal ions onto tea seed shell (TSS) is feasible, endothermic, and spontaneous in nature. Regeneration of TSS was carried out using 0.2M HCl as eluent and reused for subsequent adsorptions-desorption cycles. These results indicate that Camellia sinensis seed shell can serve as a low cost adsorbent in scavenging Pb (II) and Zn (II) ions from solutions containing same.*
Keywords: *Tea seed shell, lead, kinetics, adsorption, entropy, heat change*

I. Introduction

The potential health hazard posed by the increasing load of heavy metals in various aspects of the environment is not unknown. Heavy metal contaminations abound in the aqueous waste streams of many industries such as textile mills, mines, tanneries, plastic manufacturing factories, fertilizer plants, as well as non-point sources. The dye mill for example generates a large volume of colored effluent, which if not properly treated, may affect photosynthetic activities in aquatic life because of reduced light penetration as well as its inherent toxicity[1]. The removal of heavy metal ions and dyes from wastewaters and effluents in an economic fashion remains an important problem as industrialists have spent much and other stakeholders to get their effluents treated before discharge into large water bodies. There is need for an economic and effective technique for removing heavy metal ions from wastewater and this has resulted in the search for other non- conventional materials for their removal.

Widely used techniques aimed at preferential removal of heavy metals are ion exchange and/or precipitation methods, which require the use of chemicals that are rather exorbitantly high in price and hence uneconomical. While chemicals and synthetic resins are regarded as the more active forms of adsorbents, cellulosic materials cannot be overlooked, since evidence abound that they act as low capacity ion-exchange mediums[2]. However, more economic agricultural by-products are available at little or no cost that has been reported to posses the sorptive characteristics for heavy metal ions[3-11].

In the continuous search for alternate systems for water/effluent treatment for heavy metal ions, Tea seed shell obtained from the plant Camellia sinensis, which is considered an agricultural waste product, possibly stands a chance for potential utilization. Over the last few years, efforts have been made to utilize tea seed oil as oleochemical in polymer processing[12] but no data exists for the shell as an adsorbent. Tea (*Camellia sinensis*) is an evergreen tree plant, which belongs to the camellia genus in Theacea family. The fruit is a capsule with a locullicidal dehiscence, 10-15mm high and 2-3cm in diameter with between one and four loculli, each containing one or two seeds, which is spherical to hemispherical, and brown when mature. The leaf contains a number of bioactive molecules responsible for the health promoting properties of tea such as flavonoids. The tea industry generates a large volume of shells, which has not been adequately tapped into in tea plantations. This study was thus a continuous effort at exploiting opportunities for agricultural waste management. This paper therefore reports, the performance of tea seed shell as an adsorbent for lead (II) and zinc (II) ions.

II. Materials and Methods

2.1 Preparation of adsorbent

Tea (Camellia sinensis) seed shells were 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, were sun-dried until constant weight was obtained and chopped into small particle size. The dried sample was ground then sieved through sieves with different mesh sizes and retained until ready for use. The lead and zinc salt used for this study were of analytical grade of Pb $(NO_3)_2$ and Zn $(NO_3)_2.6H_2O$ supplied by BHD chemicals Ltd., Poole, England.

2.2 Preparation of Adsorbate

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 Pb^{2+} and Zn^{2+} metal ion of 1000 mg/L concentration were prepared using lead nitrate ($Pb(NO3)_2$) and Zn $(NO_3)_2.6H_2O$ respectively. From the stock solution, aliquot of 100 m/L (initial concentration) of metal ions was prepared by serial dilution with deionized water.

2.3 Adsorption Experiments

The batch adsorption experiments were carried out in Erlenmeyer flasks (100 mL) on the removal of Pb (II) and Zn (II) ions from aqueous solution to study the kinetics, mechanisms, and thermodynamics. In the kinetic experiments, the batch adsorption studies were carried out by shaking 0.5 g of the tea seed shell (TSS) with 25 ml of different concentrations (10 – 100 mg/L) at varying pH (1-8) containing the metal ion for various contact times (10 -180 minutes) over a range of temperatures. 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 HNO_3 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 the solution by TSS was taken as the difference between initial and residual concentrations of the metal ion. All the experiments were carried out in duplicates. Percentage removal of the metal ions was estimated using the following equation:

$$RE = C_i - C_f / C_i \times 100 \qquad [1]$$

Where,
RE = Removal efficiency
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[13] :

$$q_t = (C_i - C_f)\, v / m \qquad [2]$$

where, v = volume of aqueous solution used for adsorption
m = mass of adsorbent used.

2.4 Kinetic modeling

The kinetics of Pb (II) and Zn (II) adsorption were subjected to the three models: the Lagergren first-order according to Lagergren described by [14], pseudo-second-order [15] and intra-particle diffusion models according to Weber and Morris (1963) as described by [17, 18]. The explored models were followed according to the following equations:

2.4.1 Lagergren first-order equation:

$$\text{Log}\,(q_e - q_t) = \log (q_e) - (k_1 /2.303)\, t \qquad [3]$$

where:

q_e and q_t are adsorption capacity at equilibrium and time t, respectively (mg.g-1). k1 = 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.

2.4.2 Pseudo second-order equation:

$$(t / q_t) = 1/k_2 q_e^2 + (1/q_e)\, t \qquad [4]$$

where:
k_2 = rate constant of the Pseudo second-order (g.mg-1.min-1). The plot of (t/qt) 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[19].

2.4.3 Intraparticle diffusion model

The intraparticle diffusion model can be expressed according to Weber and Morris, (1963) as:

$R = K_{id} (t)^n$ [5]

A linearized form of the equation is:

$R = \log K_{id} + n \log (t)$ [6]

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 considered as a rate factor [20].

2.5 Desorption studies

Tea seed shell (0.1 g) was saturated with 50 mL of Pb (II) solution in Erlenmeyer flask for 180 minutes at pH 5. To elute Pb (II) that was adsorbed, TSS was washed copiously with deionized water severally. This was followed by treatment with 0.2M HCl, and shaken for 180 minutes at 29^0C. The supernatant was removed and analyzed spectrophotometrically for Pb (II). Similarly, to elute Zn (II) that was adsorbed, the procedure was carried out at pH 4.

III. Results and Discussion

3.1 Adsorption capacity

The amount of Pb^{2+} and Zn^{2+} ions was calculated through equation 1 and the results presented in Figure 1. The effect of contact time on adsorption by TSS indicates that 30 minutes was required for the metal ions to achieve optimum adsorption. For Pb (II), it required 30 minutes to remove 95% of the ion from aqueous solution while it took the same time period to remove 97.5 % Zn (II) from aqueous solution. From the plot, it can be seen that metal ion uptake increases with contact time for the adsorbent, however, adsorption of both ions tends to decrease after 30 minutes, and no significant increase was observed even after 180 minutes contact period. It is clear that TSS can adsorb an appreciable amount of these ions within a short period.

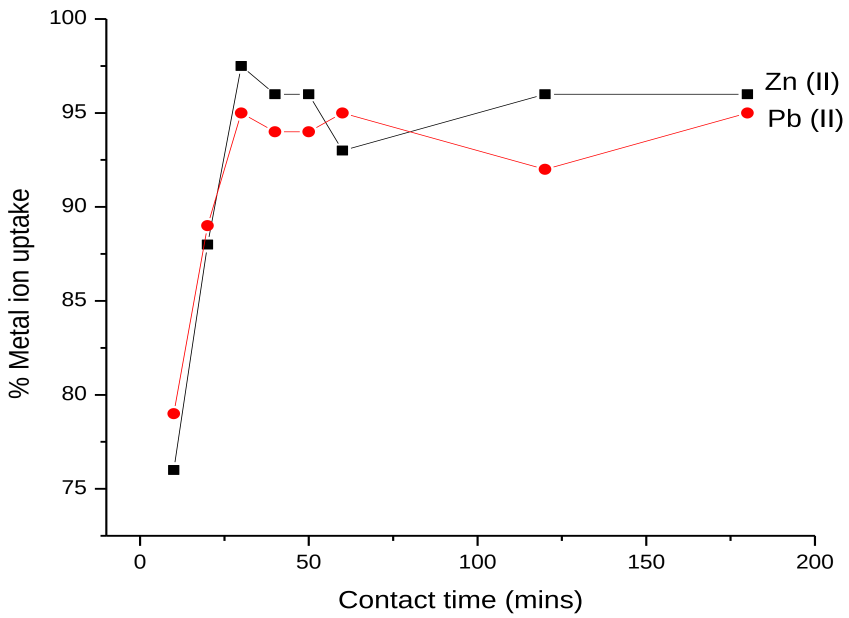


Figure 1. Effect of contact time on the adsorption of Pb^{2+} and Zn^{2+} by Tea seed shell

3.2 Effect of pH on adsorption

It is well known that the adsorption of metal ions by adsorbents is pH dependent. Metal ion adsorption on the surface of an adsorbent is described in terms of molecular mechanisms, which may probably include cation exchange in the interlayer and specific adsorption that results from surface complexation. Metal ion complexation is affected by hydrogen ions because of the affinity they have for the adsorption sites. The effect of initial pH on the adsorption of Pb and Zn ions by TSS was studied and the result shown in Figure 2. From the figure, it is observed that there was an increase in the adsorption of the heavy metal ions with increase in pH from 1- 4, where maximum adsorption of 87% was recorded for Zn and 1-5 and with maximum adsorption of 96% for Zn (II) and Pb (II) respectively. TSS contains functional groups that are favorably disposed to Pb (II) and Zn (II) ion. As the pH of the solution increased, these functional groups are exposed thereby favoring the attraction of the metal ions with positive charge, hence the increased adsorption. At this pH, the surface charge on the adsorbents increases, thereby enhancing the physical adsorption on the functional groups.

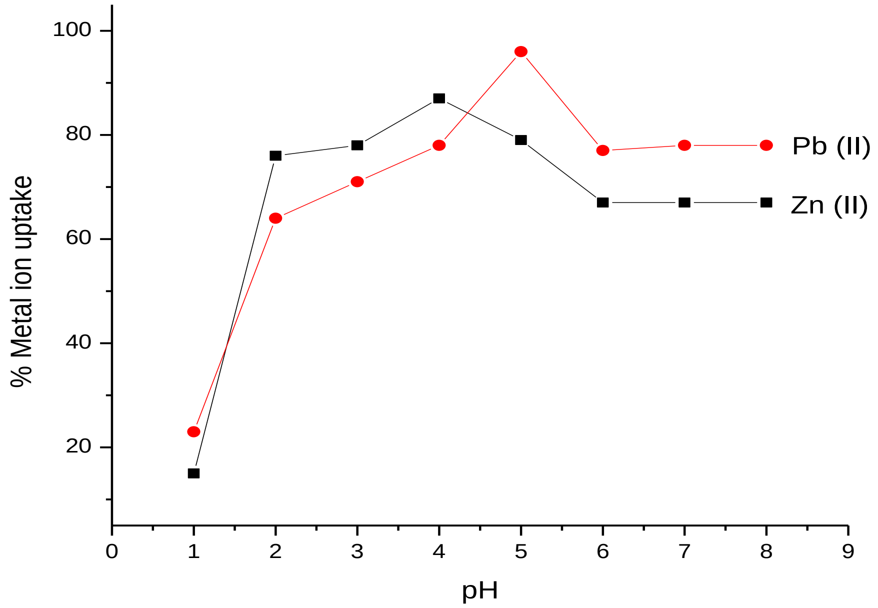


Figure 2. Effect of pH on the adsorption of Pb (II) and Zn (II) ion onto Tea seed shell

3.3 Effect of adsorbent dose

Heavy metal ions adsorption is also a function of the quantity of adsorbent available for adsorption. Figure 3 shows the effect of adsorbent dose on the percentage removal of Pb (II) and Zn (II) ion onto Tea seed shell. It is observed that percentage removal of metal ion increased with increase in adsorbent weight between 0.25 and 0.5 g for both metal ions. The optimal level of Pb and Zn ions removal by TSS is thus established at 0.5 g. It was noted that a higher percentage of the Zn (II) was removed at this dosage than for Pb (II).The observed difference in the level of adsorption may be explained based on the difference in ionic radii of the two metals. Adsorption of heavy metals having smaller ionic radius has been reported to be superior [21].

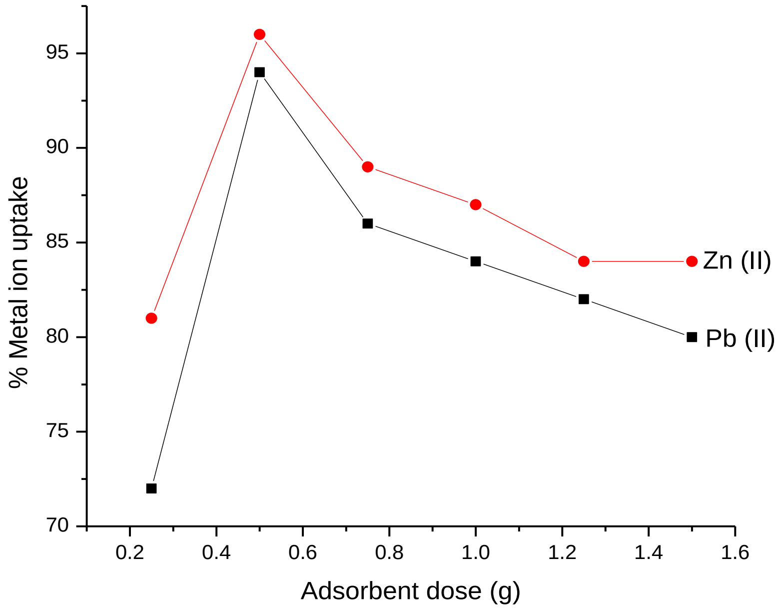


Figure 3. Effect of adsorbent dose on the uptake of Pb (II) and Zn (II) by Tea seed shell

3.4 Adsorption Kinetics

Kinetic data obtained from the study was fitted to the equations (3-6). The results obtained indicate that only the pseudo second order equation was able to satisfactorily fit the kinetic data for tea seed shell on Pb (II) and Zn (II) in the whole data range and as such results presented. A plot of the data range is shown in figure 4, while the kinetic parameter and correlation coefficient are shown in table 1.

Table 1 Pseudo second order parameters for Pb (II) and Zn (II) adsorption by tea seed shell.

Constants	Pb (II)	Zn (II)
K_2 (g/mg min)	0.6301	0.581
q_e (mg/g)	21.45	40.98
R^2	0.9999	0.9997

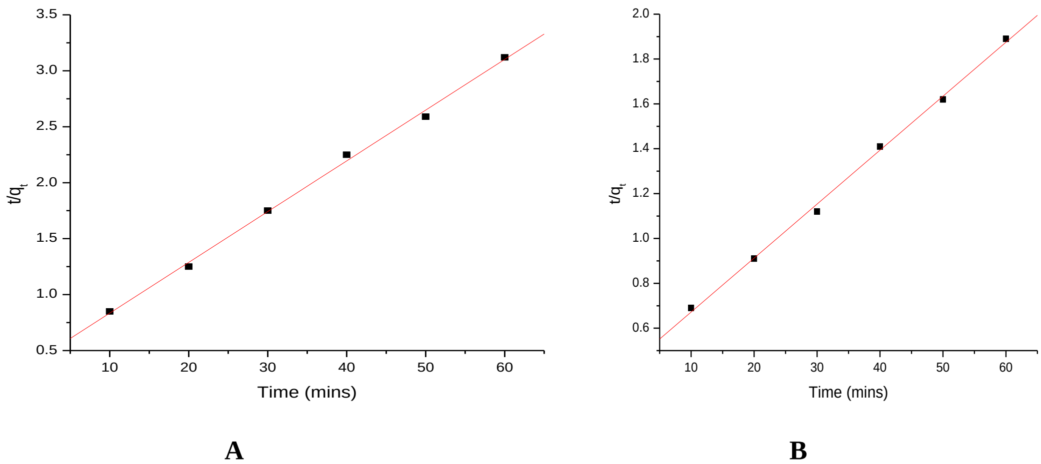


Figure 4. Pseudo –second order kinetic plot of the adsorption of A [(Pb (II)] and B [Zn (II)] by Tea seed shell

The Pseudo second order equation was used, and plots of t/q_t versus t gave linear graphs from which q_e and K_2 were estimated from the slope and intercept respectively of the plots. The correlation coefficients were 0.9991 and 0.9778 for Pb (II) and Zn (II) ions respectively. This suggests that pseudo -second order kinetics can be considered as the sorption process for Pb (II) and Zn (II) onto tea seed shell.

3.5 Weber-Morris intraparticle diffusion model

Weber- Morris intraparticle model was used to analyze the experimental data in order to estimate its fitness with the experimental data. Table 2 presents the kinetic parameters of the data. It was observed that R^2 values for the two metal ions are in the range of 0.9309 - 0.9889. As shown in the table, K_{id} which is the rate factor of the adsorption mechanism is high for both metal ions. The implication of this is that the adsorbent is effective in the uptake of these metal ions.

Table 2 Kinetic parameters of Pb (II) and Zn (II) intraparticle diffusion onto tea seed shell

Constants	Pb (II)	Zn (II)
N	0.0041	0.0067
K_{id} (min^{-1})	94.47	89.65
R^2	0.9799	0.9889

3.6 Adsorption Thermodynamics

To investigate the thermodynamic behavior of the adsorption of Pb (II) and Zn (II) ions onto modified TSS, thermodynamic parameters such as change in free energy (ΔG^o), change in enthalpy (ΔH^o), and change in entropy (ΔS^o) of the adsorption process were estimated. The adsorption of Zn^{2+} and Pb^{2+} onto the adsorbents can be regarded as a heterogeneous and reversible process when equilibrium is reached. The apparent equilibrium constant for the process can be shown [22, 23] to be:

$$K_c = C_{ad}/C_e \qquad [7]$$

Change in Gibbs free energy of adsorption process is as follow:

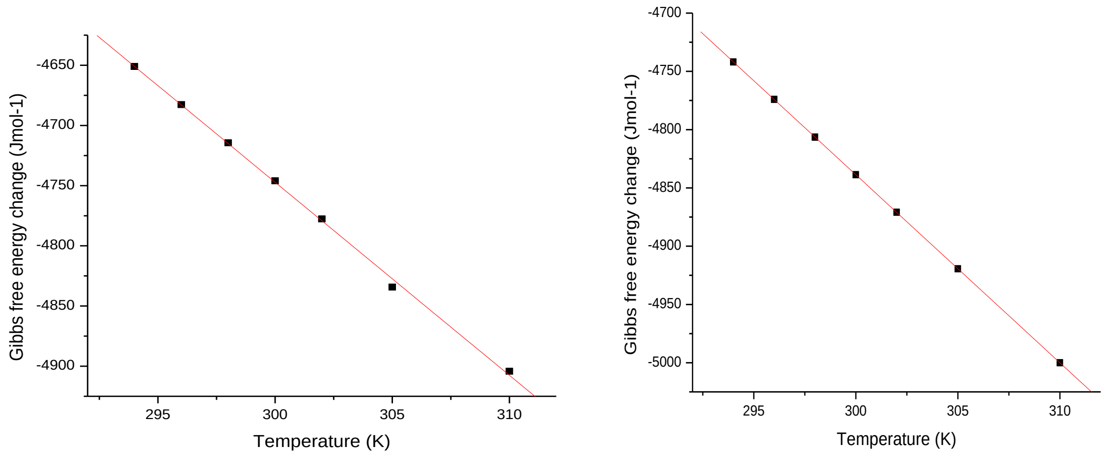
$$\Delta G^o = -RT \ln Kc \qquad [8]$$

Where ΔG^o = standard Gibbs free energy change of adsorption
R =universal gas constant (8.314 $Jmol^{-1}k^{-1}$)

T = temperature (K)

From thermodynamics,
$\Delta G^o = \Delta H - T\Delta S$ or $\Delta G^o = - \Delta (T) + \Delta H$ [9]

A plot of T against ΔG^o gives a straight line with slope $-\Delta S$ and intercept of ΔH.
For this study, a plot of T against ΔG^o is shown in figure 5.



A **B**

Figure 5 Change Gibbs free energy with temperature of A [Pb (II)] and B [Zn (II)] adsorption by tea seed shell

From the plot, a slope of -16.14 $Jmol^{-1}K^{-1}$ was obtained and an intercept value of 45.12 $kJmol^{-1}$ for Pb (II) while Zn (II) has slope of -16.20 $Jmol^{-1}K^{-1}$and intercept value of 45.23 $kJmol^{-1}$. This implies that the entropy and enthalpy values are 16.14 $Jmol^{-1}K^{-1}$ and 45.12 $kJmol^{-1}$ for Pb and Zn ions respectively. It is obvious that the value of the free energy decreases with increase in temperature for the removal of both metal ions. The implication of this is that the adsorption of Pb (II) and Zn (II) onto TSS is endothermic and the negative values of ΔG^o indicate the spontaneity of the adsorption process. The positive value of standard entropy, ΔS^o, indicates increased disorderliness at the solid/solution interface occurring in the adsorption process, thereby reflecting the affinity of TSS toward the metal ions. The overall free energy change obtained for Pb (II) and Zn (II) ions are -4.910 and -4.990 $kJmol^{-1}$ at 310 K respectively. This negative result also supports the physiosorption nature of the adsorption of Pb (II) and Zn (II) onto tea seed shell.

3.7 Adsorption-Desorption of TSS

The purpose of any adsorbent is its ability to be used repeatedly; therefore, the stability of such adsorbent must to be guaranteed. The reusability of TSS was confirmed based on the adsorption-desorption ability. High efficiency of Pb (II) and Zn (II) were recovered in the regeneration process thus confirming its viability. The reproducibility of TSS was also confirmed when several adsorption-desorption cycles were performed. Results obtained revealed 94.1 and 97.3% for Pb (II) and Zn (II) respectively in the first cycle.

IV. Conclusion.

The study investigates the sorption of Pb (II) and Zn (II) ions onto tea seed shell. From the results, pH affects the adsorption of these metal ions onto TSS. The rate of adsorption followed the pseudo second order kinetics. Thermodynamic results confirm the endothermic and spontaneous nature of the adsorption process. Adsorption-desorption result also revealed the viability of TSS. It is therefore obvious that TSS is an effective adsorbent for heavy metal ions removal.

Acknowledgement

The authors thank the management of the Cocoa Research Institute of Nigeria and the Federal University of Agriculture, Abeokuta for the use of their laboratories.

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