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Equilibrium Sorption Studies of Hg (II) Ions from Aqueous Solution using Powdered Swamp Arum *(Lasimorpha senegalensis*) Seeds.

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ABSTRACT: The potential of swamp arum *(Lasimorpha senegalensis*) seeds as a low-cost adsorbent for the removal of Hg (II) ions from aqueous solution was investigated in this study. The influence of initial metal concentration on the percent adsorption of Hg (II) ions onto powdered swamp arum seeds was studied in a batch system and the filtrate was analyzed using Atomic Absorption Spectrometry (AAS). The percent adsorbed for 10, 20, 40, 60 and 80 mg/L of the aqueous solution were 97.7, 98.9, 99.3, 99.7, and 96.5% respectively. Three isotherms; Langmuir, Freundlich, and BET were used to model the equilibrium sorption of Hg (II) ions onto powdered swamp arum seeds, with a correlation coefficient of 0.998, 0.784 and0.842 respectively. The Langmuir model fitted the equilibrium data best, with a correlation coefficient of 0.998 and a maximum adsorption capacity q_m, of 5.917 mg/g. Thus, indicating monolayer coverage on the adsorbent. The results showed that swamp arum seed have the potential to be applied as alternative low-cost biosorbent in the remediation of heavy metal contamination in waste water. ©JASEM
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KEYWORDS: Equilibrium, sorption studies, ions, solution, swamp arum, seeds.

Introduction

Heavy metal contamination exists in aqueous waste streams of many industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating. (Liang *et al*., 2009; Issabayeva *et al*., 2010; Lu and Gibb, 2006). As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increasing incessantly (Serencam *et al*., 2007).

Heavy metals such as mercury, tin, lead, cadmium are toxic to organisms. Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes (Issabayeva *et al*., 2010). Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable and persistence nature (Ahluwalia and Goyal, 2005).

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Uddin *et al*., 2009).Recently, considerable attention has been given to removal of heavy metals by biosorption, which is a process of passive binding of cations by biological material (Serencam *et al*., 2007). The use of some plant materials for the remediation of solutions of toxic heavy metals has been reported; mango leaves powder (Murugan *et al*. 2010), almond shells (Mehrasbi et al., 2008), bael leaves (Chakravarty et al., 2009), bael leaves (Kumar and Kirthika, 2010), sulfuric acid-carbonized coconut shell(Sekar et al., 2004), activated charcoal prepared from coconut shell (Gaikwad, 2004), grape stalk wastes (Villaescusa et al., 2003) and Mango peel waste (Iqbal et al., 2008).

Swamp arum (*Lasimorpha senegalensis*) is a plant found in swamps and wet woods, along streams and in other wet areas of the Pacific Northwest, where it is one of the few native species in the arum family (Armitage, et al., 2011). The plant grows from rhizomes that measure 30 cm or longer, and 2.5 to 5 cm in diameter.

Literature search shows that very scanty information on swamp arum exists which are on local uses only; hence in the present study, the removal of mercury (11) ions from solution onto powdered swamp arum **(***Lasimorpha senegalensis)* seeds at different experimental mercury (11) ions concentration was investigated to determine its effectiveness as a novel and low-cost adsorbent. The study also aims at

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determining the suitability of the equilibrium sorption isotherm models; Langmuir, Freundlich and BET for the adsorption process.

MATERIALS AND METHODS

*Preparation of Adsorbent (Swamp Arum)*In this study, swamp arum (*Lasimorpha senegalensis*) seeds were used as adsorbent for the removal of Hg (II) ions from solution. The seeds were obtained from a swamp in Amassoma Community in Southern Ijaw Local Government Area of Bayelsa State, Nigeria. Mature swamp arum seeds were collected and washed thoroughly under running tap water to remove dust and other adhering particles. The seeds were then rinsed with distilled water and allowed to dry under sunlight for one day, and finally dried in an oven at a temperature of about 80^{o}C for 24 hours. The dried seeds were ground into fine powder using a grinding mill and stored in an airtight plastic container for further use.

Preparation of Hg (II) Ion Solution A stock solution of Hg (II) ions containing 1000mg/L was prepared from Mercury (II) chloride, $HgCl_2$. 1.35g of $HgCl_2$ was accurately weighed and dissolved in distilled water in a 1000ml volumetric flask and made up to the 1000ml mark. Appropriate dilution was carried out on the stock solution in order to obtain desired concentrations of Hg(II) ions for the adsorption experiment.

Adsorption experiment: A 50ml solution of mercury (II) ions containing 10 mg/L was measured and transferred into a conical flask with 1g of the powdered swamp arum seeds added. The mixture was then placed on a mechanical shaker and agitated at a speed of 150rpm for 40 minutes. This was repeated for all the different concentrations; 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L. At the end of the 40 minutes agitation time the mixture was filtered using Whatmann filter paper and the filtrate analyzed for residual mercury ions using Atomic Absorption Spectrophotometer (AAS).

Analysis of Experimental data: The equilibrium adsorption capacity (q_e) was determined using the mass balance expression given in equation 1.

$q_e = \frac{(C_o - C_e)}{M} V$ … (1) Where V = volume of solution (L), M = mass of adsorbent (g), C_o = initial concentration of the metal ion; C_e = equilibrium concentration. The experimental data was also analyzed using the Langmuir, Freundlich and BET isotherms. The linearized form of the Langmuir isotherm model was expressed in equation 2

$$\frac{Ce}{q_e} = \frac{1}{q_m K_L} + \frac{Ce}{q} \quad \text{… (2)}$$

Where;
C_e = Concentration of metal ions at equilibrium (mg/L), q_e = Amount of metal ions adsorbed at equilibrium (mg/g), K_L = Langmuir isotherm constant related to free energy of adsorption (L/mg), q_m = Maximum adsorption capacity (mg/g). The plot of Ce/q_e against Ce should give a straight line with slope of $1/q_m$ and intercept of $1/q_mK_L$.

The linearized form of the Freundlich isotherm model was expressed in equation 3
Log q_e = log K_F + $\frac{1}{n}$ log C_e … (3)

Where; K_F = Freundlich constant expressing the relative adsorption capacity of adsorbent, n = constant indicating the intensity of adsorption. The plot of log q_e against log Ce should give a straight line with slope of $\frac{1}{n}$ and intercept of $K_{F.}$
BET model is expressed in equation 4

$$\frac{C_e}{(C_s - C_e) q_e} = \frac{1}{K_b q_m} + \frac{(K_b - 1)}{(K_b q_m)} \frac{(C_e)}{(C_s)} \quad \text{… (4)}$$

Where; K_b = BET Constant, C_s = solute concentration at the saturation of all layers (mg/L), q_m = constant indicating maximum adsorption capacity (mg/g), q_e = amount of metal ions adsorbed. A plot of $C_e(C_s-C_e)q_e$ against $C_{e/}C_s$ should give a straight line with slope of K_b-1/K_bq_m and intercept of $1/K_bq_m$.

RESULTS AND DISCUSSIONs

The effect of initial metal ion concentration on the percent adsorption of Hg (II) ions and presented in Figure I.

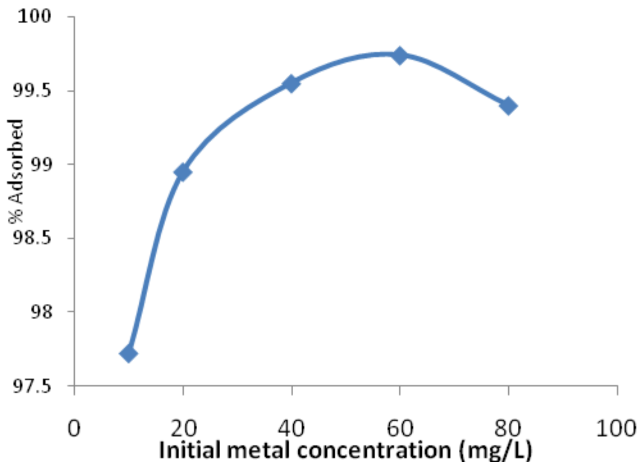

Fig.1: Effect of concentration on percent adsorption of Hg^{2+} ions onto powdered swam arum seeds

As shown in Figure 1, the amount of Hg^{2+} ions adsorbed increased with increase in initial metal ion concentration. This is as a result of the increase in the number of metal ions competing for available binding sites on the adsorbent at higher concentration levels (Mahvi, et al., 2007). This trend was similar to that observed by(Abasi, et al.,2011) who studied Adsorption of iron (III), lead (II) and cadmium (II) Ions by unmodified raphia palm (Raphia hookeri) fruit endocarp.

From the experimental data obtained in this study; the Langmuir, Freundlich and BET curves were plotted.

The Langmuir isotherm model plot of C_e/q_e versus C_e for the sorption of Hg^{2+} ions using powdered swamp arum seeds was taken and presented in figure 2.

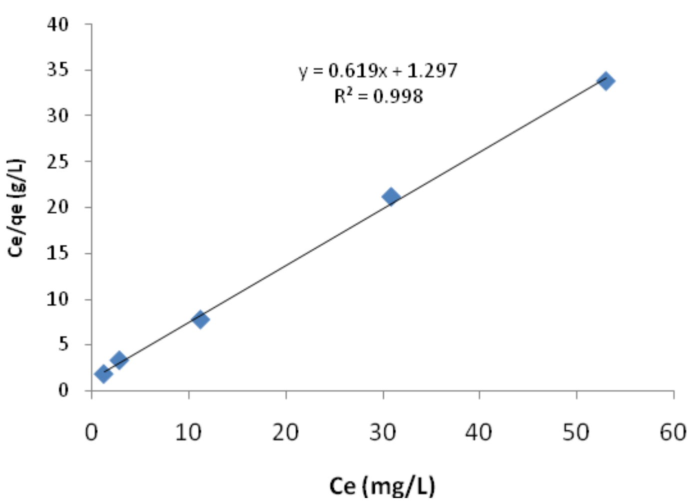

Fig2: Langmuir Isotherm plot for the adsorption of Hg^{2+} ions onto powdered swamp arum seeds

While the Freundlich isotherm plot of log q_e against log C_e as well as the BET isotherm plot of $C_e/(c_s-c_e)q_e$ against c_e/c_s were also taken and presented in Figures 3 and 4.

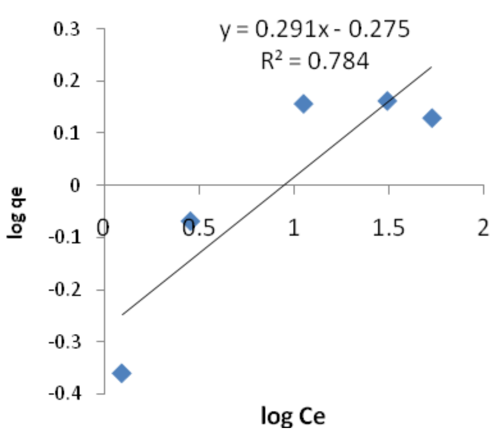

Fig.3: Freundlich Isotherm plot for the adsorption of Hg^{2+} ions onto powdered swamp arum seeds

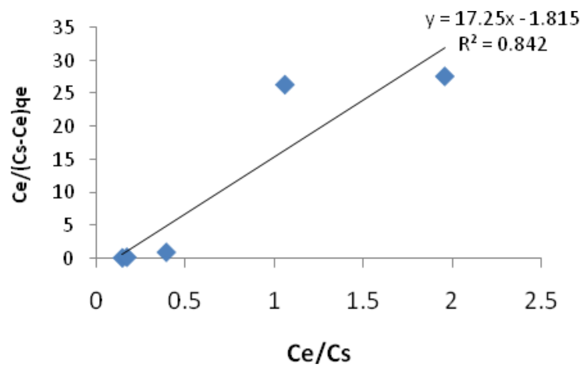

Fig.4: BET Isotherm plot for the adsorption of s Hg^{2+} ions onto powdered swamp arum seeds

From Figures 2, 3 and 4; the Langmuir, Freundlich and BET isotherm parameters were computed and with their regression coefficient (R^2) values were represented in table 1

Table 1: Langmuir, Freundlich, and BET isotherm parameters

Langmuir			**Freundlich**			**BET**		
R^2	**q_m (mg/g)**	**K_L (L/mg)**	**R^2**	**K_F (mg/g)**	N	**R^2**	**q_m (mg/g)**	K_b
0.998	5.917	0.130	0.784	0.5308	3.436	0.842	0.0512	-8.504

From table 1, it was found that the correlation coefficient (R^2) value for the Langmuir plot was 0.998, which was close to unity, thus indicating that the data conformed well to the Langmuir isotherm model. The R^2 value was similar to that obtained by (Iqbal, et al., 2008) with R^2 value of 0.998 for the adsorption of Cd (II) and Pb (II) ions from aqueous solution using mango peel waste. The correlation coefficient (R^2) values for the Freundlich and BET plots were 0.784 and 0.842 respectively which were lower than that for the LangmuirR^2 value of 0.998. Thus, the Langmuir isotherm gave the best correlation coefficient (R^2) for the sorption process and this indicates that Hg (II) ions were adsorbed onto the surface of powdered swamp arum seeds in a monolayer pattern. The Langmuir maximum uptake capacity q_m, for the adsorption of Hg (II) ions was 5.197 mg/g which was higher than the adsorption capacities for BET with an uptake capacity q_m of 0.0512 mg/g.

The Freundlich plot of log q_e against log C_e in Figure 3 gave a straight line with slope of $1/n$ and intercept of K_F. The value of K_F and n obtained were 0.5308 and 3.436 respectively. The n value is a constant indicating the intensity of adsorption, which shows that the sorption process was favourable, since values of n in the range of 2 to 10 are good, 1 to 2 are moderate and less than 1 are poor sorption characteristics (Chen et al., 2010).

Figure 4 shows the BET plot for the adsorption of Hg (II) ions onto powdered swamp arum seeds and from the slope and intercept the BET constants q_m (0.0512) and K_b(– 8.564) were obtained.

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