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Isotherm studies on biosorption of As(III) and Hg(II) ions from aqueous solution using cellulosic biosorbent derived from Okra (*Abelmoschus Esculentus*) stem.

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Abstract— *An effective biosobent was developed from cellulosic biosorbent produced from Okra stems and their various biosorption characteristics were studied for removal of toxic metal ions As(III) and Hg(II) from their aqueous solutions. A series of experiments were conducted in a batch system to assess the effects of the system variables such as pH, initial metal ion concentration and temperature. The biosorbent studied exhibits high efficiency for the metal ions adsorption. The equilibrium adsorption data were analyzed by the Langmuir, Freundlich, Temkin and Dubnin-Rudishkelvish isotherm models. The equilibrium data indicates the following order to fit the isotherms: Freundlich is greater than Temkin is greater than Dubin-Radushkelish is greater than Langmuir. The maximium adsorption capacity Hg(II) and As(III) ions were found to be 6.180 mg/g and 7.930 mg/g, 0.802 mg/g and 14.104 mg/g for UOS and MOS respectively. It is also found that unmodified okra stem showed maximum adsorption for* Hg^{2+} *at pH 6 (9.918 mg/g) and pH 8(9.9938 mg/g). Also As(III) ions showed maximum adsorption at pH 4(9.6816) for unmodified and pH 8(9.9954 mg/g) for modified okra stem. Different thermodynamic parameters, like Gibbs free energy (*ΔG*), enthalpy (*ΔH*) and entropy (*ΔS*) of the adsorption process have also been evaluated. The thermodynamic parameters of As(III) and Hg(II) ions biosorption indicated, the process was spontaneous and endothermic. The results showed in percent mean value of sorption for As(III) and Hg(II) ions as 99.37 % and 99.96 % for neat Okra cellulosic biosorbent, and 99.95 % and 99.96 % for modified Okra cellulosic biosorbent. These results showed that the neat material can be effective without introducing any new chemical substances to the environment through the modification exercise. The results indicated that the biosorbent studied was found to be a promising alternative for the adsorption of As(III) and Hg(II) ions from aqueous solution. The sorption affinity for the two metal ions studied showed As(III) > Hg(II).*

Keywords— Okra cellulosic material; sorption; biosorbent; As^{3+}; Hg^{2+}; sorption model.

1. INTRODUCTION

The rate at which industrial effluents containing toxic substances are discharged into the environment especially water bodies have been on the increase and as a result, the aquatic environment is under stress due to growing population, technological development, urbanization and economic growth [1]. The heavy metal ions are not only toxic to living organisms in water, but also causes harmful effects to plants, animals and humans through food chain transfers. The main source of heavy metal contamination is from various industrial, agricultural and domestic activities, such as mining operations, metal smelting and plating, electric device manufacturing, power plants, waste incinerators, battery manufacturing, domestic effluents and agricultural run-off [2].
Since most heavy metal ions are accumulative in nature, effective removal of heavy metal ions from aqueous solutions and waste effluents through various technologies (physical and chemical) is important in the protection of environmental quality and public health [3]. Various conventional methods have been used in the removal of heavy metal ions, including chemical precipitation, reverse osmosis, ion exchange, solvent extraction, evaporation, electrolysis and adsorption [4]. Most of these methods with exception of adsorption have some disadvantages such as high cost, incomplete removal, high reagent requirement and generation of toxic sludge. The major advantages of adsorption over conventional treatment methods include low cost, high efficiencies, minimization of chemical and biological sludge. Also these methods have significant disadvantages, which include: incomplete removal, high energy requirements, production of toxic sludge or waste products that also require further disposal and become economically unviable for the removal of heavy metals at lower concentration [5].

Moreover, either chemical or physical method has its merits and limitations in application and they are often limited by technical and economical issues [6]. These toxic substance especially heavy metals are non-biodegradable, bio-magnifies in the food chain and are accumulated in tissues [7]. They have the ability to bind with protein molecules and prevent DNA replication and subsequent cell division [8]. Therefore, there is need for cost effective alternative technology to remove metals from aqueous system because of the problem associated with conventional methods. The removal of heavy metal ions from wastewater is a very difficult task due to the high cost of treatment methods

This is why okra stem, which is a biological and agricultural waste biomass, is being tested for its potential to remove metal ions from aqueous medium. This biosorbent is readily available, economically feasible and above all biodegradable.

Okra is cultivated for its green non-fibrous fruits or pods containing numerous seeds. The fruit are harvested when immature and eaten as vegetable .The roots and stems are used for clarification of sugarcane juice from which gur or brown sugar is prepared [9]. Mature fruits and stem containing crude fiber are used in the paper industry. Besides being low in calories, okra has plenty of vitamins, calcium, potassium and other mineral matters. The mucilage and fiber found in okra helps adjust blood sugar by regulating its absorption in the small intestine [10].

A good adsorbent should have the following characteristics: It should be highly porous, should have large surface area with more specific adsorption sites and should require less time for adsorption equilibrium.

Plant wastes are cheap as they have no or very low economic value [11]. The chemical modification of plant wastes as adsorbents can solve problems such as low adsorption capacity, high chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. .

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. The ability of metals to disrupt the function of essential biological molecules such as protein, enzyme and DNA is the major cause of their toxicity [12].

Displacement of certain metals essential for cell growth by similar metal is another cause of toxicity. In this study arsenic and mercury will be examined due to their major impact on the environment.

Mercury

Mercury exist in three forms; elemental mercury, organic and inorganic mercury. Sources of mercury include metallurgical industries [13]. Mercury is used in various products such as batteries, electrical switches, fluorescent light bulbs, mercury lamp and paints.

Toxic levels of mercury have been associated with tremorgngivits, psychological changes, spontaneous abortion, congenital malformation, brain and central nervous system damage [14].

Arsenic

Arsenic pollution are from the discharge of various industries such as smelting, petroleum-refining and ceramic manufacturing industries, pesticides, herbicides [15]. Harmful effects of arsenic pollution has two division-acute poisoning which includes cancer of the skin, intense abdominal pain, nausea, diarrhea resulting from gastro-intestinal tract damage. Chronic poisoning include: anaemia and leukocytopenia [16].

In this study, chemically modified and unmodified cellulosic material(Okra stems) were used as biosorbent in the removal of metal As^{3+} and Hg^{2+} from aqueous solutions in a batch sorption system. The effects of pH, initial metal ion concentrations and temperature of the unmodified and modified okra stem will be investigated to determine the most suitable adsorption isotherms for the adsorption process for Hg and As ions removal from aqueous solutions.

2. MATERIALS AND METHODS.

The adsorbent used for this research were collected from Olokoro, Abia State. Synthetic wastewater was employed for the sorption studies. All reagents used were of analytical grade. Amoung them are 0.1 M NaOH, 0.1 M HNO_3, HgCl , As_2O_3, absolute ethanol and Toluene diisocyanate. 1000 mg/L each of stock solution of analytical graded $HgCl_2$ and As_2O_3 was prepared by dissolving exact quantity of the salts in deionized water. The range (10 to 50 mg/L) of concentrations of Hg^{2+} and As^{3+} was prepared from the stock solution. The initial concentration of metal ion solutions used for the sorption study was 50mg/L.

Preparation of the adsorbent.

The Okra stems collected were sun dried, cut and ground using an electric blender and sieved to a particle size 50µm.

Activation of the Adsorbent

The biosorbent was activated using alkaline pulping process. Alkaline pulping/kraft pulping process involve the extraction of cellulose from wood by dissolving the lignin that binds the cellulose fibres together.

The sieved samples were soaked in 50% industrial NaOH solution (White liquor) for seven days for effective pulping. This is to enable the white liquor chemically dissolve the lignin that binds the cellulose fibers together in the okra stem. After the seventh day, the waste liquor known as black liquor from the pulping process was separated from the pulp. The pulp obtained was washed with plenty of deionized water until a pH of 7.0 was obtained and filtered with a morcelin bag. However, the sample were re-soaked in 70% NaOH solution for 2 days, washed and re-soaked in 70% NaOH for a day. Thereafter, there were washed to a

neutral pH, filtered, air dried and stored in different containers according to their various adsorbent sizes ready for sorption studies. This activated adsorbent was termed unmodified Okra stem (UOS).

Chemical modification of the adsorbent

Okra stem was chemically modified by toluenediisocyanate (TDI) . About 50g of the pulp was weighed from the air-dried activated Okra stem into a refluxing flask, and 150ml of TDI added into it. The mixture was reflux for 30 min before 20 ml of a blowing agent (water) was added, and refluxed for an hour. After which the content was filtered and the residue dried. This adsorbent was termed modified Okra stem (MOS). The okra stem was first pre-treated by pulping with ethanolic sodium hydroxide and further modified with Toluenediisocyanate (TDI) in order to create a large surface area to enhance the binding sites on the modified okra stem and increase the efficiency of the biosorbent for removal of mercury and arsenic ions from aqueous solutions.

Batch adsorption studies

Experiments were conducted in 5 different 250 ml Erlenmeyer flasks containing 30 cm3 varied concentration (10, 20, 30, 40 and 50 mg/L) of Hg(II) and As(III) ions and adsorbent seize of (50 µm of unmodified and modified okra stem) dosage of 0.125 g was added to the different flasks. Flasks were agitated using a shaker, the mixture filtered using Whatman No.41 filter paper after 120 min and the filterate analysed spectrophotometrically using UNICAM(Solar AAS 500) atomic absorption photospectroscopy and at different pH (2, 4, 6, 8 and 10) agitated for 120 min and filtered.

3. Data Analysis.

The amounts of Hg(II) and As(III) ions adsorbed by the adsorbents during the series of batch investigations were determined using a simplified mass balance equation.

$$q_e = (C_i - C_e)\,V/m \text{ in mg/g} \quad (1)$$

Where q_e is equilibrium sorption capacity (mg/g), C_i is Initial concentration in (mg/L), C_e Equilibrium or residual concentration after adsorption in (mg/L), V is volume of adsorbate solution in (L) and m is mass of the adsorbent in (g).

4. Results and Discussions.

Effects of pH.

The effect of the pH on the adsorption of Hg^{2+} and As^{3+} onto the unmodified and modified okra stem are shown in figure 1 and 2. The influence of pH on adsorption of these metals onto unmodified and modified okra stem was investigated by varying the pH from 2 to 10 and keeping the volume of metal ion solution constant at a temperature of 303K and agitation time of 120 min. Results show that the amount of metal ion adsorbed from the solution by the adsorbent increased from pH 2 to 6 for unmodified and from 2 to 4 for modified okra stem. It is observed that after the optimum pH was attained, there was a decrease in sorption. At low pH, the protons compete with the metal ions for the binding sites on the adsorbent surface leading to a reduced adsorption of the metal ions by the adsorbent as a result of electrostatic repulsion effect. At higher pH, the proton concentration decreases, thereby creating more binding sites on the adsorbent leading to enhanced metal uptake. Comparing the sorption capacities of the unmodified and modified okra stem, it is found that unmodified okra stem showed maximum adsorption for Hg^{2+} at pH 6 (9.918 mg/g)(pH 10: 9.956 mg/g) and pH 8(9.9938 mg/g). Also As^{3+} showed maximum adsorption at pH 4(9.6816) for unmodified and pH 8(9.9954 mg/g) for modified okra stem. The adsorbents generally show affinity for the metal ions in this order: $As^{3+} > Hg^{2+}$ at the initial concentration of 50mg/L used.

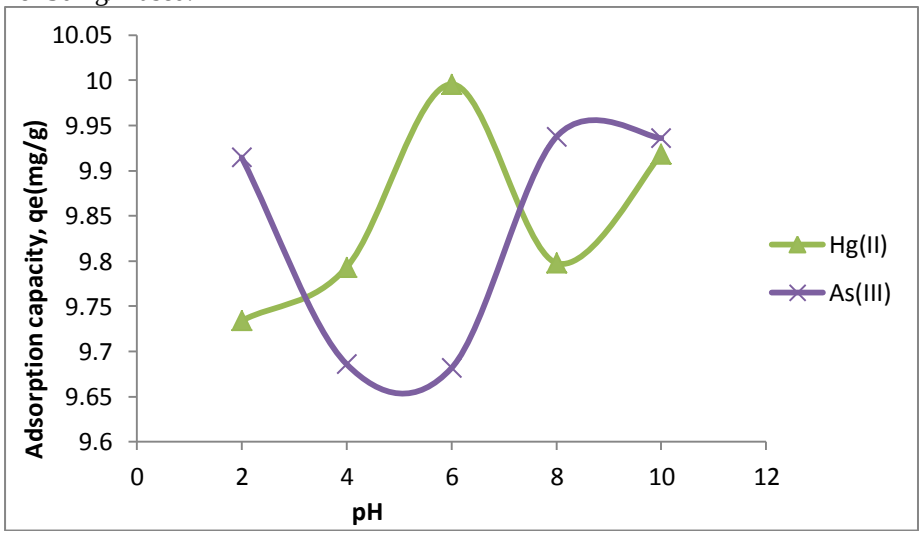

Figure 1: Plot of adsorption capacity versus pH for unmodified okra stem (UOS)

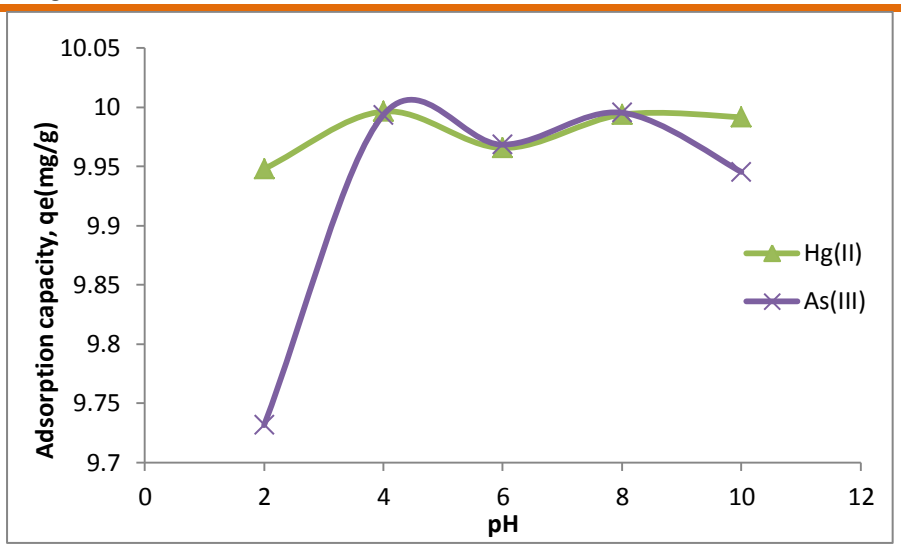

Figure 2: Plot of adsorption capacity versus pH for modified okra stem (MOS)

Effect of initial metal ion concentrations.

The effect of initial concentration on the amount of Hg^{2+} and As^{3+}adsorbed by the adsorbents are shown in Figures 3 and 4. From Figures 3 and 4, it can be observed that as metal ion concentration increased from 10mg/L to 50mg/L, adsorption capacity for both unmodified and modified okra stem increased to a maximum where there is saturation for all the metal ions used in the study. This observation is in order because at lower metal ion concentration, adsorption sites may not have been saturated. However, at higher concentrations, the adsorption sites are saturated, leading to the decrease in the adsorption efficiency of the adsorbents for the metal ions. The amount of Hg^{2+} and As^{3+} adsorbed onto unmodified okra stem increased from (1.9992 mg/g and 1.9989 mg/g) to (9.9978 mg/g and 9.9909 mg/g) in the concentration range of 10mg/g to 50mg/g respectively. For the modified okra stem, adsorption capacities for these metals increased from (1.9996 mg/g and 1.9989 mg/g) to (9.9990 mg/g and 9.9978 mg/g). Comparing the sorption capacities of the biosorbents, it is observed that modified okra stem showed better adsorption for the two metals under the conditions of our study. It is also observed that the amounts of Hg^{2+} and As^{3+} adsorbed for both adsorbents were high. This may be due to nature of the anion of the metal salt used. $HgCl_2$ and As_2O_3 are found to be less soluble in water. However, highly soluble compound is less easily adsorbed.

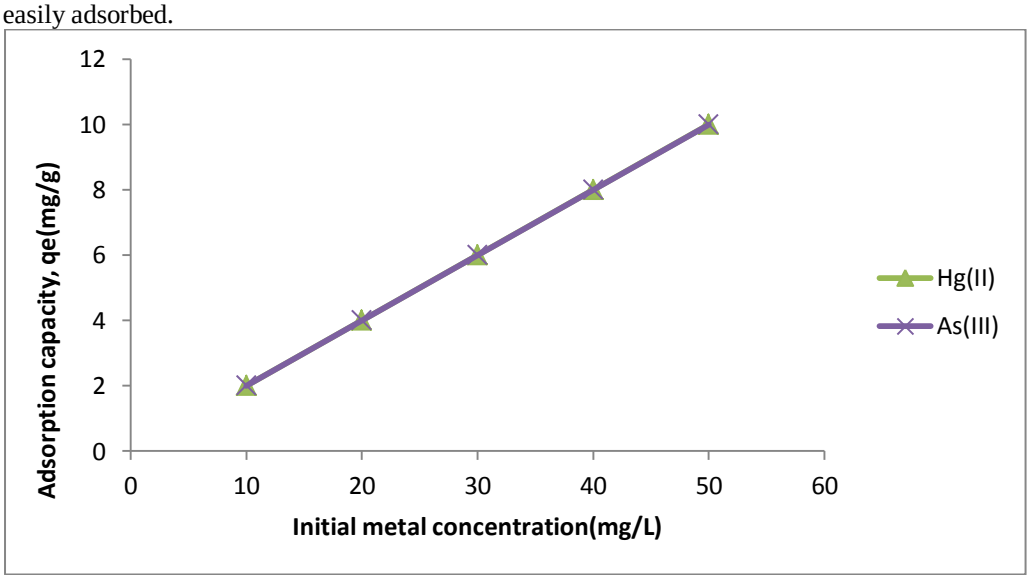

Figure 5: Plot of adsorption capacity of metal ions versus initial concentration for unmodified

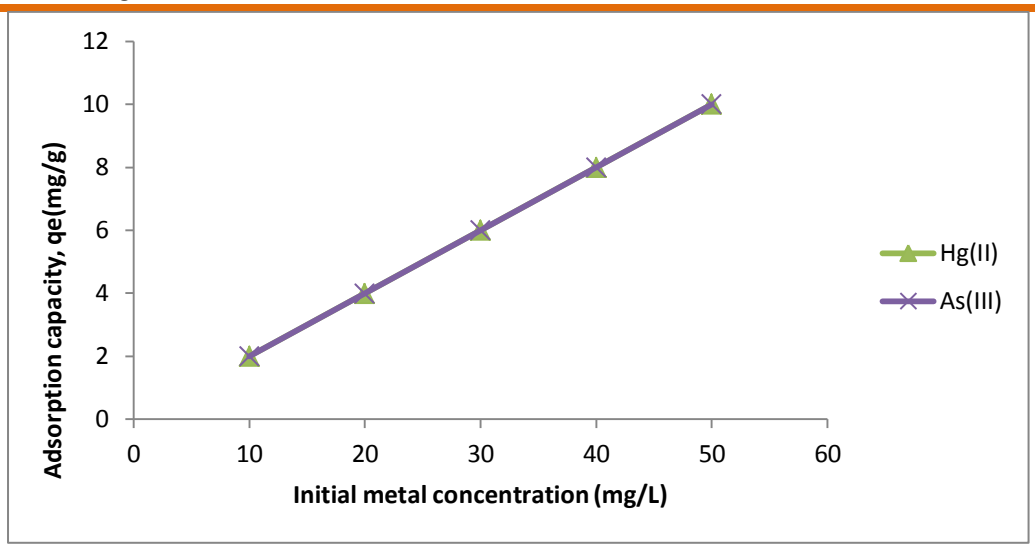

Figure 6: Plot of adsorption capacity of metal ions versus initial concentration for modified Effect of temperature.

Figures 7 and 8 showed a plot of adsorption capacity versus temperature (313,323,333,343 and 353)K. The effect of the solution temperature on the adsorption capacity was investigated for Hg^{2+} and As^{3+} ions solution at initial metal ion concentrations of 50 mg/g. The plots of adsorption capacities versus temperature for unmodified and modified okra stem are shown in Figures 7 and 8. Table 1 showed that the amount adsorbed decreased with increasing temperature for the two metal ions. This is mainly due to the decreased surface activity at a higher temperature indicating that the adsorption between the two metal ions on unmodified and modified okra stem is exothermic in nature. Similar views are reported by [17]. The reason could also be due to weakening of interactive forces between the metal ions and the adsorbent at higher temperatures which is consistent with physisorption.

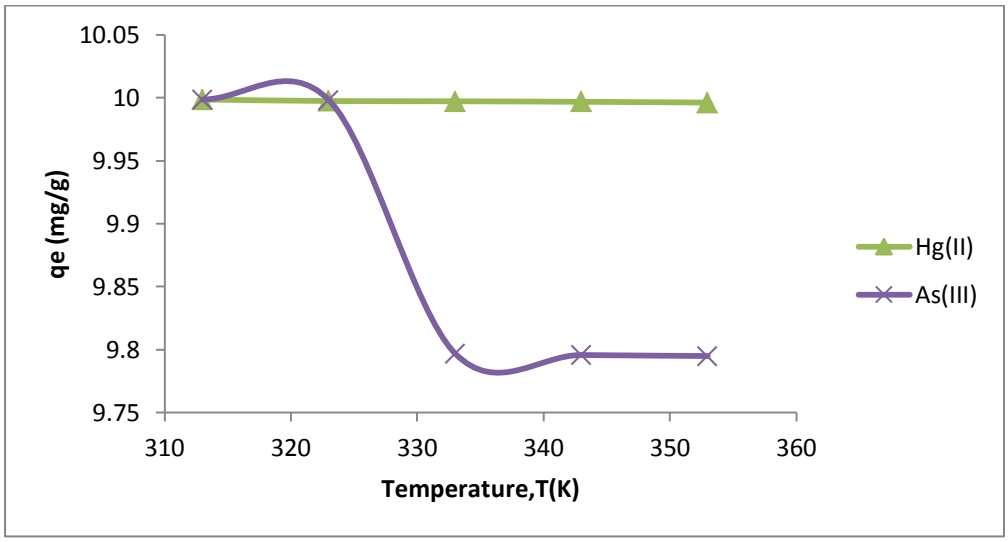

Figure 7: Plot of adsorption capacities of the metal ions versus temperature for unmodified okra stem

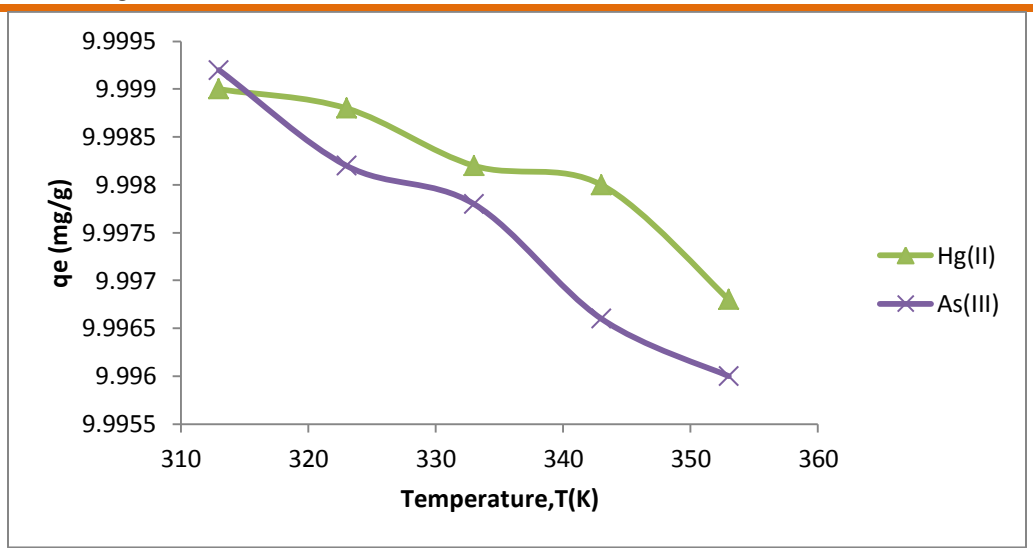

Figure 8: Plot of adsorption capacities of the metal ions versus temperature for modified okra stem

SORPTION ISOTHERMS

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. The two widely accepted equilibrium adsorption isotherms are Langmuir and Freundlich isotherm. Several other isotherm exists, such as:Temkin, Flory-huggins, Dubinin-Radushkevich, Harkin- jura, BET isotherm.

Langmuir isotherm model

The Langmuir model is based on assumptions that adsorption occurs at specific homogenous sites, energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface, and is written as:

$C_e/q_e = 1/q_{max}K_L + C_e/q_{max}$ 2

Where q_e is the adsorption capacity in mg of adsorbate per gram of adsorbent, C_e is the residual (equilibrium) metal ion concentration in solution, q_{max} is the maximum adsorption capacity corresponding to monolayer coverage and K_L is the Langmuir isotherm constant, which is related to the adsorption energy (dm^3/mg). The plot of C_e/q_e vs C_e gives a straight line with linear regression coefficients (Figure 9 and 10). From the intercepts and slopes, constant q_{max} and K_L were evaluated. A dimensionless equilibrium parameter, R_L, can express the essential characteristics of Langmuir isotherm.

$$R_L = \frac{1}{1 + KLCo} \qquad 3$$

The value of RL indicates the type of isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L > 1$): linear ($R_L = 1$); or unfavorable ($R_L > 1$). In this study, the value of R_L was less than 0.5 for As(III) ions on modified okra stem only and negatives for the rest indicating the Langmuir adsorption isotherm to be a favorable adsorption isotherm for As(III) ion only.

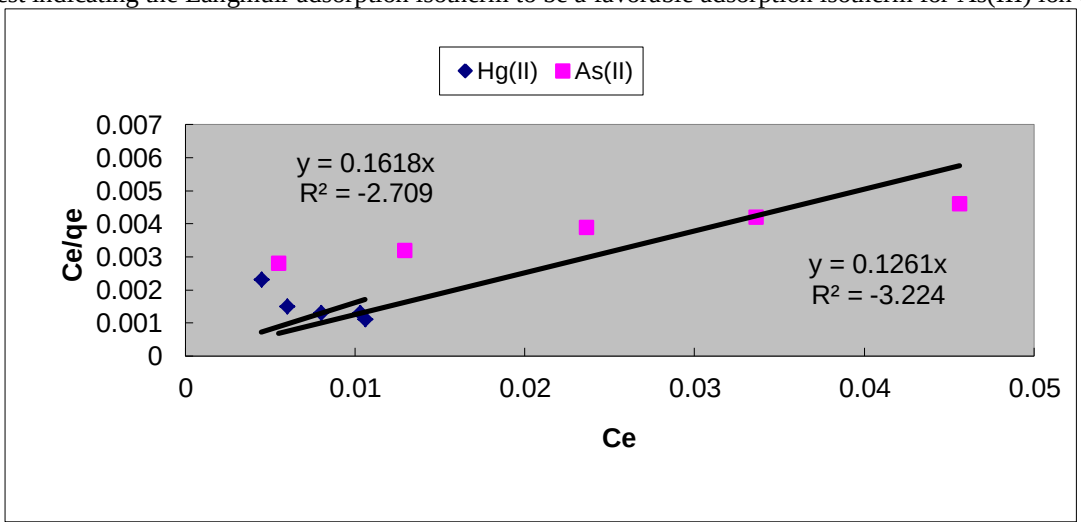

Figure 9:Langmuir isotherm of plot of Ce/qe vs Ce for adsorption of metal ions onto Unmodified okra stem

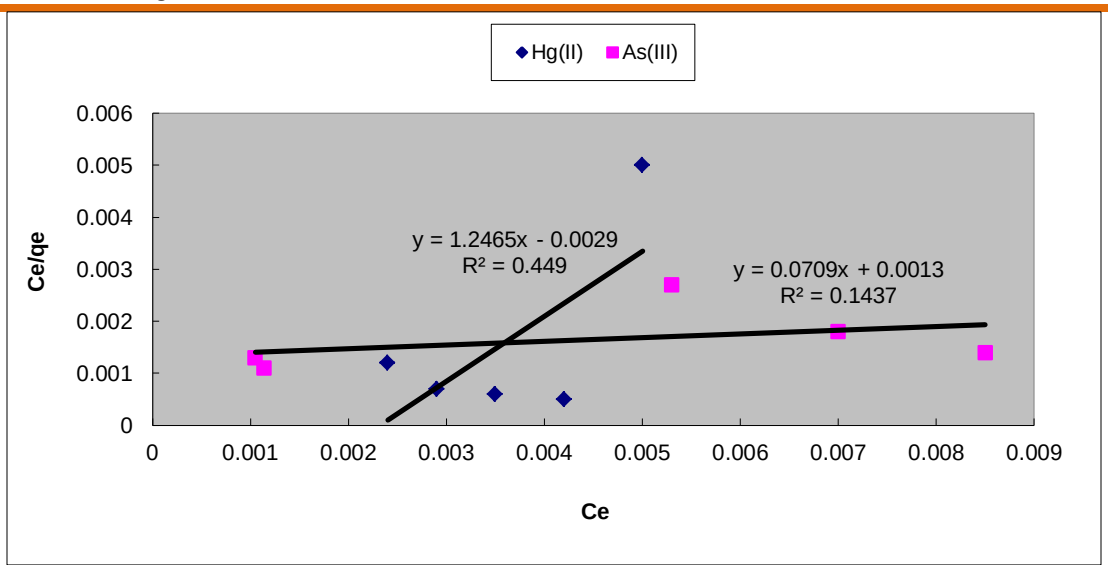

Figure 10:Langmuir isotherm plot of Ce/qe vs Ce for adsorption of the metal ions onto Modified okra stem

Table 2. Langmuir isotherm constants and correlation coefficients(R^2 values) for sorption of metal ions onto unmodified and modified okra stem

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
~~q_{max} (mg/g)~~	~~6.180~~	~~7.930~~	~~0.802~~	~~14.104~~
K_L(dm3/mg)	-	-	-421.85	54.539
R^2	-2.709	-3.224	0.449	0.144

Freundlich equilibrium isotherm

The Freundlich equilibrium isotherm assumes a heterogeneous surface with a uniform distribution of heat of adsorption over the surface. The linearised form of Freundlich adsorption isotherm is represented as:

$$\text{In} = \text{In } k_f + \text{In Ce} \qquad 4$$

where K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity(heterogeneity factor) respectively. The Freundlich plots are shown in Figures 11 and 12 which represents linear plot of $\text{In}q_e$ vs $\text{In}C_e$, according to Freundlich isotherm equation. The values of Freundlich constants are presented in Table 3. Assessment of the R^2 values for the unmodified and modified okra stem shows that the adsorption of the metal ions was best described by the Freundlich model. The correlation coefficients (R^2) were generally high for unmodified and modified okra stem, with values greater than 0.952 for Hg^{2+} and As^{3+}. The high value of the Freundlich constant K_F indicates that the adsorption process was favorable. Moreover, the high R^2 values indicate that the Freundlich isotherm clearly described the adsorption of the metal ions onto the adsorbent. According to Anusiem [18] the fit of experimental adsorption data to Freundlich model indicates that the forces of adsorption by the adsorbents are governed by physisorption.

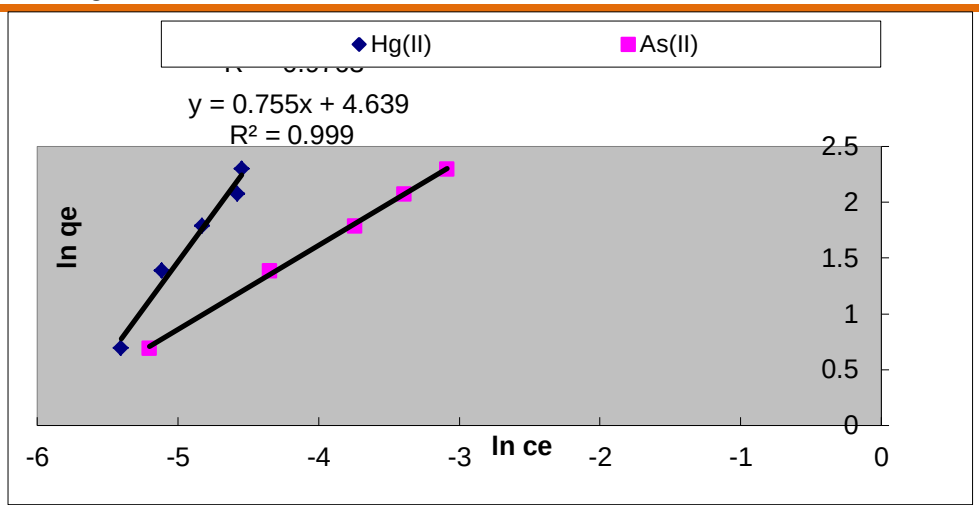

Figure 11: Freundlich plot of Inq_e vs In Ce for adsorption of the metal ions onto unmodified okra stem

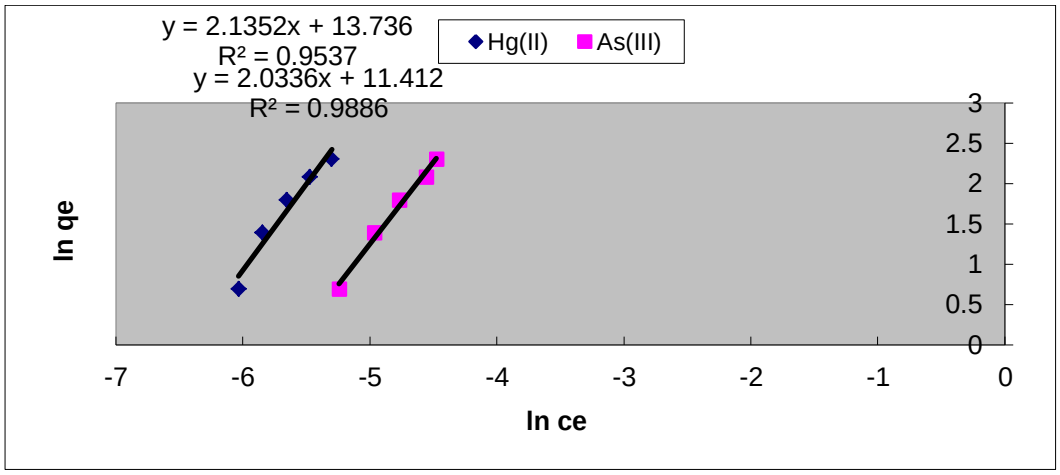

Figure 12: Freundlich plot of Inq_e vs InCe for adsorption of the metal ions onto modified okra stem

Table 3 Freundlich Isotherm constants and correlation coefficients(R^2 values) for sorption of metal ions onto unmodified and modified okra stem

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
N	0.583	1.32	0.47	0.49
K_F(L/g)	23155	103	918043	90219
R^2	0.976	0.999	0.953	0.988

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D-R) model was applied to the equilibrium data to assess the nature of adsorption process, i.e whether it is physical or chemical adsorption. The linearised D-R adsorption isotherm is represented as [19]:

$\ln q_e = \ln q_D - BD\varepsilon^2$ 5

$\varepsilon = RTIn(1 + \frac{1}{Ce})$ 6

A plot of Ce vs qe gives a straight line as shown in Figure 13 and 14 with slope of B_D and intercept of In q_D. The parameters B_D and q_D were given in table 4. Where q_D is the theoretical saturation capacity (mg/g) , is a constant relating to the adsorption energy ($mol^2K\ J^{-2}$), R is gas constant ($JK^{-1}mol^{-1}$) and T is the temperature (K). The constant B_D, gives an idea of the mean energy, E (kJ $mol^{-1}K^{-1}$), of adsorption per mole of the adsorbate as it is transferred to the surface of the adsorbent from the infinite distance in the solution and this energy is usually evaluated from the relation in equation.

$$E = \frac{1}{\sqrt{2BD}} \qquad 7$$

The adsorption is physiosorption when the energy of activation is 5 to 40 kJ/mol and chemisorptions when the energy of activation is 40 to 800 kJ/mol [20]. From table 4, it was suggested that the adsorption of these metal ions by modified okra stem is physiosorption in nature.The Dubinin-Radushkevich plots are shown in Figures 13 and 14. Figure 9 and 10 showed very low correlation coefficient (R^2) values for the unmodified okra stem for the two metal ions. D-R isotherm is not able to describe the experimental data properly for the unmodified absorbent but could do that for the modified because of the high correlation coefficients.

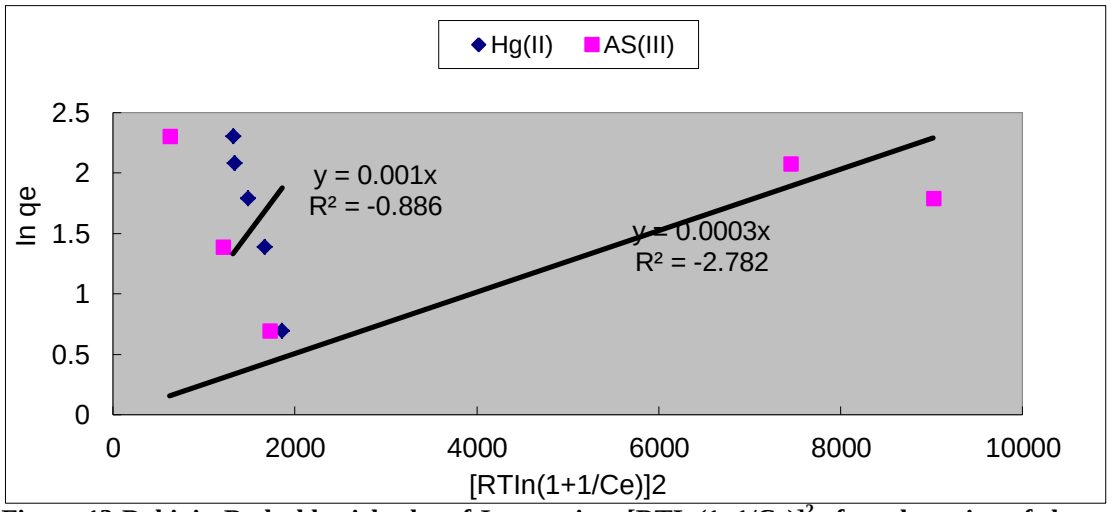

Figure 13:Dubinin-Radushkevich plot of Inq_e against $[RTIn(1+1/Ce)]^2$ for adsorption of the metal ions onto unmodified okra stem

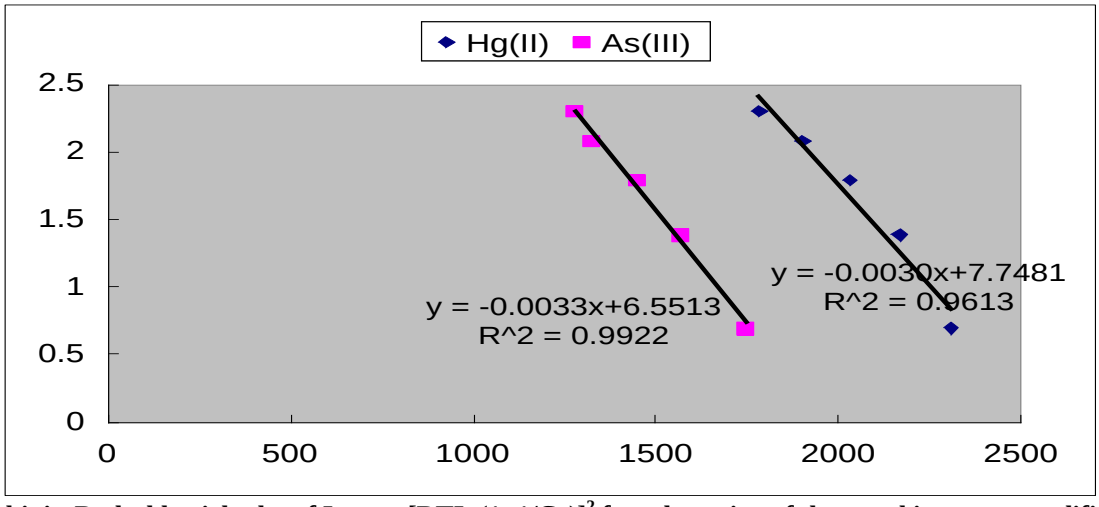

Figure 14:Dubinin-Radushkevich plot of Inq_e vs $[RTIn(1+1/Ce)]^2$ for adsorption of the metal ions onto modified okra stem

Table 5 Dubinin-Radushkevich constants and correlation coefficients(R^2 values) for sorption of metal ions onto unmodified and modified okra stem

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
$B_D(mol^2KJ^{-2})$	-0.001	0.000	0.0030	0.0033

q_D(mg/g)	-	-	2317	700
E(kJmol^{-1}K^{-1})	-	-	12.91	12.31
R^2	-0.88	-2.78	0.9613	0.9922

Temkin isotherm

The Temkin isotherm assumes the effect of some indirect interactions amongst adsorbate particles and suggests linear decrease in the heat of adsorption of all the molecules in the layer. Temkin isotherm equation is given as [21].

$$q_e = \beta_T \ln\alpha_T + \beta_T \ln Ce \qquad 8$$

A plot of Ce vs qe gives a straight line as shown in Figure 15 and 16 with slope of β and intercept of βIn α. The parameters α and β were given in table X. Where β = (RT)/b, T is the absolute temperature in Kelvin and R is the universal gas constant 8.314 J (molK)$^{-1}$. The constant b is related to the heat of adsorption [22]. The Temkin plots are shown in Figures 15 and 16 and it could be observed that the R^2 values (0.949 and 0.952) and (0.949 and0.966) of Hg^{2+} and As^{3+} adsorption onto unmodified and modified okra stem, respectively imply that Temkin Isotherm model could describe the experimental data of this process.

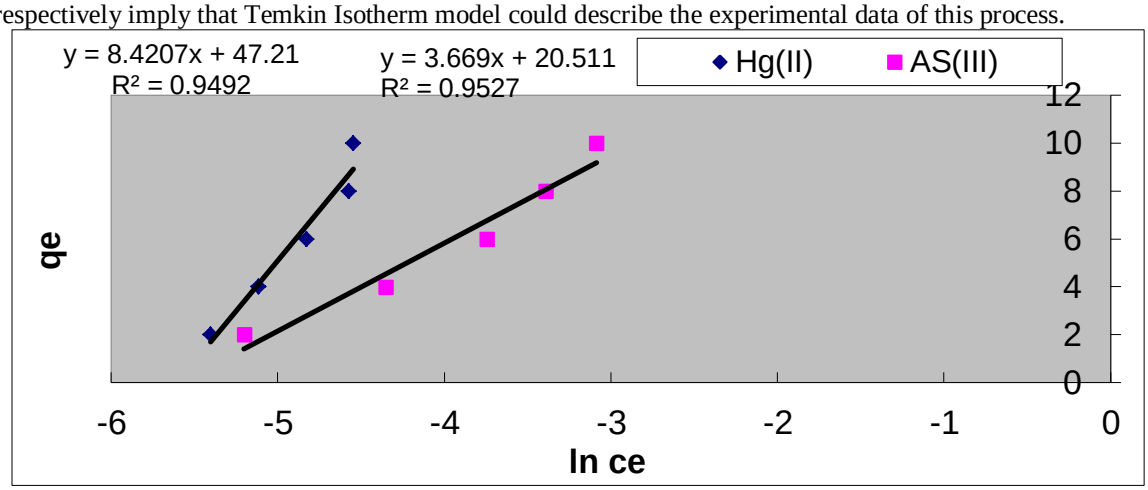

Figure 18: Temkin isotherm plot of q_e vs In Ce for adsorption of the metal ions onto unmodified okra stem

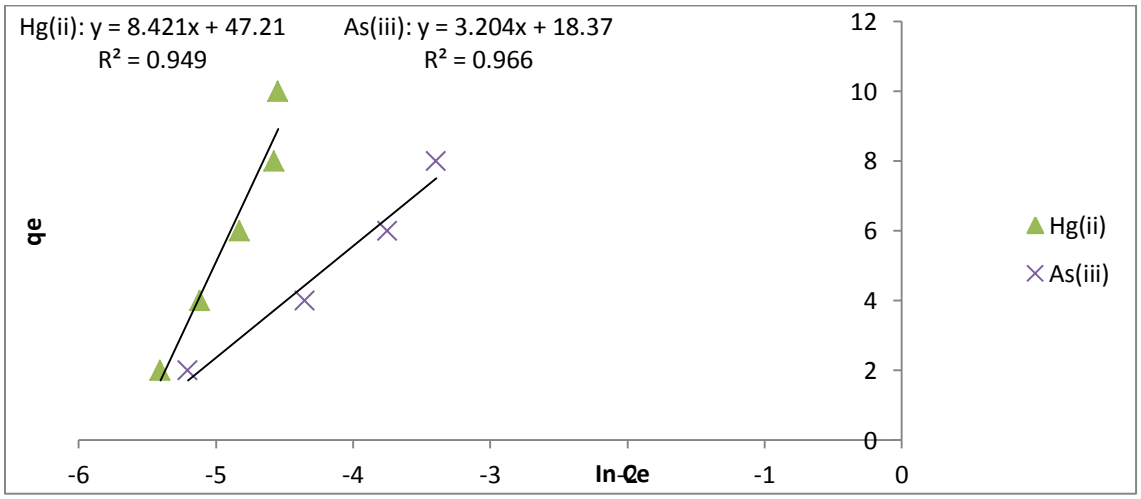

Figure 19:Temkin isotherm plot of q_e vs InCe for adsorption of the metal ions onto modified okra stem

Table 6 Temkin isotherm constants and correlation coefficients(R^2 values) for sorption of metal ions onto unmodified and modified okra stem

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
α(L/g)	272.30	267	272.11	30.04

β (mg/L)	8.42	3.67	8.42	3.20
B	0.00334	0.00145	0.00334	0.00127
R^2	0.949	0.953	0.949	0.966

THERMODYNAMIC STUDIES

Thermodynamic parameters like standard free energy change ($\Delta G, kJ/mol$), standard enthalpy change($\Delta H, kJ/mol$), and standard entropy change($\Delta s, kJ/mol$) were determined using the following equation:

$$\Delta G = -\text{RTInK} \quad (9)$$

$$K = \frac{Csolid}{Cliquid} = \frac{Ci-Ce}{Ce} \quad (10)$$

$$\Delta G° = \Delta H - T\Delta S \quad (11)$$

$$\text{In K} = -\Delta G/\text{RT} \quad (12)$$

$$\text{In K} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

Where K is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/L), C_{liquid} is liquid phase concentration at equilibrium (mg/L), T is absolute temperature in Kelvin and R is gas constant (8.314J/K.mol). Equation 13 which is van't Hoff equation was used to study the nature of sorption process. A plot of In K versus the reciprocal of temperature (1/T) gives a straight line from which $\Delta H$and ΔS were calculated from the slope and intercept respectively(Figures 20 and 21).It is observed from the results shown in Tables 9 and 10 that ΔH values are all positive for the two metal ions on both unmodified and modified okra stem. The positive values of ΔH indicates that the process is endothermic. The free energy of specific adsorption ΔGo (kJ mol-1) is calculated from the following expression.

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

The negative values of ΔG (Table 9) at different temperatures studied indicate feasibility of the process and its spontaneous nature. If adsorption takes place spontaneously, then the free energy must diminish during the process so that ΔG^o must have a negative value. Moreover, as the temperature increased, the ΔG values were found to have decreased, suggesting that the metal ions adsorption were more favorable at lower temperatures.

The positive values of ΔH^o for the system confirm the endothermic nature of the process. The positive values of ΔS observed for the adsorption of the metal ions suggested the increase randomness at the solid-liquid interface during adsorption process. The metal ions in the aqueous media were hydrated. When the metal ions get adsorbed on the adsorbent surface, the water molecules previously hydrogen bonded to the metal ions get released and dispersed in the solution, this results in the increased in the entropy. The positive values of entropy changes also reflect good affinity of the metal ions towards the adsorbent.

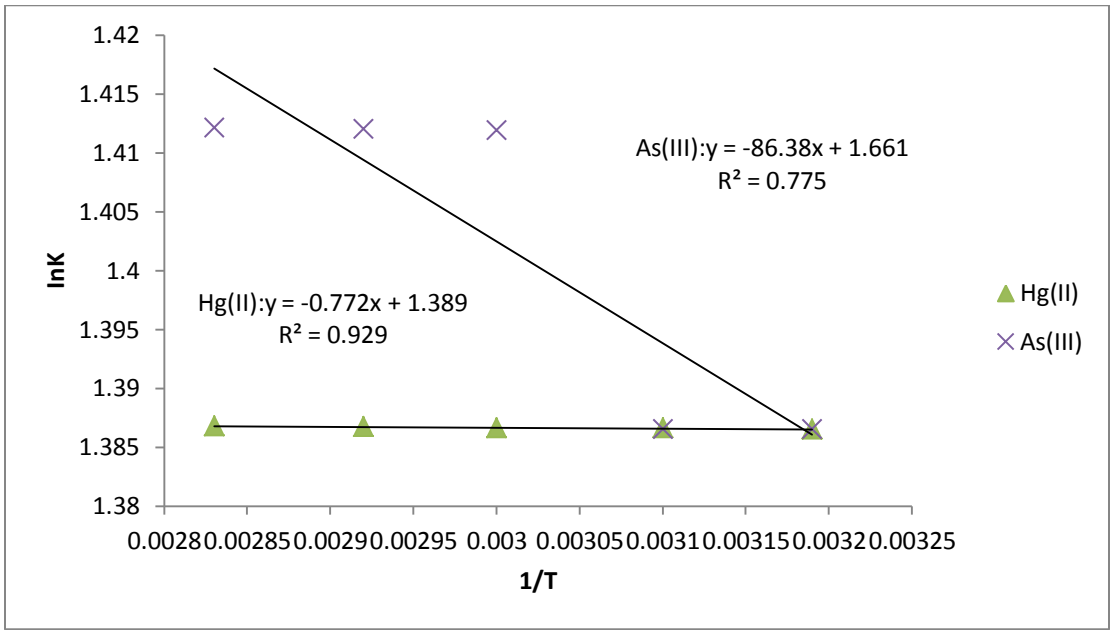

Figure 20: Van't Hoff plot for the sorption of metal ions onto unmodified okra stem at temperature 313K,323K,333K,343K and 353K

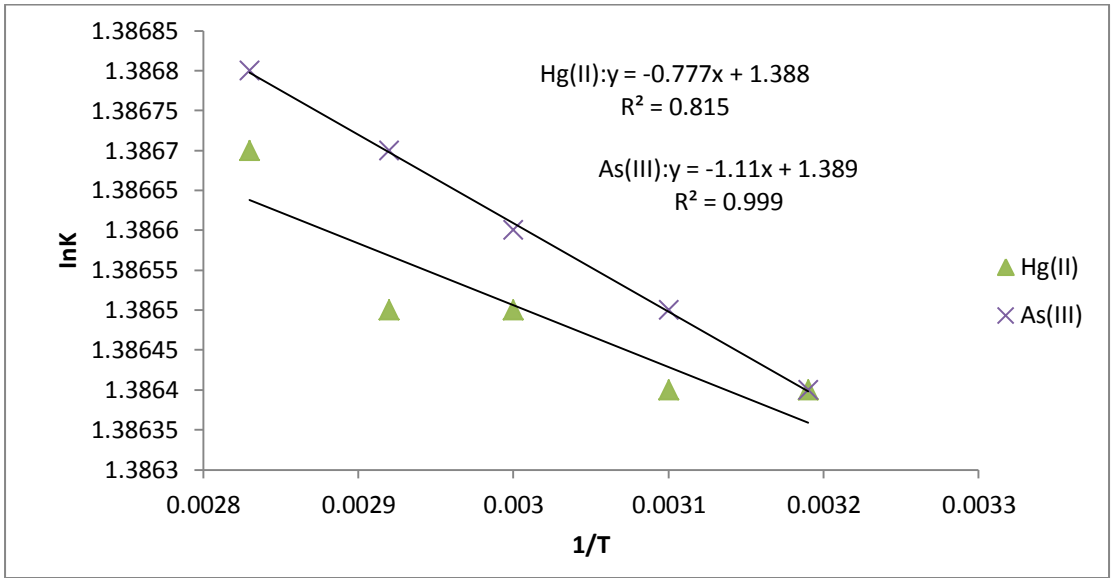

Figure 21: Van't Hoff plot for the sorption metal ions onto modified okra stem at temperature 313K,323K,333K,343K and 353K

Table 10: Thermodynamic values as calculated from the van't Hoff plots for modified and unmodified okra stem

Thermodynamic parameters.	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
ΔH (kJ/mol)	0.006	0.718	0.006	0.006
ΔS (kJ/mol)	0.012	0.014	0.012	0.012
ΔG (kJ/mol) at 313 K	-3.750	-3.664	-3.750	-3.747
ΔG (kJ/mol) at 323 K	-3.870	-3.804	-3.870	-3.867
ΔG (kJ/mol) at 333 K	-3.990	-3.944	-3.990	-3.987
ΔG (kJ/mol) at 343 K	-4.110	-4.084	-4.110	-4.107
ΔG (kJ/mol) at 353 K	-4.230	-4.224	-4.230	-4.227

5. CONCLUSION

The biosorption of Hg(II) and As(III) ions onto unmodified okra stem and modified okra stem was proven to be an efficient process. The amount of metal ions adsorbed was found to vary with pH, temperature, concentration and dynamics of the process. The maximum uptake of metal ions by unmodified and modified okra stem occurred at a pH 6 for Hg(II) and pH 8 for As(III). The Langmuir, Freundlich, Dubnin-Radushkevich and Temkin isotherm models. The Freundlich isotherm models were used for the mathematical description of the biosorption equilibrium of these metal ions onto unmodified okra stem and modified okra stem. The Freundlich isotherm model was found to provide the best fit of the experimental data, followed by Temkin and Dubnin-Radushkevich which gave a fairly good fit. The thermodynamic parameters G (J/mole), H (J/mole) and S (J/K/mole) indicated the endothermic nature of biosorption and increased randomness at the solid-solution interface during adsorption respectively. Results obtained from this study indicated that okra stem which is an agricultural waste and pollutant, could be used as a potential sorbent for the removal of Hg(II) and As(III) ions from aqueous solution in a batch system. Since okra stem is readily available, economically feasible, biodegradable and above all it's in tandem with the popularization of green chemistry, green environment and green technology for sustainable development, it can be used as an economical sorbent for the real industrial effluent.

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