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Original Research Article

Kinetic Studies of the Adsorption of Hg^{2+} Ions (in Aqueous Solution) on Powdered Swamp Arum (Lasimorpha Senegalensis) Seeds

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ABSTRACT

The kinetics of biosorption of Hg (II) ions from aqueous solution using powdered swamp arum seed was investigated to ascertain its suitability as a low cost adsorbent. Batch biosorption technique was used to investigate the effect of contact time on the removal of Hg (II) ions from solution. The results show that powdered swamp arum seeds were a very effective and novel adsorbent for Hg (II) ions from aqueous solution. The percentage removal of Hg (II) ions increased with increase in contact time up to 60 minute where equilibrium was attained. Two kinetic rate equations were used for analyzing the experimental data. The percent removal of Hg (II) ions was 90.2% at 10 minutes, 93.28, 96.53, 99.73 and 99.73% respectively for 20, 40, 60 and 80 minutes. The rate equations were very suitable for describing the adsorption process with regression coefficient (R^2) values of greater than 0.9. However, the pseudo second order model was more suitable for the experimental data since it had a higher regression coefficient value of 0.999. The pseudo second order constant, k_2 (0.400) was also found to be higher than the first order constant, k_1 of 0.00002. Thus, the results of these findings show that powdered swamp arum seeds could be effectively utilized for the removal of Hg (II) ions from aqueous solution.

Keywords: kinetic studies, adsorption, aqueous solution, swamp arum, seeds.

INTRODUCTION

Over the past several decades, the intensification of industrial activities has led to increased amounts of heavy metals being dumped into the environment. [1] The rate at which these metallic substances are discharged into the environment, especially water bodies, is increasing at an alarming rate. Heavy metal ions are of great concern because of their toxic nature, bioaccumulating tendency, detrimental effects on human life and public health, and negative impacts on the environment. [2] According to the United States Environmental Protection Agency (EPA), the metals of most concern include arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, mercury, tin and zinc. [3] Some heavy metals are essential for enzymatic activities. However, they may inhibit enzyme activity when natural concentrations are exceeded. As a result most heavy metals whether essential or not are potentially toxic to living organisms. [4] Land-based operations that introduce heavy metal pollutants into the sea include mining, milling, smelting activities, metal plating, refining and assorted manufacturing processes.

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. [5] The plant grows from rhizomes that measure 30 cm or longer, and 2.5 to 5 cm in diameter.

Recently, research efforts have been directed towards the use of agro-wastes and unused abundant plant materials for the removal and recovery of toxic and valuable metals from aqueous systems and industrial effluents. The use of some agro wastes for the remediation of solutions of toxic heavy metals has been reported; orange peel and orange peel xanthate, [6] peanut shell, [7] EDTA modified peanut shells, [8] potato peels, [9] potato peels waste in removing Ni (II) ion, [10] rice husk ash, [11] using rice husk ash for competitive adsorption of Cd (II) and Ni (II) ions from aqueous solution, [12] ability of rubber leaves powder to adsorb Pb (II) ion from aqueous solution, [13] rubber leaves powder, [14] dried sunflower leaves. [15]

Literature search shows that very scanty information on swamp arum exists on local uses only; hence in the present study, the removal of mercury [11] ions onto powdered swamp arum (*Lasimorpha senegalensis)* seeds at different experimental contact time was investigated. The study also aimed at using the kinetic models; pseudo-first and pseudo-second order so as to determine their suitability for the adsorption process.

MATERIALS AND METHODS

Collection and Preparation of swamp arum seeds

The mature swamp arum fruits were obtained from a swamp in Amassoma community of Southern Ijaw Local Government Area, Bayelsa State, Nigeria. The seeds were detached from the fruit, washed with water to remove dust and any adhering particles, rinsed with distilled water and dried under sunlight for one day and then in an oven at 80 ºC for another 24 hours. The dried seeds were crushed and ground to powder using a grinding mill. The powdered swamp arum was stored in an airtight plastic container for the batch adsorption experiments.

Preparation of Stock Solution of Hg^{2+} ions

A stock solution of 1000 mg/L of Hg^{2+} ions was prepared from its salt, $HgCl_2$, by dissolving 1.35g of $HgCl_2$ in 1000 mL of distilled water.

Batch adsorption experiments

Batch experiments were carried out at room temperature by adding 2.0 g of powdered swamp arum fruits to 60 mg/L of Hg (II) ions solution in a conical flask, agitated at the rate of 150 rpm at time intervals of 10, 20, 40, 60 and 80 minutes. At the end of the agitation time, the mixture was filtered using Whatmann filter paper and the filtrate was analyzed for residual Hg^{2+} ions using atomic absorption spectrophotometer (AAS).

Analysis of Experimental data

The uptake of Hg (II) ions from solution by the adsorbent was calculated using equation (1)

$$\% \text{ Uptake} = \frac{Co - Ce}{Co} \times 100 \text{ ---------------- } \mathbf{(1)}$$

Where;

Co =Initial concentration of Hg (II) (mg/L)

Ce = Concentration of Hg (II) at equilibrium (mg/L)

The pseudo-first order kinetic model was used to find out its suitability for the adsorption process. The pseudo-first order expression is given in equation (2)

$$\log qe - logqt = \log qe - \frac{K1t}{2.303} \text{ -------------- } \mathbf{(2)}$$

Where;

q_e = Amount of metal ions adsorbed at equilibrium (mg/g)

q_t = Amount of metal ions adsorbed at time t (mg/g)

k_1 = pseudo first-order rate constant (min^{-1})

A plot of log ($q_e - q_t$) versus t should give a straight line and from the slope and intercept the parameters k_1 and q_e are determined.

The pseudo-second order model was also used to analyze the experimental data in this study. It is mathematically expressed in equation (3)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(3)}$$

Where h is the initial sorption rate (mg/min). The initial sorption rate, h, is given as:

h = $K_2 q_e^2$ ---------------------------- **(4)**

Where K_2 is the pseudo-second-order rate constant (g/ (mg/min). The parameters h and q_e are determined experimentally from the intercept and slope of a plot of t/q_t against t. From equation (4), the pseudo-second order rate constant k_2 is calculated.

RESULTS

The effect of time on the percent removal of Hg^{2+} ions by powdered swap arum seeds was obtained by plotting percent adsorbed against time and presented in Figure 1. Two observations can be made from the figure; the amount of Hg^{2+} ions adsorbed using powdered swamp arum seeds increased with increase in contact time and the contact time required to attain equilibrium was dependent on the resident time of contact between the Hg^{2+} ions and the adsorbent.

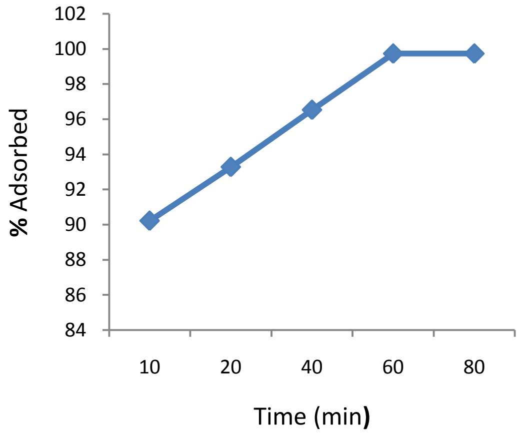

Fig.1: Effect of time on the percent removal of Hg^{2+} ions from aqueous solution using powdered swamp arum seeds

For the same concentration, the percentage removal of heavy metal increases with increase in contact time till equilibrium was attained. The optimal contact time to attain equilibrium was 60 minutes with a maximum percent removal of 99.73.

The pseudo-first and pseudo-second order rate model plots for the adsorption of mercury (II) ions onto swamp arum seeds were also taken and are presented in Figures 2 and 3. From the figures, the pseudo-first order and pseudo-second order model parameters were calculated and with their regression coefficient (R^2) values are presented in Table 1.

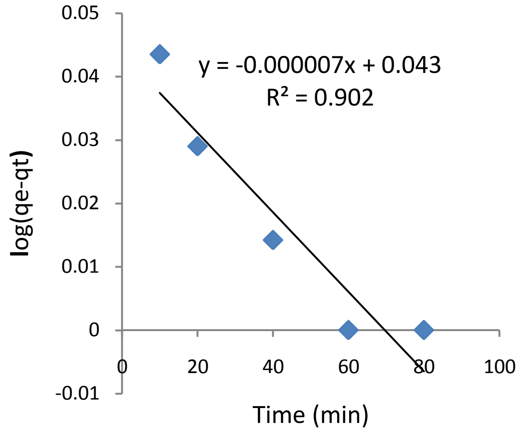

Fig.2: Pseudo-first order plot for the removal of Hg^{2+} ions onto powdered swamp arum seeds

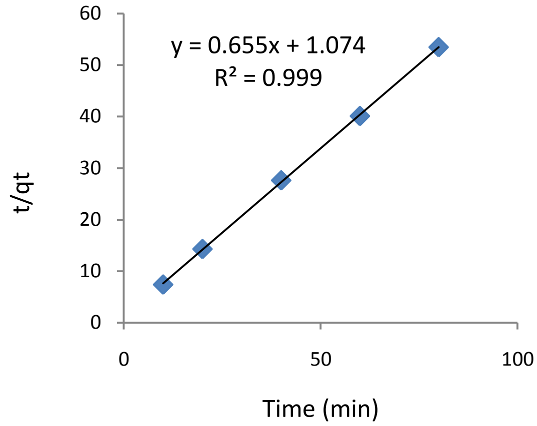

Fig. 3: Pseudo-second order plot for the removal of Hg^{2+} ions onto powdered swamp arum seeds

Table 1: Pseudo first and second rate order model parameters

Pseudo first order			Pseudo second order			
k_1	q_{e1}	R_1^2	k_2	q_{e2}	h	R_2^2
0.00002	1.104	0.902	0.400	1.526	0.931	0.999

Figure 2 shows the linear plot of log (q_e - q_t) against t at constant Hg (II) ions concentration of 60 mg/L. The pseudo first-order rate constant, K_1, (min^{-1}) and the pseudo first-order adsorption capacity, q_{e1}, (mg/g) values were determined from the slope and intercept of the linear plots in Figure 2. Table 1 gave the values of k_1 and q_{e1}, as well as the R_1^2 value for the pseudo-first order kinetic model plot.

Figure 3 shows the linear plot of t/qt against t at constant Hg (II) ions concentration of 60 mg/L. The values of q_{e2} and h were calculated from the slope and intercept of the plot respectively. Table 1 gives the values of k_2 (0.400) and q_{e2} (1.526), as well as the R_2^2 value (0.999) for the pseudo-second order plot.

DISCUSSION

The results in figure 1 show that the uptake of Hg^{2+} ions was fast at the initial stages of the contact period, and thereafter, it became slower near the equilibrium. This may be due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the Hg^{2+} ions on the adsorbent and bulk phases. Similar results were obtained by other researchers. [6-8]

Table 1 shows the rate parameters and equilibrium sorption capacities of the pseudo first and pseudo second order equations. From Table 1, it was observed that the value of the correlation coefficients R_1^2 and R_2^2, were all high (>0.90). This shows that the results fitted both the pseudo-first and the pseudo-second order models. However, the pseudo-second order correlation coefficient value (R_2^2=0.999) was found to be higher than that of the pseudo- first order value (R_1^2 =0.902). Again, the equilibrium sorption capacity (1.526 mg/g) for the pseudo-second order (q_{e2}) was found to be higher than the sorption capacity (1.104 mg/g) for pseudo-first order (q_{e1}) as shown in Table 1. This was because the pseudo-second order kinetic model assumed that the sorption rate was proportional to the square of number of unoccupied sites. [16] These results suggest that the sorption of Hg^{2+} ions onto the powdered swamp arum seeds follows better the pseudo-second order model. Thus, suggesting a chemical reaction mechanism. The pseudo- second order kinetic model considers the rate-limiting step as the formation of chemisorption bond involving sharing or exchange of electrons between the sorbate and the sorbent. Similar results were also reported when kinetic data from different authors, including the adsorption of Pb (II) ions onto orange peel and orange peel xanthate, [7] adsorption of Cu (II) and Cr (III) onto peanut shell, [8] adsorption of Hg (II) and Cd (II) using EDTA modified peanut shells [9] and removal of Cu (II) ions from aqueous solution using potato peels [10] were studied.

CONCLUSION

In this study, the ability of swamp arum sorbent to remove Hg (II) from aqueous solution was investigated. The result of this study indicates that the uptake of Hg (II) ions by powdered swamp arum seeds was dependent on time of adsorption. The uptake of Hg (II) ions increased with increasing contact time until equilibrium was attained in 60 minutes of contact. The kinetic data obtained from this study fitted well to both pseudo-first order and pseudo-second order models with high values of coefficient of regression (R^2). However, the pseudo- second order model was more suitable based on their R^2 values. The results show that powdered swamp arum seeds were effective for the removal of Hg (II) ions from aqueous solution. Since swamp arum used in this work is free, abundant and locally available, the resulting sorbent is expected to be economically viable, novel adsorbent for the removal of Hg (II) ions from aqueous solution.

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