Kinetics of Cadmium Adsorption in Aqueous Media Using Banana Stem Biomass

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ABSTRACT

Kinetics of cadmium adsorption on banana stem biomass in an aqueous media was investigated. Cadmium is of particular concern because its presence in aquatic ecosystems even at low concentrations could be toxic to human health. Adsorption is one of the methods used to remove cadmium from aquatic environments. Selected amounts of cadmium ion concentrations (0.1, 0.5, 1.0, 1.5 and 2 ml/L) were added to 0.1g, 0.2g, 0.5g, 0.7g and 1g powered dry banana stem biomass respectively and allowed to stand for predetermined times (10min, 20min, 30min, 60min, 70min and 80 min). The solution was centrifuged, filtered and the amount of Cd remaining in the solution determined using Inductively Coupled Plasma Spectrometer. The results obtained were used to determine the kinetics of Cd release from the aqueous media. The study revealed that banana stem biomass was able to adsorb cadmium ions up to 40mg/kg when the particle size of the banana biomass used was 600 µm. The adsorption of banana-stem biomass for cadmium ions followed Langmuir and Freundlich isotherms. The kinetics study also showed that the adsorption process for cadmium ions followed pseudo first order and pseudo second order with coefficient correlation equal to 0.999 and 0.989 respectively. The adsorption capacity (K_f) of banana-stem biomass for cadmium calculated from Freundlich isotherm was 2.797 while the adsorption capacity (Q_c) calculated from Langmuir isotherm at 295K was 23.25.This study showed that banana stem biomass is a potential adsorbent for remediation of cadmium from water bodies.

Keywords: *Cadmium, adsorption, kinetics study, banana stem biomass*

I. INTRODUCTION

Environmental pollution by heavy metals is of health concern due to the toxic nature of cadmium even at low levels. Cadmium constitutes one of the pollutants found in the environment arising from anthropogenic and industrial activities. The presence of heavy metals in the ecosystem is known to pose danger to human health. According to [1] adsorption is one of the methods that can be used to remove heavy metals from aqueous media.

Adsorption is the surface phenomenon of binding molecules or particles in a solution onto a surface of an adsorbent [2]. Adsorption is considered as one of the most effective and economical technology compared to others for removal of toxic metals from effluents. Hence the aim of this study was to prepare powdered banana stem as an adsorbent biomass to investigate the kinetics and eqiulibria of cadmium ions in aqueous solution.

II. METHODOLOGY

2. 1 Preparation of adsorbents

The waste banana stem biomass weighing 168g was collected from a banana farm in Kisii and sundried to reduce water content to below 10%. The sundried biomass was then transferred to the oven and further dried to reduce the mass to 146 grams. The dry banana stem biomass was milled using a machine type AR11 (Zhengzhou CY Scientific Instrument Co., Ltd) to obtain a powdered biomaterial. The powder was washed several times with doubly distilled water to remove any soluble coloring matter and again air dried. The dry powdered banana stem biomass was sieved through a 2mm sieve and stored in air tight plastic containers for subsequent analysis.

2.2. Preparation of stock solution

Standard commercial solution (1000 ppm) of cadmium metal was used to prepare working standards for the determination of cadmium ions in aqueous media. The working standards were 0.1, 0.2, 0.5, 1, 2, 5 ppm each. All working standards were obtained from the standard commercial solution by dilution. 0.1M HNO_3 and 0.1M NaOH were used to adjust the pH of the stock solutions.

2.3 Adsorption studies and cadmium analysis

HL-200I digital weighing machine (KERN Co Ltd) was used in weighing the adsorbent. 0.1g, 0.2g, 0.5g, 0.7g and 1 g of dry powered banana stem biomass were taken and cadmium ion concentration in ml/L; (0.1, 0.5, 1.0, 1.5 and 2) was added. The mixture was allowed to stand for 18 hours then a centrifuge (Kleinknecht) was used to separate the banana biomass from the metal solution. An Inductively Couple Plasma Emission (ICPE) spectrometer was then used to determine the Cd^{2+} remaining in the solution. The concentration of cadmium was determined in triplicate and the mean values were used in data analysis.

2.4 Adsorption kinetics

Adsorption capacity for cadmium metal by banana stem biomass was investigated at pH value of 5.6, 1 ppm concentration, 298K temperature and at 10 minutes intervals in the range of 10 minutes to 80 minutes. The data from the adsorption of cadmium ions by banana stem biomass were modeled by Lagergren's Pseudo-first order and Pseudo-second order [3] kinetic equations. Pseudo first-order kinetic is given by equation (1):

$$\text{In}\ (q_e - C_e) = \text{In}\ C_e - K_1 t \qquad (1)$$

Pseudo second-order kinetic model is given by equation (2):

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and the time t (min) respectively C_e is the concentration of heavy metal adsorbed.

K_1 and K_2 are Pseudo first and second order rate constants of adsorption respectively.

The value of K_1 was calculated from the slope of the linear plot of In (q_e- C_e) versus InC_e. K_2 was obtained from a plot of 1/q_t versus t.

2.5 Adsorption isotherms

Adsorption of cadmium ions were in the range of 0.1 ppm to 2 ppm at constant pH (5.6), time (30 min), temperature (295K) when increase in adsorbent dosage was investigated. The analysis of the adsorption isotherms of heavy metal ions was carried out by applying the Langmuir [4] and Freundlich [5] equations. Langmuir isotherm is given by equation (3):

$$C_e/q_e = 1/b.Q_o + C_e/Q_o \qquad (3)$$

where C_e and q_e are concentrations (mg/l) and amount (mg/l) of heavy metal adsorbed respectively, b is the Langmuir constant related to the free adsorption energy (l/mg), and Q_o is a constant related to the area occupied by a monolayer of the adsorbent, reflecting the maximum adsorption capacity (mg/g). A plot of C_e/q_e versus C_e was used to obtain Q_o and b.

The linearized Freundlich isotherm model is given by the equation (4):

$$\text{In}\ q_e = \text{In}\ k + 1/n\ \text{In}\ C_e \qquad (4)$$

where n is Freundlich adsorption intensity, k is a constant for the system relating to the bonding energy. The ultimate adsorption coefficient k was found from the intercept of a plot of In q_e versus InC_e.

2.6 Thermodynamic properties

Thermodynamic properties and thermal effects on adsorption were studied by varying the temperature in the range of 298K to 323K at 1 ppm concentration of Cd^{2+} ions, 1gadsorbent and pH value of 5.6. Thermodynamic parameters; Gibbs free energy ΔG^o (kJ/mol), enthalpy changes ΔH^o (kJ/mol) and entropy change ΔS^o (kJ/mol K) were calculated from the data obtained. Gibb's free energy was calculated using the equation (5):

$$\Delta G^O = -RT\ \text{In}\ K_a \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where, R is universal gas constant (0.008314 kJ/mol K), T is absolute temperature (K), K is adsorption equilibrium constant from Langmuir isotherm.

Enthalpy change was calculated using the equation (6):

$$\Delta H^o = \Delta G^o + T \Delta S^o \qquad (6)$$

A plot of ΔG^o versus T was done and the values of ΔH^o and ΔS^o calculated from the slope and intercept of the plot.

III. RESULTS AND DISCUSSION

3.1 Thermodynamic properties

When the percentage of cadmium removed was plotted against temperature, it was observed that the percentage of Cd removed increased with temperature until 308K and then it decreased (Fig.1).

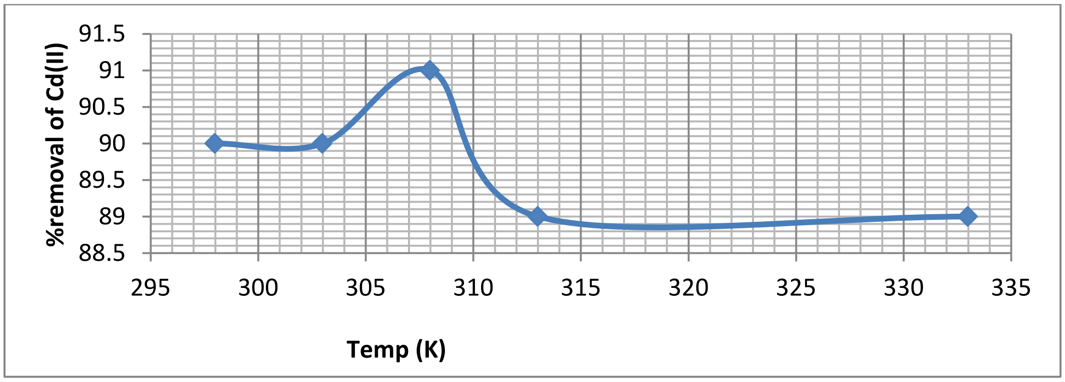

Figure 1: A plot of percentage removal of cadmium versus temperature

The results indicated that at higher temperatures, the kinetic energies of the heavy metal ions increased, resulting in more binding with polar functional groups of the adsorbent [6]. However, above 308K, adsorbent material was decomposed by heat which decreased adsorption capacity [7]. A plot of ΔG^o versus T (Fig. 2) was used to calculate the values of ΔH^o and ΔS^o from the slope and intercept of the plot.

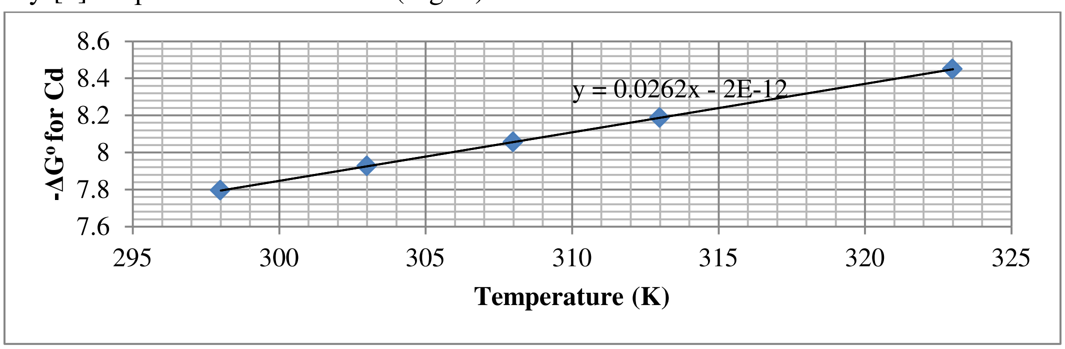

Figure 2: A plot of ΔG^o versus Temperature

The calculated Thermodynamic parameters are recorded in Table 1

Table 1: Thermodynamic properties for adsorption of cadmium by banana stem biomass

Metal ion	**ΔH^o (kJ/mol)**	**ΔS^o (kJ/mol K)**	**ΔG^o (kJ/mol)**		
			300 K	**310 K**	**320 K**
Cd^{2+}	2.00E-12	-0.026	-7.85	-8.11	-8.36

The results in Table 1 showed that ΔG^o values were negative and increased in their absolute values with temperature. This indicated a spontaneous adsorption process. ΔH^o value was positive for cadmium ion indicating that adsorption process was endothermic. Change in entropy (ΔS^o) value was negative which suggested that the Cd^{2+} ions were fairly stable on the adsorption sites of banana stem biomass.

3.2 Adsorption kinetics

The value of K_1obtained from the slope of the linear plot of In (q_e- C_e) versus In C_e was 1.232 (Fig.3). The value of K_2 was 7.17(Fig.4). Data fitted well in Pseudo first-order and Pseudo second-order models since (R^2) values were greater than 0.99. R^2 values that are less than 1 could be as a result of the remaining sites becoming unfilled because of charge repulsion [8].

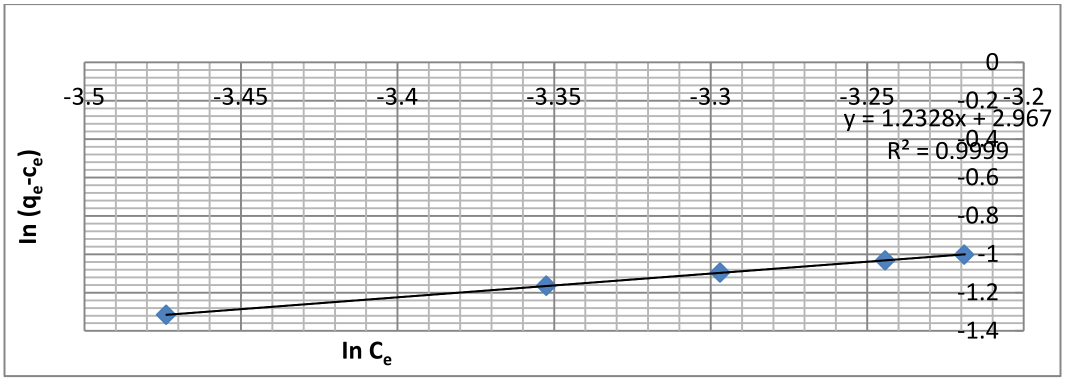

Figure 3: A fit of Pseudo first-order adsorption for Cd(II) ion

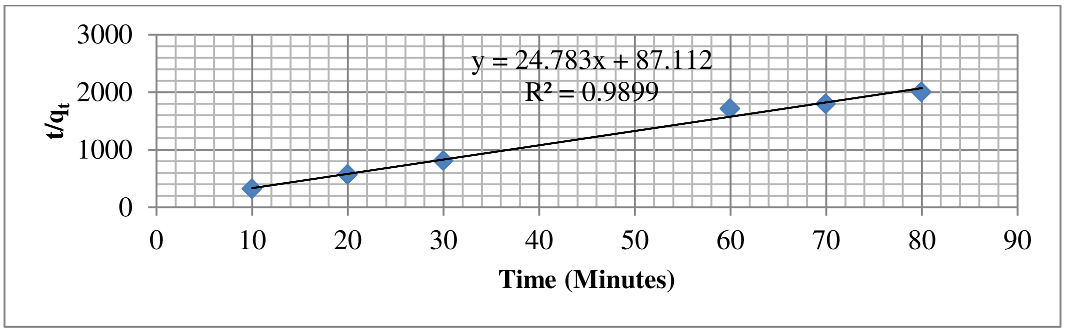

Figure 4: A fit of Pseudo second-order adsorption for Cd(II) ion

3.3 Adsorption isotherms

Adsorption capacity, Q_o, for the Cd^{2+} at 295K was 23.25mg/g and b was 3.07l/g (Fig.5).The lower value of 'b' (3.07) indicates that the particle radii of banana stem biomass were small towards adsorption [9].The ultimate adsorption coefficient, k, calculated from Freundlich model was 2.797 while n was obtained from the reciprocal of the gradient and was 1.64 (Fig.6). Adsorption intensity 'n' values of Freundlich isotherm model demonstrate that the Cd^{2+} adsorption by powdered banana stem biomass is favorable at low temperatures as the magnitude lied between 1 and 3 [10]. R^2 values indicate that Freundlich and Langmuir isotherms hold good for cadmium.

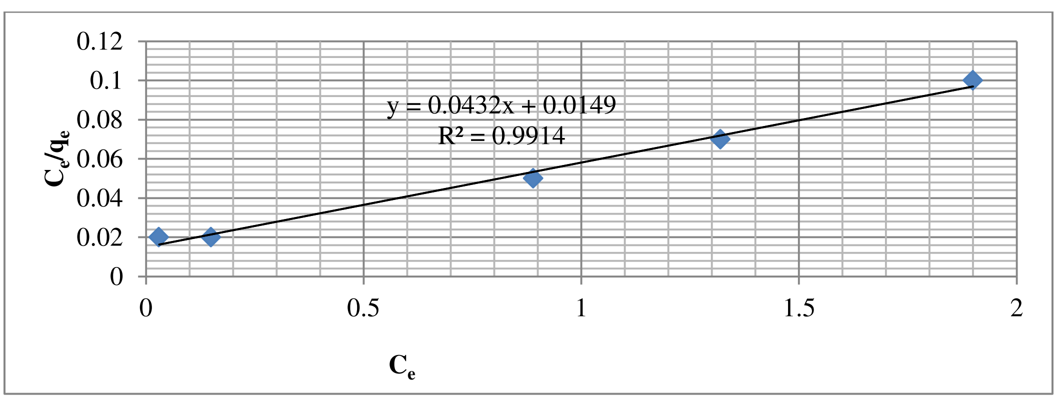

Figure 5: Langmuir isotherm for Cd(II) ion

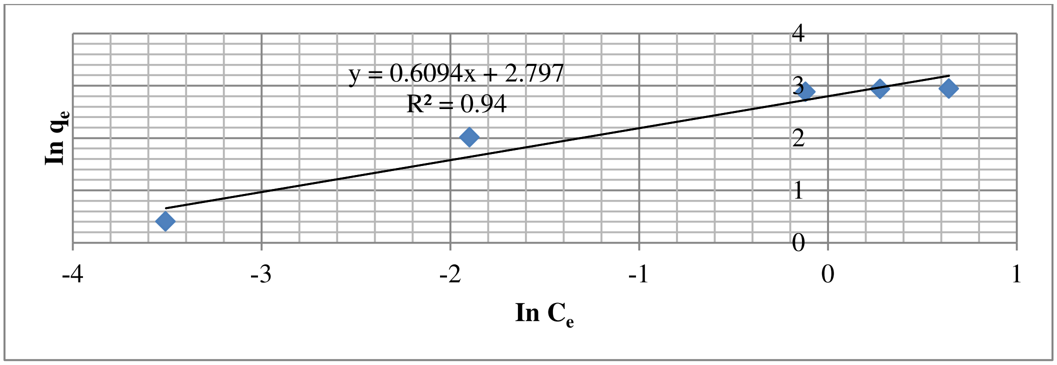

Figure 6: A fit of Freundlich isotherm for Cd(II) ion

IV. CONCLUSION

The results showed that cadmium adsorption onto banana stem biomass followed Pseudo first and second-order kinetic models. Langmuir isotherm was found to hold good for adsorption of Cd(II) ions. Thermodynamic parameters applied in this study indicated that the adsorption process of Cd^{2+} ions by powdered banana stem biomass is spontaneously favorable and endothermic in nature and the randomness decreased during adsorption process.

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