Thermodynamics of adsorption of mercury (II) ions from aqueous solution using powdered swamp arum *(Lasimorpha senegalensis)* seeds

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ABSTRACT
This study describes the adsorption thermodynamics of mercury (II) ions from aqueous solution onto powdered swamp arum seeds at different experimental temperatures to determine its effectiveness as a novel and low-cost adsorbent. The study also aims at determining the suitability of some thermodynamic models for the adsorption process. Batch adsorption experiments were carried out as a function of temperature. The thermodynamic parameters; enthalpy (ΔH), entropy (ΔS) and Gibbs's free energy (ΔG) changes were determined. The negative ΔG values indicate the feasibility and spontaneous nature of the adsorption process. The enthalpy change (ΔH) of the process was determined to be -15 kJ/mol; the negative sign indicates that the adsorption was exothermic. The value of the entropy change (ΔS) was found to be -0.035kJ/mol.K, which indicates that the degree of disorderliness of the sorbate reduced as they got adsorbed onto the surface of the adsorbent.

Keywords: *Thermodynamics; adsorption; aqueous solution; swamp arum; seeds*

INTRODUCTION

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. Unlike organic pollutants the majority of which are susceptible to biodegradation, heavy metals will not degrade into harmless end products, and therefore accumulated in living organisms, causing various diseases and disorders [1]. Therefore the elimination of heavy metals from water and wastewater is important to protect public health.

The major source of mercury pollution in the aquatic environment is chlor-alkali production, pulp paper, oil refining, electrical, rubber processing and fertilizer industries [2].

Mercury is one of the toxic metals found in most wastewaters. Mercury has adverse effect on the central nervous system, pulmonary and kidney functions, and causes damage to chromosomes [3]. Once mercury enters the food chain large concentrations of mercury compounds accumulate in humans and animals. The tolerance limit of Hg (II) into inland surface water is 10 μg/L and in drinking water -1 μg/L [2].

In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metals from wastewater and water supplies [1]. For high strength and low volumes of wastewater, heavy metal removal by adsorption is a good proposition [4].

Among many water treatment technologies, utilizing plant residues as adsorbents for the removal of metal ions and dyes from wastewater is a prominent technology [5]. High efficiency and low cost among others are the major advantages of this technique over conventional treatment techniques [6]. The use of some agro wastes for the remediation of solutions of toxic heavy metals have been reported; mango tree [7], senna alata bark [8], sesame leaf [9], peanut shell [10], fluted pumpkin waste [11], Raphia palm tree [6], palm shell [12], Rosmarinus officinalis leaves [13], mussel shell [14] palm shell powder [12] Bombax buonopozense [15], modified agricultural waste [16] B.eurycoma seed coat [17].

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 [18]. 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 adsorption of mercury (11) ions from solution onto powdered swamp arum **(***Lasimorpha senegalensis)* seeds at different experimental temperatures was investigated to determine its effectiveness as a novel and low-cost adsorbent. The study also aims at determining some thermodynamic parameters for the adsorption process.

MATERIALS AND METHODS

Adsorbent Preparation: Swamp arum (Lasimorpha senegalensis) fruit bunches was collected from a swamp forest in Amassoma town of Southern Ijaw Local Government Area of Bayelsa State, Nigeria. The seeds were removed from the fruit bunches and were washed with running tap water to remove all dirt. The seeds were then rinsed with distilled water and air dried for 24 hours. Thereafter, they were oven dried at a temperature of 80^{o}C for 24 hours. The dried samples were ground into powder using grinding machine. The ground samples were then stored in air-tight plastic containers for the adsorption studies.

Preparation of Hg^{2+} ion solution: A Stock solution of 1000 mg/L Hg^{2+} ions was prepared from its salt, $HgCl_2$. This was done by weighing 1.35g of $HgCl_2$ and transferred into a 1000 mL volumetric flask. The salt was then dissolved with distilled water and the solution made up to the 1000 mL mark of the flask. From the stock solution a 60 mg/L concentration of the metal ion was prepared by serial dilution using a 50 mL measuring cylinder. This was done by transferring 3 mL of stock solution into a 50 mL measuring cylinder and made up to the mark with distilled water.

Determination of effect of temperature

To five 250 mL conical flasks were introduced 50 mL each of 60 mg/L solution of Hg^{2+} ions. 2 g of the powdered adsorbent was then weighed and added to each of the conical flasks. The conical flasks were then corked and labeled temperatures of 25, 40, 50, 60 and 70^{o}C respectively. The flasks were then heated on a thermo electron corporation precision water bath to the appropriate temperature for 40 minutes at 150 rpm. The suspensions were then filtered using Whatmann filter paper and the residual Hg^{2+} ion concentration (C_e) analyzed using Atomic Absorption Spectrophotometer (AAS).

Analysis of Experimental data

The percentage removal of metal ion by powdered swamp arum seed was calculated by using equation 1

$$\%R = \frac{Co - Ce}{Ce} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

Where %R is the percent removal of Hg^{2+} ions from solution, Co is initial metal ion concentration in solution (mg/L) and Ce is the metal ion concentration in solution at equilibrium (mg/L).

The equilibrium constant (K_c) for the adsorption process was calculated using equation 2

$$Kc = \frac{Co - Ce}{Ce} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

The thermodynamic parameters, ΔS, ΔH, and ΔG were obtained from the expressions in equations (3) and (4) respectively.

$$\ln Kc = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

$$\Delta G = -RTLnKc \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where ΔS is entropy change, ΔH is enthalpy change, ΔG is Gibbs free energy change, R is gas constant (8.314J/mol. K) and T is the temperature in Kelvin.

RESULTS

Effect of temperature: The effect of temperature on the percent adsorption of Hg^{2+} ions onto powdered swamp arum seeds was studied and is presented in Figure 1.

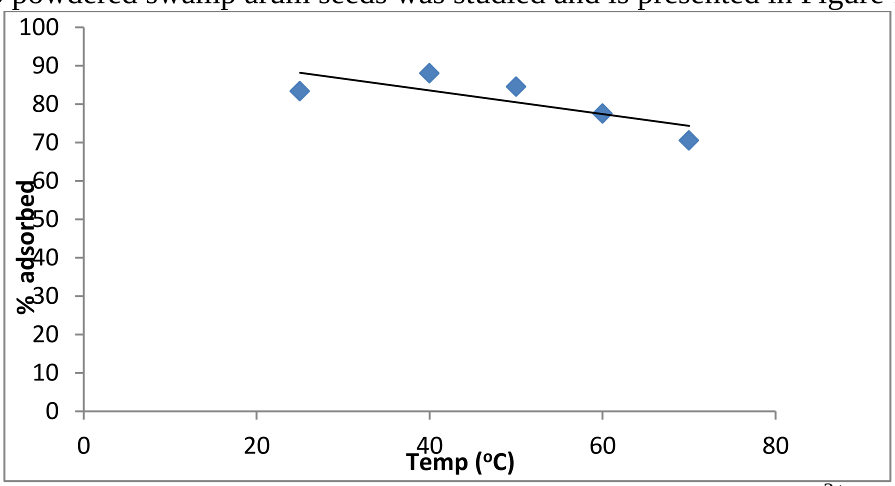

Figure 1: Effect of temperature on the percent removal of Hg^{2+} ions onto powdered swamp arum seeds

From figure 1, it was shown that increase in temperature decreases the percent adsorption of Hg^{2+} ions from solution.

Thermodynamics of the sorption process: In order to determine the thermodynamic behavior of the sorption process of Hg (II) ions onto powdered swamp arum seeds from aqueous solution, the thermodynamic parameters such as the change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were evaluated. This was done by plotting ln K_c versus 1/T of equation 3 and presented in Figure 2. From the slope and intercept of Figure 2, the parameters ΔH and ΔS were determined. While the parameter, ΔG for each temperature was evaluated from equation 4. The parameters thus evaluated and the regression coefficient (R^2) obtained from Figure 2 were listed in Table 1.

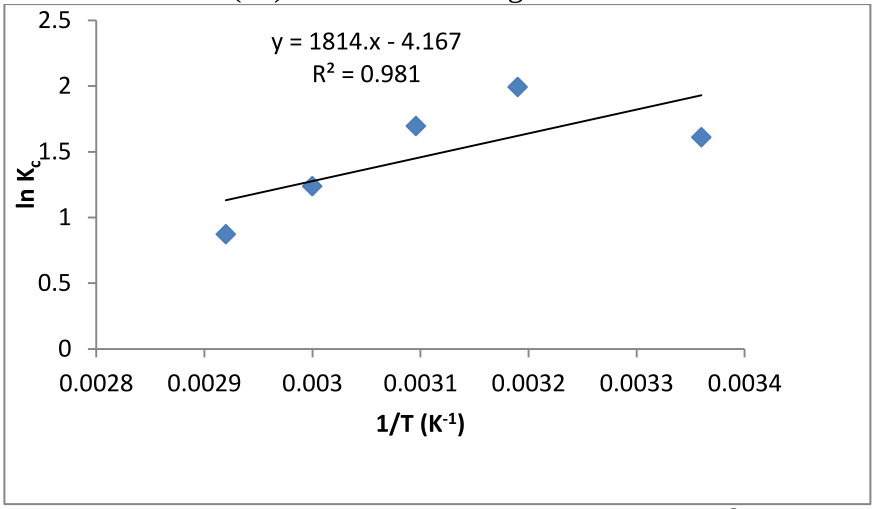

Figure 2: Plot of ln K_c against 1/T for the adsorption of Hg^{2+} ions onto powdered swamp arum seeds.

Table 1: Thermodynamic parameters and regression coefficient (R^2) value for the adsorption of Hg^{2+} ions onto powdered swamp arum seeds.

Temp (^{o} C)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol K)	R^2
25	-3.9844			
40	-5.18479	-15.082	-0.035	0.981
50	-4.55421			
60	-3.42388			
70	-2.48440			

DISCUSSION

The decrease may be due to weak interaction between Hg^{2+} ions and powdered swamp arum seeds. A rise in temperature increases the kinetic energy of Hg^{2+} ions and therefore their binding strength to the surface of the adsorbent becomes less, thus lowering the extent of adsorption. Similar findings have been reported [6, 13], using Raphia palm tree for the removal of Iron (III), Lead (II) and Cadmium (II) ions and carbonized Rosmarinus officinalis leaves (ACROL) on the removal of mercury (II) ions from aqueous solutions.

As shown in Table 1, the Gibb's free energy change (ΔG) values were all negative. The negative ΔG values indicate the feasibility and spontaneous nature of the adsorption process. The ΔG values obtained in this study for the Hg^{2+} ion were all less than -10 kJ/mol, suggesting that physical adsorption was the predominant mechanism in the sorption process.

The enthalpy change (ΔH) of the adsorption process was found to be -15 kJ/mol, the negative sign indicates that the adsorption was exothermic i.e., the adsorption takes place with the release of energy. On the other hand, the value of the entropy change (ΔS) was -0.035 kJ/mol.K. The negative value of the entropy change indicates that the degree of disorderliness of the Hg^{2+} ions reduced as they got adsorbed onto the surface of the adsorbent. This is similar to the findings of [13], using carbonized Rosmarinus officinalis

leaves on the removal of Hg^{2+} ions from solution.
The high regression coefficient (R^2) value of 0.981 shows that the thermodynamic equation was suitable for describing the adsorption process.

CONCLUSION

The present study evaluates the efficiency of powdered swamp arum seeds in removing Hg^{2+} ions from aqueous solution. The findings show that powdered swamp arum seeds are a novel and low-cost adsorbent for the removal of mercury (II) ions from aqueous solution. Some thermodynamic parameters were determined which were suitable for describing the sorption process.

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