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Sorption Kinetic and Intraparticle Diffusivities of As^{3+} and Hg^{2+} Detoxification from Aqueous Solution Using Cellulosic Biosorbent Derived from Okra (*Abelmoschus esculentus*) Stems.

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Abstract— *The use of biodegradable, renewable and readily available local materials like cellulosic biosorbent produced from Okra stems as biosobent for the removal of toxic metal ions As(III) and Hg(II) ions were investigated and the results of the studies modeled using conventional adsorption models. The batch sorption study was performed as a function of pH, particle size and contact time. The dynamics of the process was investigated in order to establish the exact kinetics of the process and likely mode of bonding of the metal ions to the adsorbent binding sites.The results obtained indicates that optimum contact time of 120 min was sufficient for the attainment of of equilibrium for the sorption process. The experimental sorption data were analyzed using three sorption kinetic models viz; pseudo first-order, pseudo second-order and intra-particle diffusivity models. Results obtained showed that the pseudo second-order gave the best description to the experimental sorption data with correlation coefficients (R^2 values) of 1 and 0.999 for both unmodified and modified Okra stem for the two metal ions. The calculated pseudo second-order rate constants k_2 ($g.mg^{-1}min^{-1}$) obtained from the plots gave 10, 0.0636 and 10, 0.0335 for unmodified and modified Okra stems for Hg(II) and As(III) ions respectively. The calculated equilibrium sorption capacities, qe for unmodified and modified adsorbent were found to agree closely with experimentally determined values and are the same 10, 10.101 for the two metal ions. The result also showed in percent mean value of sorption for As^{3+} and Hg^{2+} 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 mechanism of sorption tested showed a film diffusion models. 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 anthropogenic activities currently going on around the globe changes the natural flow of chemical substances and sometimes introduces new chemicals into both land, air and water environments [1,2].

Water pollution by heavy metal ions has become a serious threat today and of great environmental concern due to their toxicity and persistence in nature [3]. 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 [4]. Various chemical and physical methods have been used to remove metal ions from solutions in the last few decades. These methods include: chemical precipitation, solvent extraction, ion exchange, adsorption, electrolysis, evaporation and membrane processes [5,6]. However, each method has its merits and limitations in application and they are often limited by technical and economical issues[7]. 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[8]. Operational problems and the high cost of the afore-mentioned physico-chemical methods necessitated the use of low-cost materials of biological origin for metal removal from water[9,10]. Recent studies have shown that heavy metals can be removed using plant materials such as sour sop seeds[11], modified cassava fibre [12], coconut fibre[13], wild cocoyam[14], maize cob[15], sugar cane bagasse[16] modified and unmodified tiger nut shell [17]. The application of okra stem as a biosorbent material presents strong potential due to its main components of cellulose, pectin,hemicelluloses and lignin which contain functional groups as possible binding sites for metals[18]

Okra is an economically important vegetable crop grown in tropical and warm temperature regions of the world. Okra stem is semi woody and sometimes pigmented with a greenish or reddish tinges colour[19].

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 for clarification of sugarcane juice from which gur or brown sugar is prepared[20]. 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[21].

Heavy metal refers to any chemical element with a specific gravity that is at least five times the specific gravity of water and is toxic at high amount[22]. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breakdown soils and releasing heavy metals into streams, lakes, rivers and ground water.

1.1 Mercury

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[23].

1.2 Arsenic

Arsenic pollution are from the discharge of various industries such as smelting, petroleum-refining and ceramic manufacturing industries, pesticides, herbicides[24]. 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[25].

In this study, lingo-cellulosic material(Okra stems) were used as biosorbent in the removal of metal As3+ and Hg2+ from aqueous solutions in a batch sorption system. The effects of contact time, pH, particle size, mechanism and sorption kinetics of the unmodified and modified okra stem will be investigated.

2. MATERIALS AND METHODS.

The adsorbent used for this research were collected from Olokoro,Abisa 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 HNO3, HgCl , As2O3, absolute ethanol and Toluene diisocyanate. 1000 mg/L each of stock solution of analytical graded HgCl2 and As2O3 was prepared by dissolving exact quantity of the salts in deionized water. The range (10 to 50 mg/L) of concentrations of Hg2+ and As3+ 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, ground using an electric blender and sieved to three particle sizes of 50µm, 500µm and 1000µm.

Activation of the Adsorbent

The biosorbent was activated using alkaline pulping process.

Alkaline pulping/kraft pulping process involves 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 mins 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).

Batch adsorption experiments.

Kinetic of sorption studies were carried out according to the methods described by Imaga[26]. Kinetic sorption for As3+ and Hg2+ were carried out for the adsorbent of 50 µm at pH 6 and temperature 30oC (303K). 30 cm3 of each standard solution of metal, initial concentration of 50 ml/L was transferred into 250 ml Erlenmeyer flask and labeled. The 0.125 g of the adsorbent transferred into the flask and agitated in a shaker for different contact times (30, 60, 90, 120 and 150 mins). After each agitation time , the content of the flask was then filtered using Whatman No.41 filter paper. The residual concentrations of the metal ions 20 cm3 of the filtrate of each metal solutions was determined using UNICAM(Solar AAS 500) atomic absorption photospectroscopy. The adsorption procedure was repeated using different adsorbent (50 µm,500 µm and 1000 µm) sizes of unmodified and modified okra and filtered

DATA ANALYSIS.

The amounts of Pb(II), Cd(II), Hg(II) and As(III) ions adsorbed by the adsorbents during the series of batch investigations were determined using a simplified mass balance equation [27].

$$q_e = (C_i - C_e)\, {}^{V}/_{m} \text{ in mg/g} \qquad (8)$$

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).

3. RESULTS AND DISCUSSIONS.

MODIFICATION BY TOLUENEDIISOCYANATE ON THE OKRA STEM

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 for adsorption. Scheme 4.2 shows the presence of double bond in the processed derivatised cellulose (TDCb) which was initially absent in the standard cellulose. This indicates that a reaction may have taken place on modification with TDI to produce the double bond. Also,the IR results of the standard cellulose and the modified material in fig. x showed that there were incorporation of additional groups into the adsorbent. This other functional groups may have led to enhancement of binding sites on the modified okra stem, thereby increasing the efficiency of the biosorbent for removal of mercury and arsenic ions from aqueous solutions.

Effect of particle size.

The biosorption rate of unmodified and modified okra stem for three particle sizes (50µm, 500µm and 1000µm) was studied keeping other parameters constant. The plots of percentage adsorption of metal ions Hg2+ and As3+ versus particle sizes of Unmodified okra stem(UOS) and Modified okra stem(MOS) ranging from 50-1000µm are shown in Figures 3 and 4. The results show that for particle size of 50µm, the percentage removal of Hg2+ and As3+ from aqueous solution by unmodified and modified okra stem waste was 99.99, while for the particle size of 500µm the percentage removal of Hg2+ was greater than 90 % for both UOS and MOS and less than 90 % for As3+ in UOS and MOS. The plot of the %adsorption versus particle size revealed that modified okra stem had the highest percentage removal of the metal ions at 50µm size, while that of As3+ is less than (85.96) by unmodified okra stem at 1000µm size. It was also observed that percentage removal of the metal ions increased with decreased in particle size. Similar results for the increased efficiency of the removal of Pb2+ ions from solution with decreasing particle size was reported by Hashem[28]. The high sorption of metal ions by unmodified and modified okra stem with smaller particle size is attributed to the availability of more surface area on the adsorbent.

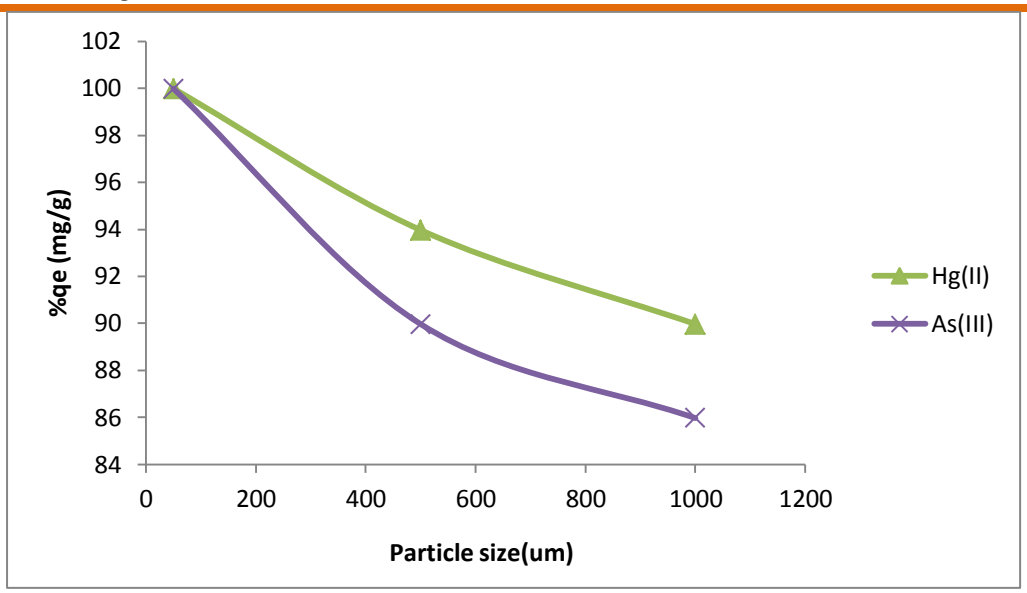

Figure 3: Plot of adsorption capacities of metal ions versus particle size for unmodified okra stem

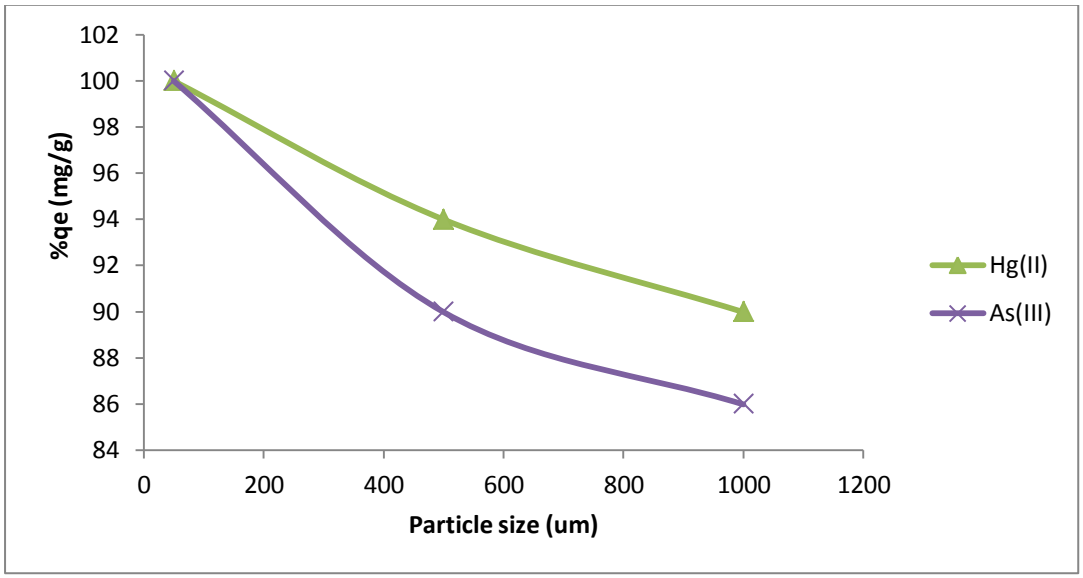

Figure 4: Plot of adsorption capacities of metal ions versus particle size for modified okra stem

Effect of contact time

Figure 5 and.6 show the plots of amount adsorbed against contact time for unmodified and modified okra stem.. Results revealed that the amount adsorbed increased with increased time for UOS and MOS for the two metal ions. The amount adsorbed by UOS and MOS maintained a regular increase from 30-150 min where saturation occurred and there were no significance difference in adsorption uptake within 90-150 min. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. However, as the contact time increased, the sites became progressively saturated and equilibrium was achieved at 120 min contact time after which the residual concentration at different times remains constant.

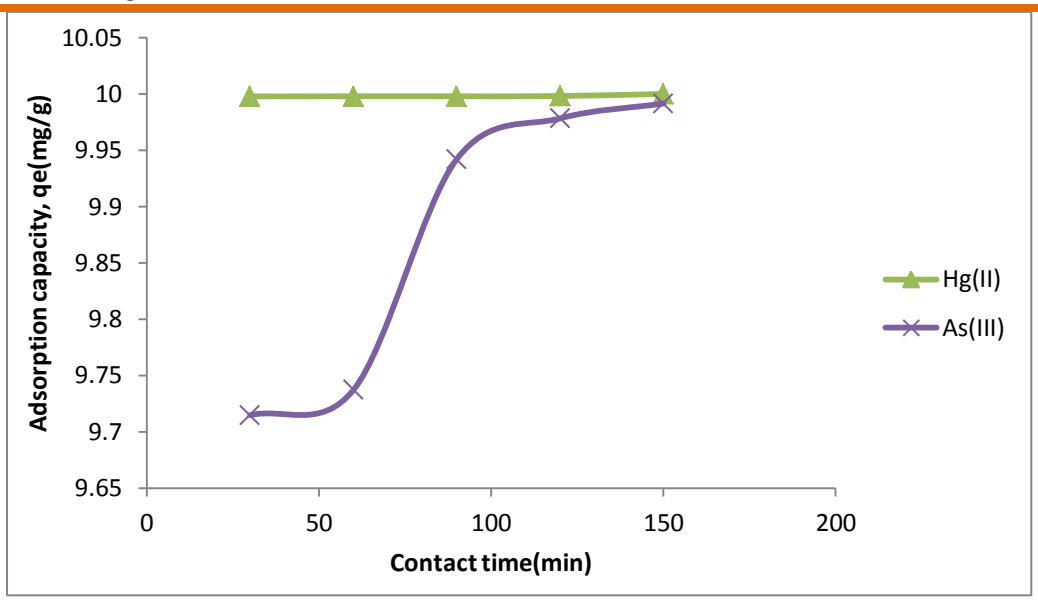

Figure 5: Plot of adsorption capacities of the metal ions versus contact time for unmodified okra stem

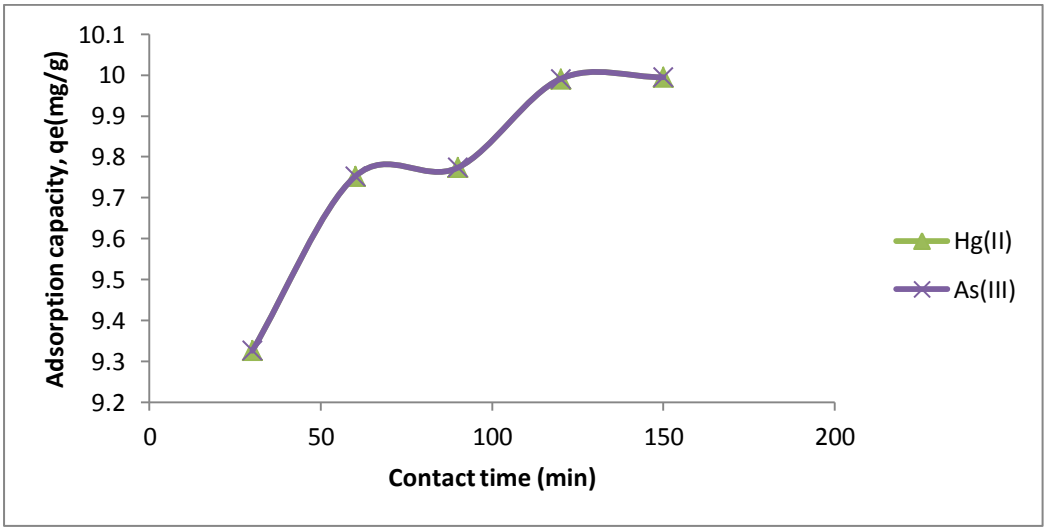

Figure 6: **Plot of adsorption capacities of the metal ions versus contact time for modified okra stem**

Adsorption Kinetics.

Kinetics describes the solute uptake which in turn controls the residence time of adsorbate uptake at the solid–solution interface[29]. Adsorption kinetics is an effective method of evaluating the rate and mechanism of metal ions adsorption onto the adsorbent.In this present study, three different adsorption kinetic models viz: pseudo first-order, pseudo second-order and the intra-particle diffusion models. [30,31] models were applied to analyze the experimental data. The conformity between the experimental data and the model-predicted values is expressed by the correlation coefficients (R2 values close or equal to 1). A relative high R2 value indicates that the model successfully describes the kinetics of the metal ion adsorption. The different kinetic models are described as follows:

Pseudo first-order model.

The pseudo first-order model assumes that the rate of metal ion adsorption is proportional to the number of free adsorption sites. The pseudo first-order equation is generally expressed as:

$$\frac{dqt}{dt} = k_1(q_e - q_t) \quad (1)$$

Where qe and qt (mg/g) are adsorption capacities at equilibrium and time, t respectively, k1 is the rate constant for pseudo first-order adsorption process (min-1). After integration and applying boundary conditions at t = 0 to time t = t and qt = 0 to qt = qt, the integrated form of equation 1 becomes:

$$\log (q_e - q_t) = \log q_e - \frac{k1t}{2.303} \quad (2)$$

The plot of log (qe – qt) versus t yield straight lines as shown in Figure 7 and 8 for umodified and modified okra stem. The values of the pseudo first-order rate constant, k1 and the equilibrium sorption capacities, qe were determined from the slopes and intercepts of the linear plots respectively. The pseudo first-order parameters (k1 and qe) and R2 values calculated from the linear plots are presented in table 1.

From table1, it can be observed that there is marked variation in the qe values for both the UMOS and MOS for the two metal ions from the experimental adsorption capacity, qe values and this indicates the non-fitting of the model to the experimental adsorption data. The fairly high R2 values obtained from the kinetic pseudo first-order confirm that the model did not give perfect fitting to the experimental adsorption data.

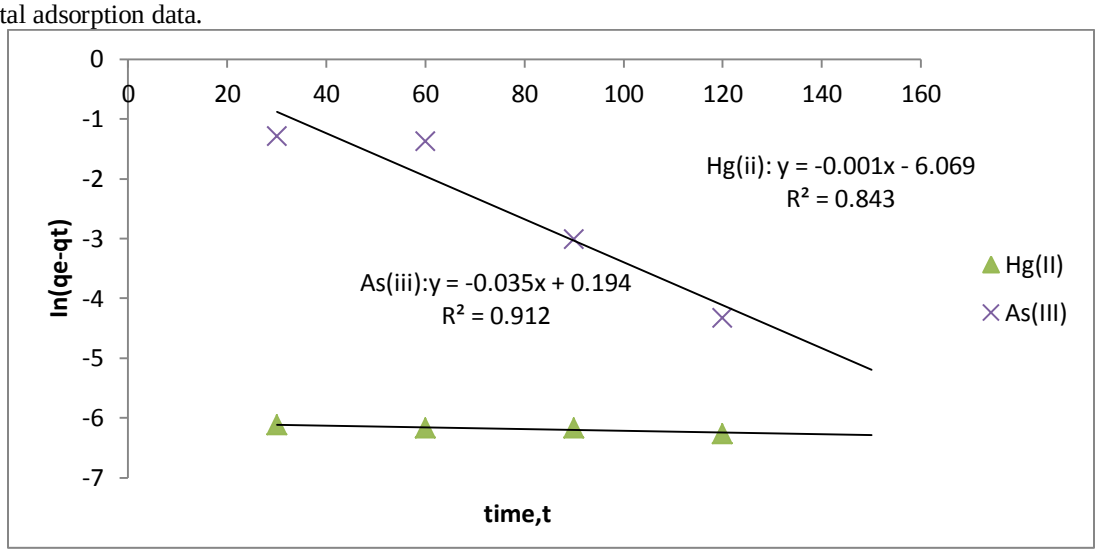

Figure 7:Pseudo-first order plot of In(qe-qt) vs t for adsorption of the metal ions onto unmodified okra stem

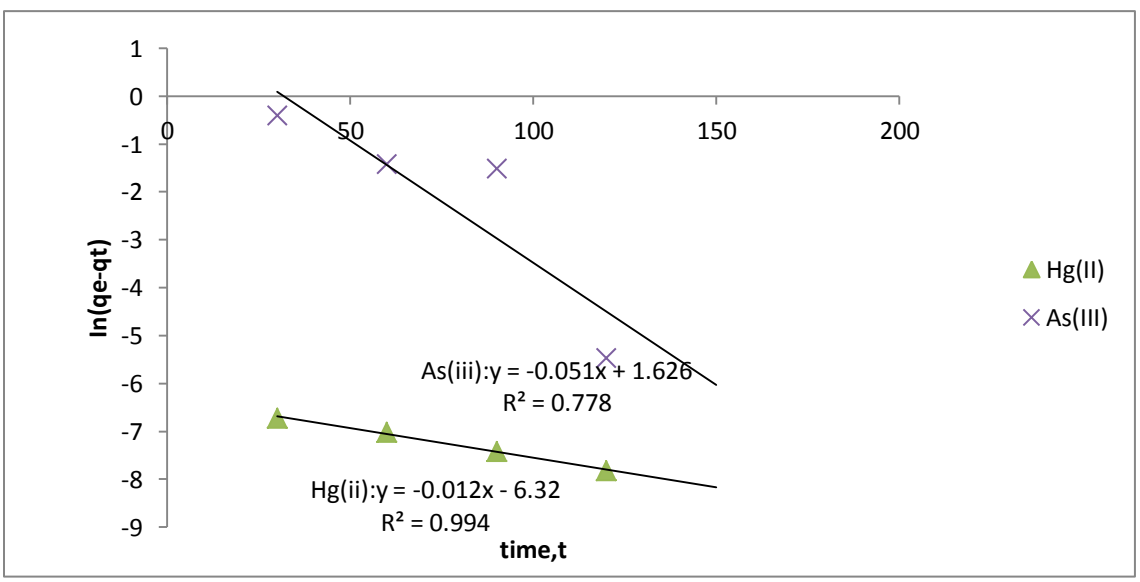

Figure 8: Pseudo-first order plot of In(qe-qt)vs t for adsorption of the metal ions onto modified okra stem

Table 1 Pseudo-first order 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
qe (mg/g)	-8.803	-1.640	-1.844	0.486
$k_1(min^{-1})$	0.001	0.035	0.012	0.05
R^2	0.843	0.912	0.994	0.778

Pseudo second-order model

The pseudo second-order kinetic model relies on the assumption that the rate-limiting step of an adsorption process may be chemical reactions involving valence forces resulting from sharing or exchange of electrons between adsorbates and the adsorbent sites[32]. The psudo second-order adsorption kinetics rate equation is expressed as:

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where k2 is the rate constant for pseudo second-order adsorption process. After integration and applying boundary conditions at t = 0 to time t = t and qt = 0 to qt = qt, the integrated form of equation 3 becomes:

$$\frac{t}{qt} = \frac{1}{k2q2e} + \frac{t}{qe} \quad (4)$$

The initial adsorption rate, ho (mg/g min-1) as t approaches zero is expressed as:

$$ho = k_2q^2_e \quad (5)$$

Equation (4) then becomes:

$$\frac{t}{qt} = \frac{1}{ho} + \frac{t}{qe} \quad (6)$$

The plot of $\frac{t}{qt}$ versus t using equation (6) gave linear relationship as shown in Figure 9 and 10 for UOS and MOS from which qe and k2 were determined from the slope and intercept of the linear plots respectively. From the pseudo second-order plots, pseudo second-order parameters k2, qe and ho (the initial sorption rate) were determined and presented in table 2.With respect to the values of the constants in table 2 and the high values of kinetic fitting parameter(R2) determination for both UOS and MOS of (1 and 0.999) respectively for the two metal ions, indicate that pseudo second-order kinetic plots gave the best fit to the experimental adsorption data. Therefore the fitting of the adsorption data into pseudo second-order model means that the rate of occupation of active sites is proportional to the square of the number of the unadsorbed sites [33,34] .The trend of kinetic adsorption of the metal ions from the calculated initial sorption rate, ho is as follows UOS and MOS (1000 and 0) and (6.489 and 3.488) for Hg(II) and As(III) ions respectively which is in line with the observation of the pseudo second-order rate constant , k2 which follow the same trend as observed in Table 2. The high the k2 values, the faster the kinetics of the adsorption process and this means that the sorption of Hg(II) ions for both UOS and MOS from solution was faster than that of As(III) ions. The values of equilibrium adsorption capacity, qe, calculated from the slope of the pseudo second-order plots revealed that greater amount As(III) ions was adsorbed than Hg(II) ions for both UOS and MOS[35].

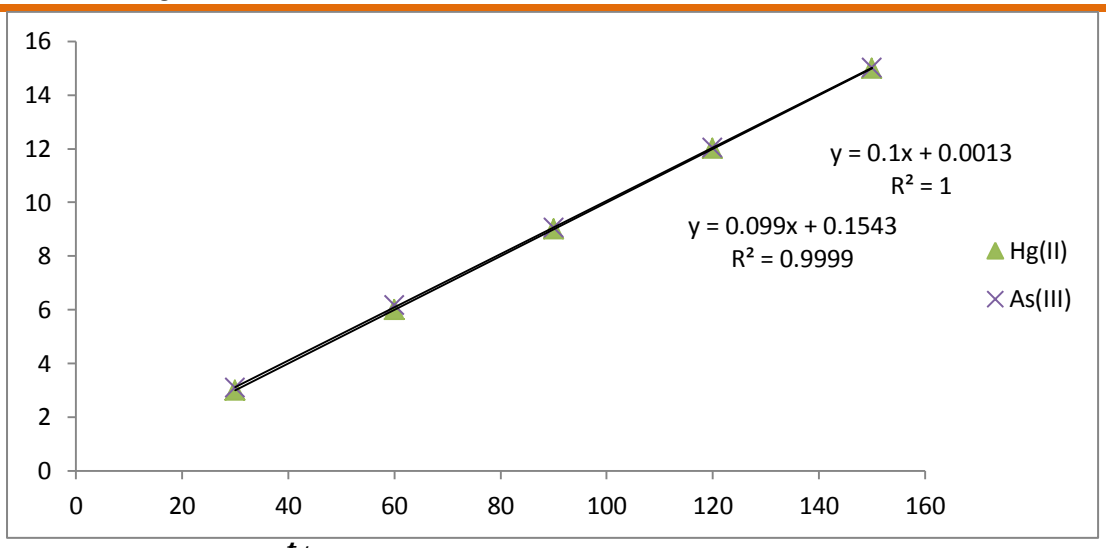

Figure 9: Pseudo-second order plot of t/q_t vs t for adsorption of the metal ions onto unmodified okra stem

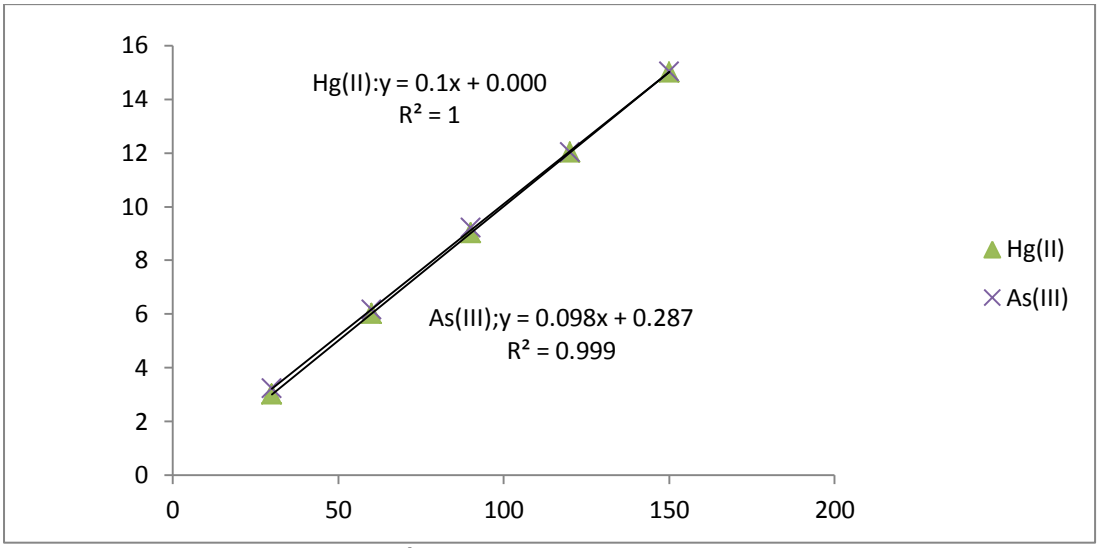

Figure 10: Pseudo-second order plot of t/q_t vs t for adsorption of the metal ions onto modified okra stem

Table 2: Pseudo-second order constant and correlation coeffecients(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
qe(mg/g)	10	10.101	10	10.204
k_2(g/mg/min)	10	0.0636	10	0.0335
h_o(mg/g/min)	1000	6.489	0	3.488
R^2	1	0.999	1	0.999

INTRAPARTICLE DIFFUSSION MODELS

3.3.1 Liquid Film Diffusivity Model

The kinetics of adsorption of metal ions on various adsorbents may be controlled by several independent processes such as bulk diffusion, external mass transfer, film diffusion, chemical reaction, and intra particle diffusion. The linear driving force concept and developed a simple relationship[36]:

$$\ln (1- \alpha e) = -K_p t + D_F \quad (7)$$

Here $\alpha_e = q_t/q_e$ is the fractional attainment of equilibrium and Kp is the rate constant.

A plot of ln $(1-\alpha_e)$ versus time (t) yields the K_P the rate constant (min^{-1}) as the slope of the graph and a dimensionless constant D_F as intercept.

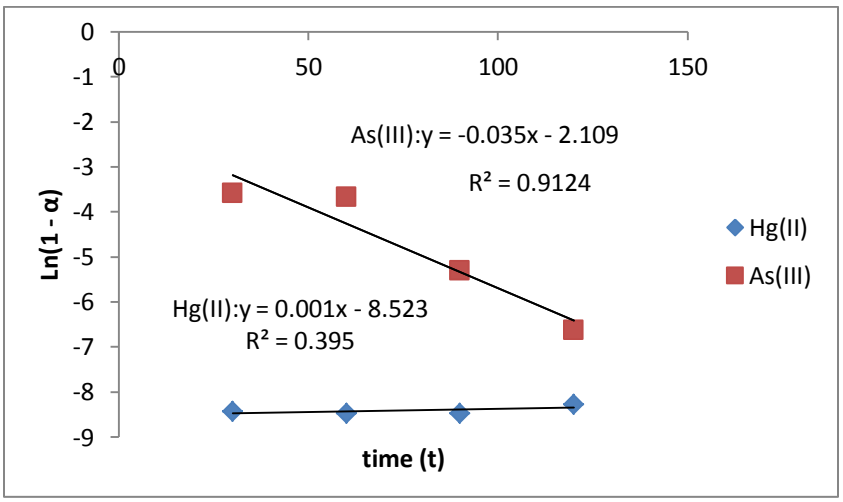

Fig 11: liquid film diffusivity model for UOS for As(III) and Hg(II) ions

From above, Hg(II) is linear(particle diffusion controlled) while As(III) is non linear(film diffusion controlled)

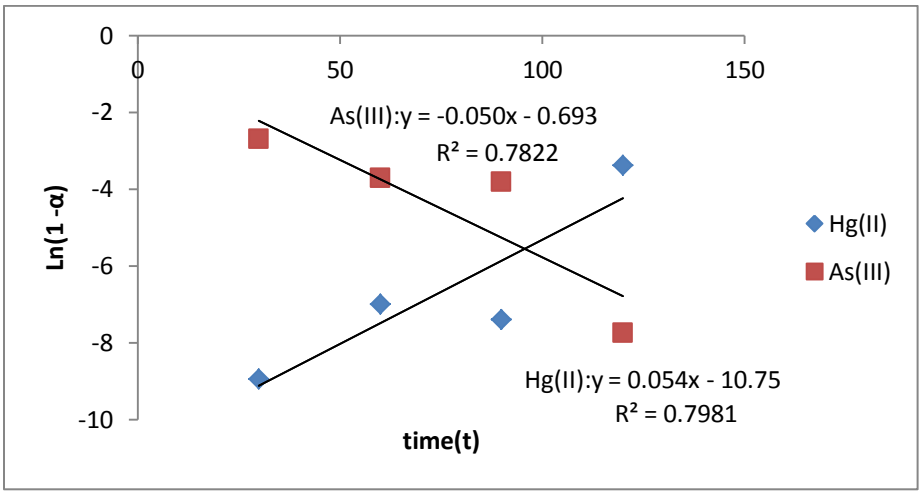

Fig 12: liquid film diffusivity model for MOS for As(III) and Hg(II) ions

Both As(III) and Hg(II) are non linear i.e there are film diffusion controlled.

If a plot of ln (1- αe) against t is a straight line, then adsorption is controlled by particle diffusion and the diffusion of the metal ions to the adsorbent surface is independent of the initial concentration of the metal ions, if it is not a straight line, then it indicates that the sorption process is controlled by film- diffusion. The fractional attainment at equilibrium is the ratio of the amounts of sorbate removed from solution after a certain time to that removed when sorption equilibrium is attained. It would definitely be expected that factors such as the number of reactive sites on the substrate and the bulkiness of the substrate would affect the rate of sorption. However, a great deal of information is gotten from the fractional attainment of equilibrium. The rate of attainment of equilibrium may be either film diffusion controlled or particle-diffusion controlled, even though this two different mechanism cannot be sharply demarcated[36].

Table 3: liquid film diffusivity constants for UOS and MOS of Hg(II) and As(III) ions.

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
Kp(min^{-1})	0.001	0.035	-0.054	0.050
D_F	-8.523	-2.109	-10.75	-0.693
R^2	0.395	0.912	0.798	0.782

The R2 value of Hg(II) and As(III) ions for UOS and MOS suggests that the diffusivity model does not entirely support the adsorption of Hg(II) and As(III) ions with the exception of As(III) ions of R2(0.912). The diffusion rate constant Kp and the linear driving force DF (diffusion parameter) obtained from the slope and intercepts of the plots are presented in table 4. A look at figure11 show that only Hg(II) ion is particle diffusion controlled while figure 12 show that both Hg(II) and As(III) ion are film diffusion controlled since the plotted graph is non- linear. Since sorption of Hg(II) ion is particle diffusion controlled (plot is linear), it could be affected by the following processes: (1) diffusion of the solute from the solution to the film surrounding the particle; (2) diffusion from the film to the particle surface (external diffusion); (3) diffusion from the surface to the internal sites (surface diffusion or pore diffusion; (4) uptake which can involve several mechanisms: physicochemical sorption, ion exchange, precipitation or complexation [13]. The mechanism of sorption depicted to be particle diffusion controlled means that intra-particle mass transfer resistance is rate limiting [37]. This means that in the presence of a mixture of the metal ions, the metal ions compete for the adsorption sites on the adsorbent. This competition affects the diffusion properties of the metal ions, hence decreases the adsorption capacity of the metal ions. The R2 values confirm this. Thus, the metal ion that successfully reaches the adsorption site faster depends on the above factors and also on the ionic radii of the metal ions. Competition among the metal ions for adsorption sites clearly affected the adsorption capacity [13]. Consequently, in an adsorption process, the metal ions from the bulk solution should move through the thin liquid film surrounding the adsorbent. The thin film may produce a diffusion barrier for the metal ion to penetrate before they arrive at the binding sites on the adsorbent. This suggests that the metal ion must overcome this film barrier to be adsorbed at the sites on the adsorbent. This mechanism is consistent with the fact that the rate of diffusion of the metal ion also affects adsorption rate. This conclusion was also arrived at by Abia and Asuquo[38].

3.3.2 Mass Transfer Model

The mass transfer kinetic model is generally expressed as [39](Abia *etal*, 2006).

$$C_o - C_t = D\exp(K_o t) \quad (8)$$

Where, C_O is the initial metal ion concentration (mg/L), C_t is the metal ion concentration at time t in mg/l, T is the shaking time in minutes, D is the fitting diameter, K_O is a constant which is the mass transfer adsorption coefficient. A linearized form of the equation (8) is written thus:

$$\ln(Co-Ct) = Ko + \ln D \quad (9)$$

If the sorption of the metal ion is depicted by the mass transfer model, then the plot of ln ($Co-C_t$) versus time should give a linear relationship from where lnD and Ko can be determined from the intercept and slope of the plot, respectively.

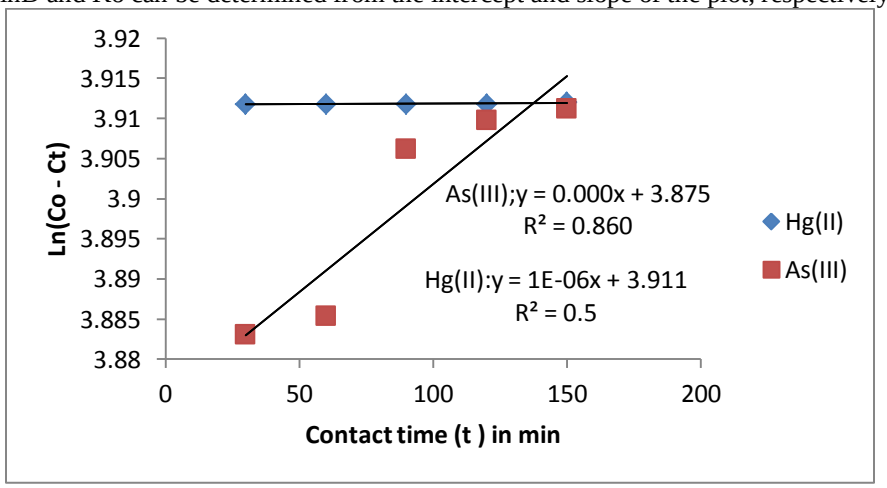

Fig 13: Mass Transfer Model of UOS for Hg(II) and As(III) ions.

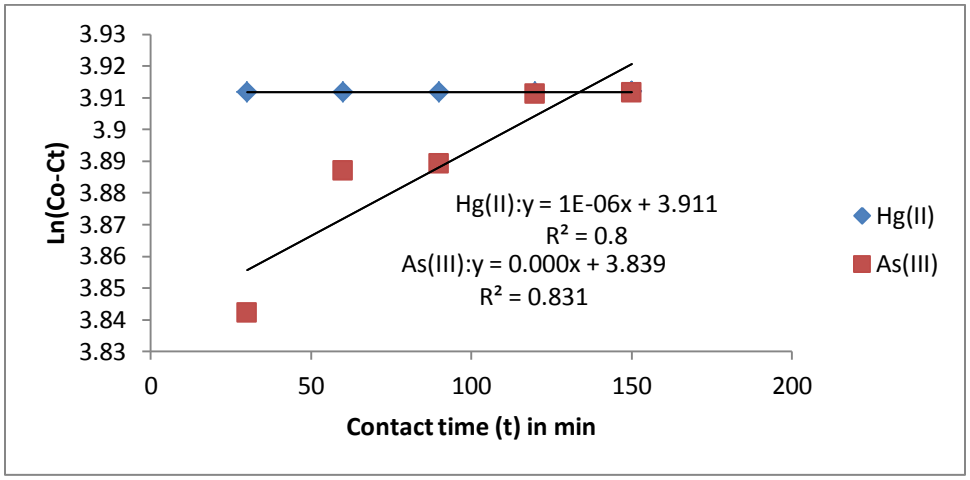

Fig 14: Mass Transfer Model of MOS for Hg(II) and As(III) ions

Table 4: mass transfer constants for UOS and MOS for Hg(II) and As(III) ions

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
K_o	1E- 06	0.00	1E-06	0.00
D	49.94	48.18	46.48	49.94
R^2	0.5	0.860	0.8	0.831

From the results, the low R^2 values suggest that the mass transfer diffusivity model does not actively support the adsorption of the metal ions in both UOS and MOS systems. Mass transfer is the movement of chemical species in a fluid mixture caused by some forms of driving force. There are two main mechanisms of mass transfer: diffusion and mass transport by convection[40]. These mechanisms (diffusion and mass transport by convection) were not mainly supported suggesting that mass transfer model did not wholly favour the sorption of hg(II) and As(III) ions.. The diffusion rate constant Ko and D (fitting parameter) obtained from the slope and intercepts of the plots are presented in table 4. A look at figures 13 and 14 shows that the plots are not very linear especially for Hg(II) ion in UOS; suggesting that the sorption process is not mainly diffusion and mass transport by convection controlled. The low R^2 (0.5) value for Hg(II) in UOS confirm this. Hence, diffusivity model parameters were then used as a film-diffusion controlled. Aikpokpodion stated that the rate of diffusion of ions between soil solution and soil surfaces is generally low due to molecular collisions that give rise to extremely strong hindrance to the movement of molecules[40].

3.3.3 Intra Particle Diffusivity Model

Intra particle diffusivity equation for description of sorption kinetics was explored using the intra-particle diffusivity model given below [41]:

$$qt = kidt^{½} + C \qquad (10)$$

Where, kid is the rate of sorption controlled by intra particle diffusivity (mgg-1min^{-1} ($^1/2$)) ,C depicts the boundary layer thickness. This model predicts that the plot of qt versus $t^{1/2}$ should be linear with kid and C as slope and intercept respectively if intra particle diffusivity is involved in the sorption process. Intra particle diffusivity is the rate controlling step if the line passes through the origin.

Mckay and Poots model

This model equation was developed by Mckay and Poots[42]. They stated that the amount of solute adsorbed can be expressed in terms of the square root of time as given in the equation:

$$q_t = Xi + K_i t^{1/2} \qquad (11)$$

where Xi is the boundary layer diffusion effects (mg/g), K_i is the rate constant for intraparticle diffusion (mg/g/min). McKay and Poots intraparticle plots are shown in Figures 14 and 15 for UOS and MOD respectively.

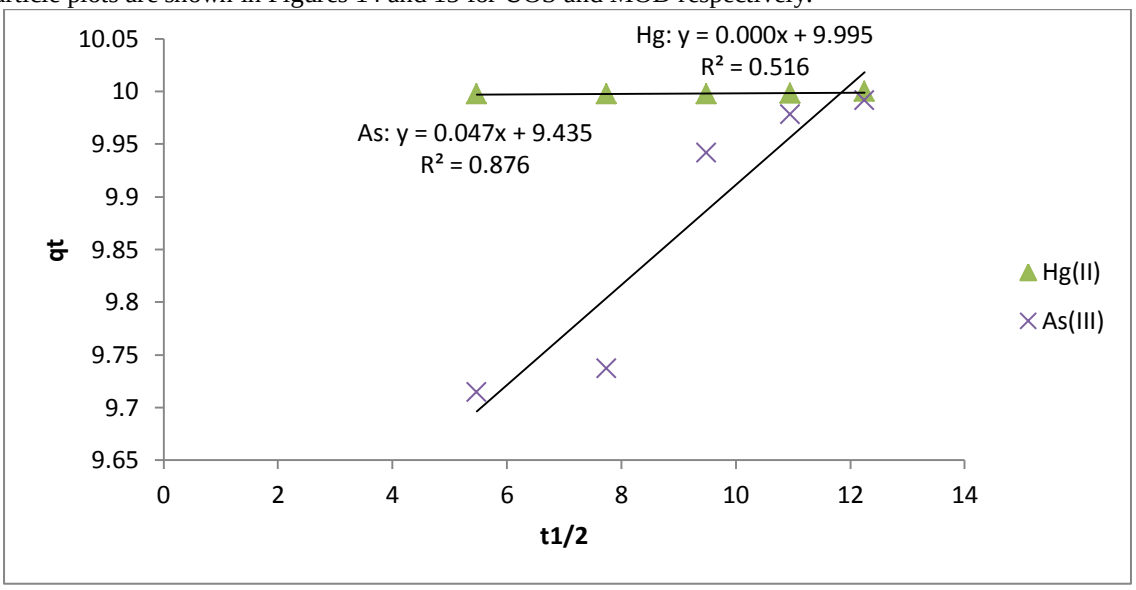

Figure 15: Mckay and Poots intrapartcle diffusion plot for adsorption of metal ions onto unmodified okra stem

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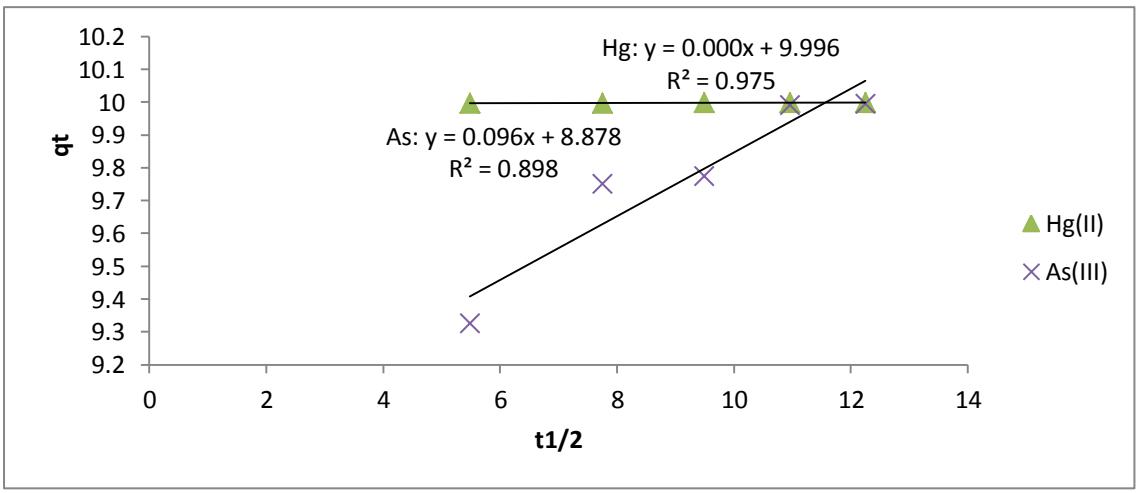

Figure 16: Mckay and Poots intraparticle diffusion plot for adsorption of metal ions onto modified okra stem

Table 5 Mckay and poots intraparticle diffusion model

Constants	Unmodified Okra Stem (UOS)		Modified Okra Stem (MOS)	
	Hg(II) ions	As(III) ions	Hg(II) ions	As(III) ions
X_i (mg/g)	9.995	9.435	9.996	8.878
K_i (mg/g/min)	0.000	0.047	0.000	0.096
R^2	0.516	0.876	0.975	0.898

The Kinetic parameters and the correlation coefficients (R^2 values) are presented in Table 5.The higher values of Xi i.e boundary layer thickness depicts higher adsorption capacities. The boundary layer gives an insight into the tendency of the metal ions to adsorb to the adsorbent phase or remain in solution. Since diffusion takes place, the boundary layer is looked upon as a viscious drag existing between the adsorbent surface and the metal ion solution diffusing across its surface. As shown in Table 5, the boundary layer thickness varied from 0.721-9.995mg/g and 2.370-9.996 mg/g for unmodified and modified okra stem respectively, which is an indication of high adsorption capacity of the metal ions by the adsorbent. Generally, it could be said that the model fits the experimental data well and also confirms that the sorption process may be intraparticle diffusion controlled due to the high R^2 values which ranged 0.516-0.876 and 0.898-0.975 for unmodified and modified okra stem respectively.

According to Itodo of the intraparticle diffusivity plot, the sorption mechanism assumes an intraparticle diffusivity model if the following conditions are met[36]: 1. High R^2 values to ascertain applicability 2. Straight line which passes through the origin for the plot area qt versus $t^{1/2}$ 3. Intercept C< 0. A validity test which deviates from 1, 2 and 3 above shows that the mode of transport is affected by more than one process [43]. The intercept C values are very high (well above zero values). Higher values of kid illustrate an enhancement rate of adsorption, whereas, larger kid values illustrate better adsorption which is related to improved bonding between adsorbate and adsorbent particles [36]. From the assertion above, the values of kid are relatively very low showing that there is no enhancement rate of adsorption which illustrates no adsorption and no better bonding between adsorbate and adsorbent particles. From the results obtained in table 5, it shows that none of these conditions (1, 2 and 3) listed above were met suggesting that the intra-particle diffusivity model adsorption mechanism does not in any way favor the adsorption of Hg(II) and As(III) ions in UOS and MOS systems. From the results obtained in table 5 , it follows that R^2, kid and a values are low suggesting that the intra-particle diffusion model adsorption mechanism does not in any way favor the adsorption of Hg(II) ion and As(III) ion with the UOS and MOS. This means that the values of kid being relatively very low shows that there is no enhancement rate of adsorption which illustrates no adsorption and no better bonding between sorbate and sorbent particles. Higher values of kid illustrate an enhancement rate of adsorption, whereas, larger kid values illustrate better adsorption which is related to improved bonding between sorbate and sorbent particles [36].

4. CONCLUSION

The biosorption of Hg(II) and As(III) ions onto okra stem was proven to be an efficient process. The influences of pH, contact time and particle size, were examined. The maximum uptake of metal ions by unmodified and modified okra stem occurred at a pH of 6 and 8 for Hg(II) respectively and pH 4 and 8 for As(III) respectively. The equilibrium adsorption was attained after 120 min. The pseudo-second order kinetic model fits best with the dynamical behavior of the adsorption of Hg(II) and As(III) ions onto okra stem.

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 solutions.. This is because it is readily available, economically feasible, biodegradable and above all its in tandem with the popularization of green chemistry, green environment and green technology for sustainable development.

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