

Sorption of Cd²⁺ From Aqueous Solutions Using Cassava (*Manihot Esculenta*) Waste: Equilibrium and Kinetic Studies

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Abstract

Removal of Cd(II) ions from aqueous solutions via adsorption using raw and acid-modified cassava tuber bark waste was investigated in a batch process. Effects of contact time, solution pH, temperature and initial Cd(II) ions concentrations on the sorption yield was evaluated. Optimum adsorption conditions were found to be pH of 5.5 and 5.0 for raw cassava tuber bark waste (RCTBW) and modified cassava tuber bark waste (MCTBW) respectively, initial Cd(II) ions concentration of 100 mg/L, temperature of 40 °C and contact time of 60 mins. The sorption process conformed Freundlich isotherm than the Langmuir isotherm. Kinetic studies showed that the uptake of Cd(II) ions by both adsorbents followed the Lagergren pseudo-first-order kinetic model. FT-IR study showed the involvement of -OH, -NH, C=O, COOH and -C-N functional group in the sorption process. Thus, cassava tuber bark waste demonstrated excellent property as an adsorbent materials for the removal of Cd(II) ions from aqueous solutions.

Keywords: Sorption, Cadmium, Kinetic, Isotherms.

Introduction

Cadmium is a hazardous heavy metal [1]. Inhalation of fine dust and fumes, or ingestion of highly soluble cadmium compounds are the most dangerous form of cadmium exposure [2]. Cadmium is introduced into the environment as a result of iron and steel production, natural source, phosphate fertilizers, sewage sludge, cadmium nickel batteries, mining, pigments, stabilizers and fossil fuel combustion [2, 3]. The most severe form of cadmium exposure in human is *itai-itai* disease (a disease which is known to cause excruciating pains in born) [4]. Other harmful effects of cadmium in living organisms include renal abnormalities,

hypertension, hepatic damage, kidney malfunction, liver and reproductive organ disorder, emphysema and atherosclerosis [2, 5, and 6]. It is obvious however, that the need for the removal of Cd(II) ion from wastewater cannot be overemphasized. Several conventional methods had been employed in the removal of Cd(II) ions and other heavy metals from the environment. Some of these methods include filtration, chemical precipitation, reverse osmosis, chemical coagulation, flocculation, ion exchange, solvent extraction and membrane technologies [7, 8, 9 and 10]. Most of these methods however suffer some setbacks such as high operational costs, inefficiency in the removal of contaminant generation of sludge

and many more [11]. Thus, the use of biological origin has emerged as one of the most effective, eco-friendly and cheap alternative means for the removal of heavy metals from the water system [1]. The uptake of both metal and non-metal species by biomass, whether living or denatured, is commonly termed as biosorption [12]. A number of reviews have appeared highlighting the potential of low-cost sorbents obtained from agricultural waste materials for the sorption of cadmium (II) ions from aqueous solution. Some of these include cassava tuber bark waste [11], corncob [13, 14], exhausted coffee [15], grape stalk [16], hazelnut [17], peanut hulls [18], rice husk [19, 20], and sawdust [21].

Cassava (*manihot esculenta*) is extensively cultivated as an annual crop in Nigeria for its edible starchy, tuberous root and as a major source of carbohydrates. Nigeria cassava production is by far the largest in the world; a third more than production in Brazil and almost double the production of Indonesia and Thailand [22]. With the current effort of the Federal government of Nigeria investing 200 billion of naira into cassava production, the waste generated from cassava will enormously increase. In this study, the ability of raw and modified cassava tuber bark waste as cheap sorbent for the removal of Cd(II) ions from aqueous solutions were examined in batch process. Different factors such as contact time, initial metal concentration, solution pH and temperature were considered. Also, equilibrium and kinetic studies on the adsorption of Cd(II) ions onto the cassava waste were carried out.

Materials and Methods

Raw Material and Chemical

All the reagents used were of analytical grade and used without further purifications. Distilled deionized water was used for the preparation of all solutions. Stock solutions of 1000 mg/L of CdCl₂ (Nile Chemicals, India) were prepared from which working solutions of several concentrations were prepared by serial dilutions. The cassava tuber bark waste samples were collected from Arigbajo farm in Ifo Local

Government Area of Ogun State, Nigeria. Samples were washed several times using distilled-deionized water and dried in the laboratory. The dried biomass was then dried in an oven at 100 °C for 6 hours and ground into powdery forms with the aids of manually-operated grinder. It was then sieved and particles having sizes less than 150 µm were obtained.

Activation of biosorbent

About 30 g of the sieved cassava tuber bark waste was soaked in 0.5 M HNO₃ (Oxford, India) for a period of 24 hours at room temperature. After this duration, it was removed and filtered through a Whatman No. 1 filter paper and rinsed with distilled-deionized water. The sorbent was dried in an oven at 100 °C for 8 hours. It was then removed and stored in an airtight container. This was referred to as modified cassava tuber bark waste (MCTBW). The remaining sorbent was referred to as raw cassava tuber bark waste (RCTBW).

Sorption Studies

The batch sorption studies were carried out on a rotary shaker at a speed of 150 rpm in 250 mL Erlenmeyer flasks which contained 20 mL of Cd(II) ions and 0.6 g of the biomass. The pH of the solution was adjusted with 0.1 M HNO₃ or KOH prior to the addition of the sorbent. The samples were taken at definite time intervals of 5, 10, 15, 20, 30, 40, 50 and 60 mins and were filtered immediately to remove the sorbent and the metal ions contents of Cd(II) were analyzed using UNICAM 969 solar Atomic Absorption Spectrophotometer. All the experiments were carried out in triplicate and the average value recorded. The percentage removal (% E) of Cd(II) ions was estimated using equations (1) and (2):

$$q_e = \frac{C_i - C_e}{W} V \quad (1)$$

$$\text{Sorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Where C_i and C_f are the initial and final concentration of copper (II) ions in 'mg/L', C_e is

the equilibrium concentration of copper (II) ion in 'mg/g', W is the mass of the adsorbent in 'g' and V is the volume of the solution in L .

Characterization of Cassava Tuber Bark Waste

The crystal structure and phase stability of the cassava tuber bark waste sample was measured using X-ray diffraction patterns on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation in the range of $10 - 45^\circ$ (2θ). Scanning electron microscopy (SEM) was used to investigate the morphology of the biomass before and after adsorption using a Hitachi (Japan) S-3000H electron microscope with an accelerating voltage of 15kV. The absorption peaks of the cassava tuber bark waste

were performed before and after sorption of Cd by using FT-IR transmission by KBr method. Homogenized pellet of grinded KBr powder was hard-pressed with SHIMADZU MHP-1 mini hand press. The scans were done in the mid IR region of $400\text{-}4000 \text{ cm}^{-1}$ with 45 scan repeat using SHIMADZU 8400S FT-IR instrument.

Results and Discussions

Characterization of Cassava Tuber Bark Waste

The XRD pattern of cassava biomass showed amorphous regions with peaks at 16.3° , 18.6° and 22.4° as shown in Fig. 1a. The diffraction peaks at $2\theta = 16.1^\circ$ and 22.4° correspond to the (101) and (200) planes for cellulose.

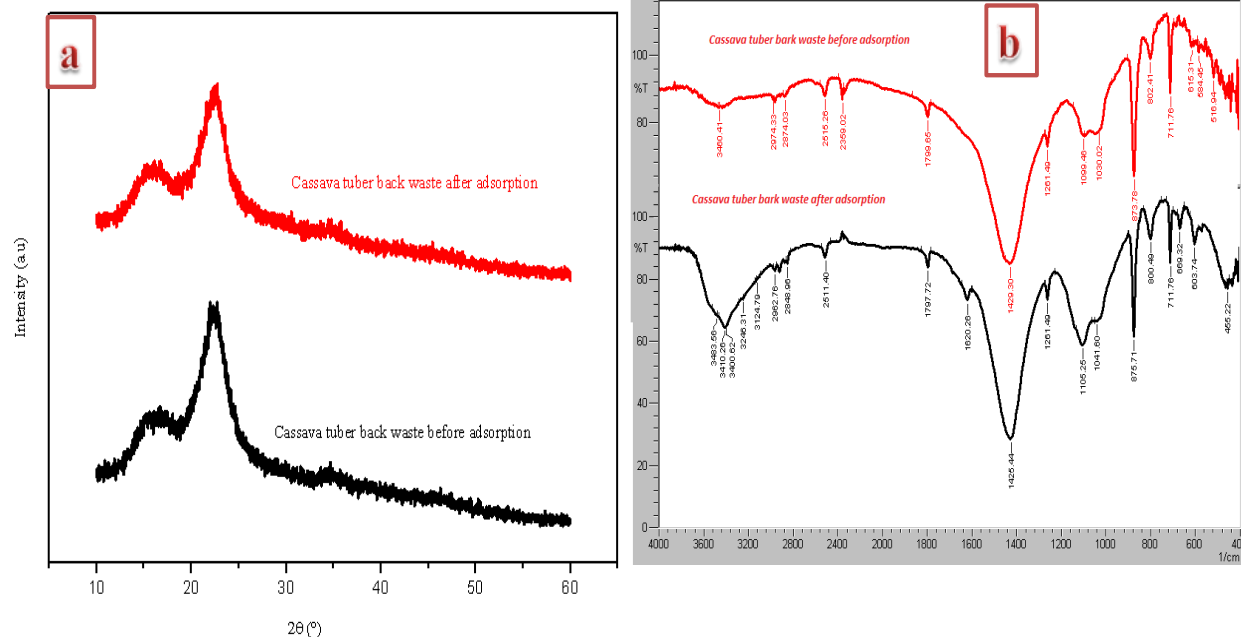


Fig. 1. (a) XRD and (b) FT-IR spectral of Cassava Tuber Back Waste before and after Cadmium Adsorption

The various functional groups which are present of the cell walls of natural and Cd (II) ions loaded cassava tuber bark wastes were investigated as presented in Fig. 1b. The broad peaks from 3400 to 3460 cm^{-1} are indication of $-\text{OH}$ and $-\text{NH}$ groups. The band at 2974 cm^{-1} is ascribed to C-H stretching of aliphatic alkanes, while that at 2511 cm^{-1} is attributed to S-H

stretching. The bands at 1797 and 1799 cm^{-1} are associated with C=O group. The peak at 1620 cm^{-1} is attributed to C=C bonds, while the peaks at 1261 cm^{-1} indicate $-\text{SO}_3$ group. The peaks between 1105 and 1099 cm^{-1} are assigned to C-O bond. The stretching observed between 1030 and 1041 cm^{-1} is associated with $-\text{CN}$, while that which was observed from 711 to 875 cm^{-1} were

attributed to C-H of aromatic ring. On comparison of the FT-IR spectra of cassava tuber bark waste before and after adsorption of Cd, clear band shifts and decrease in intensity at some bands were noted. Among these functional groups are -OH stretching, -NH stretching, -C=O stretching, -CN stretching and aliphatic C-H stretching. These functional groups present on surface of cassava tuber bark waste could be responsible for the sorption of Cd(II) ions. Fig. 2 shows the scanning electron microscopy (SEM) of cassava tuber bark waste before (A) and after adsorption (B) of cadmium ion. The surface morphology of biomass possesses a rough surface with multilayer surfaces which contained abundant porous structures of different sizes which are responsible for the high adsorption capacity of the cassava tuber bark waste biomass.

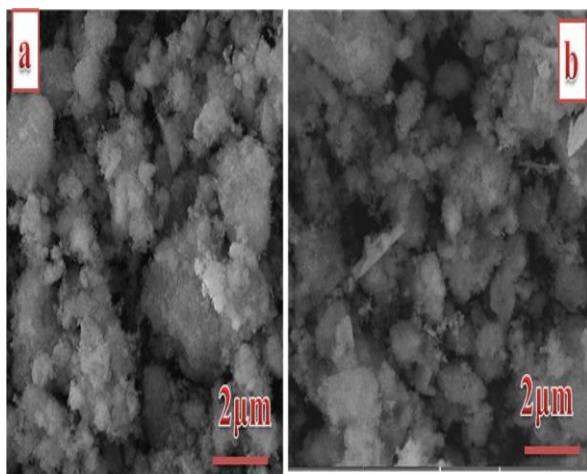


Fig. 2: SEM of Cassava Tuber Back Waste (a) before and (b) after Adsorption of Cassava Tuber Back Waste

3.2. Effect of solution pH on Cd(II) ions uptake.

In order to examine the effect of solution pH on the sorption of Cd(II) ions onto RCTBW and MCTBW, the batch sorption process was studied at different pH of 2, 3, 5, 6 and 8. Maximum uptake of Cd(II) ions by RCTBW was attained at a pH of 6, while that of MCTBW was attained at a pH of 5 (Fig. 3). The percentage removal of Cd(II) ions by RCTBW increases from 52.4 to

77.8 % when the pH was raised from 2 to 6, it then decreased to 40.8 % at a higher pH of 8. Upon treatment with nitric acid, the percentage removal increases from 67.4 to 94.6 %. When the pH was raised from 2 to 5, the percentage removal decreased. At low pH, the overall surface charge on the cells will become positive, which will inhibit the approached of the positively charged metal cations. But as the pH increases, deprotonation occurs which enhances the adsorption of the metal ions by the sorbent. This is in agreement with Nale *et al.* [23] and Zeid *et al.* [24].

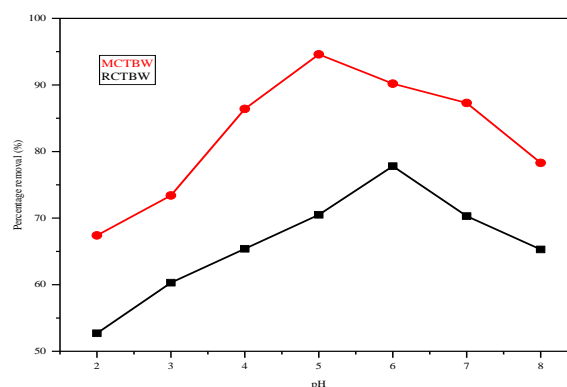


Fig.3: Effect of pH on the Uptake of Cd(II) ions on RCTBW and MCTBW

Effect of Contact Time and Initial Cd(II) ions Concentration.

The variation in Cd(II) ions uptake at different initial metal concentrations of 20, 30, 40, 50, 60, 80 and 100 mg/L at different time interval of 10, 20, 30, 40, 50, 60, 80 and 100 mins is shown in Fig. 4a. Maximum uptake of Cd(II) was achieved at a contact time of 60 mins for both biomasses. The amount of Cd(II) ions adsorbed increased from 6.3 to 17.2 mg/g when the contact time was raised from 20 to 60 mins at 20 mg/L. The uptake increased tremendously from 33.4 to 73.2 mg/g when the contact time was raised from 20 to 60 mins at 100 mg/L. The uptake of Cd(II) ions was however rapid at the initial stage of the sorption process owing to the large surface area on the sorbents. But as the reaction proceeds, these vacant sites are gradually filled up by the Cd(II) ions, thus, the process became slower. Similar observations

were reported in other studies [25, 26]. The effect of initial Cd(II) ions concentration was also studied. As shown in Fig. 5, the percentage removal of Cd(II) ions increases with an increase in initial Cd(II) ions concentration. Higher initial concentration provided an important driving force to overcome mass

transfer resistance of the adsorbate between the aqueous and solid phases and thus increased the uptake of the cadmium by the adsorbent This finding is in accordance with similar reports [27, 28].

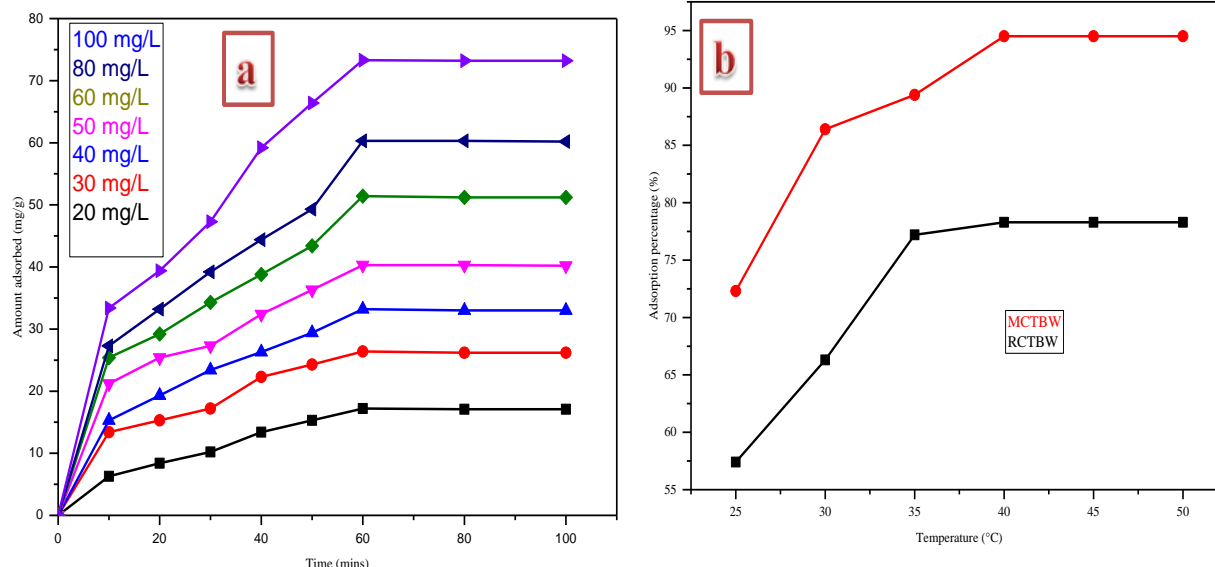


Fig. 4: (a) Effects of Contact Time, Initial Cd(II) ions Concentration and (b) Effect of Temperature on Uptake by RCTBW and MCTBW

Effect of Temperature on the Uptake of Cd(II) ions by RCTBW and MCTBW.

The influence of temperature on Cd(II) ions uptake by RCTBW and MCTBW was examined at different temperature of 25, 30, 35, 40, 45 and 50 °C and the results are shown in Fig. 4b. Maximum Cd(II) ions was attained at a temperature of 40 °C. The percentage removal of RCTBW increased from 57.4 to 78.3 %, while that of MCTBW increased from 72.3 to 94.5 % as the temperature increased from 25 to 40 °C. Increase in metal ions uptake at a higher temperature may be a result of increasing tendency of the adsorbate to diffuse across the cell wall of the adsorbent. The results of this work in agreement with the observations of Shen and Duvnjak [13] and Remos *et al.* [14], but differ from the reports of Saltal *et al.* [29] and El-Sayed *et al.* [30]

Adsorption Isotherm Modeling.

The relationship between the concentration of the remaining Cd(II) ions at equilibrium and adsorption capacity of both raw and acid-modified biosorbents was evaluated using both the Langmuir and Freundlich Isotherms [31]. The Langmuir model suggests a monolayer adsorption on a homogeneous surface in which there is no interactions between adsorbed molecules. The linearized form of the Langmuir equation is given by equation 3 [31]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b_{q_{max}}} \tag{3}$$

Where C_e and q_e represent concentration at equilibrium and amount of Cd (II) ions adsorbed at equilibrium, b stands for adsorption affinity which is related to the heat of adsorption in dm^3/g and q_{max} represents the sorbent adsorption

capacity. The plots of $\frac{C_e}{q_e}$ against C_e for the uptake of Cd(II) ions by RCTBW and MCTBW is shown in Fig. 5a with a slope of $\frac{1}{q_{max}}$ and an intercept of $\frac{1}{b_{q_{max}}}$ from where the values of q_{max} and b were estimated and the physical parameters are presented in Table 1.

Adsorption intensity (R_L) from the Langmuir model is given as:

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

Where C_o is the initial metal concentration in mg/L and the parameters are presented in Table 1.

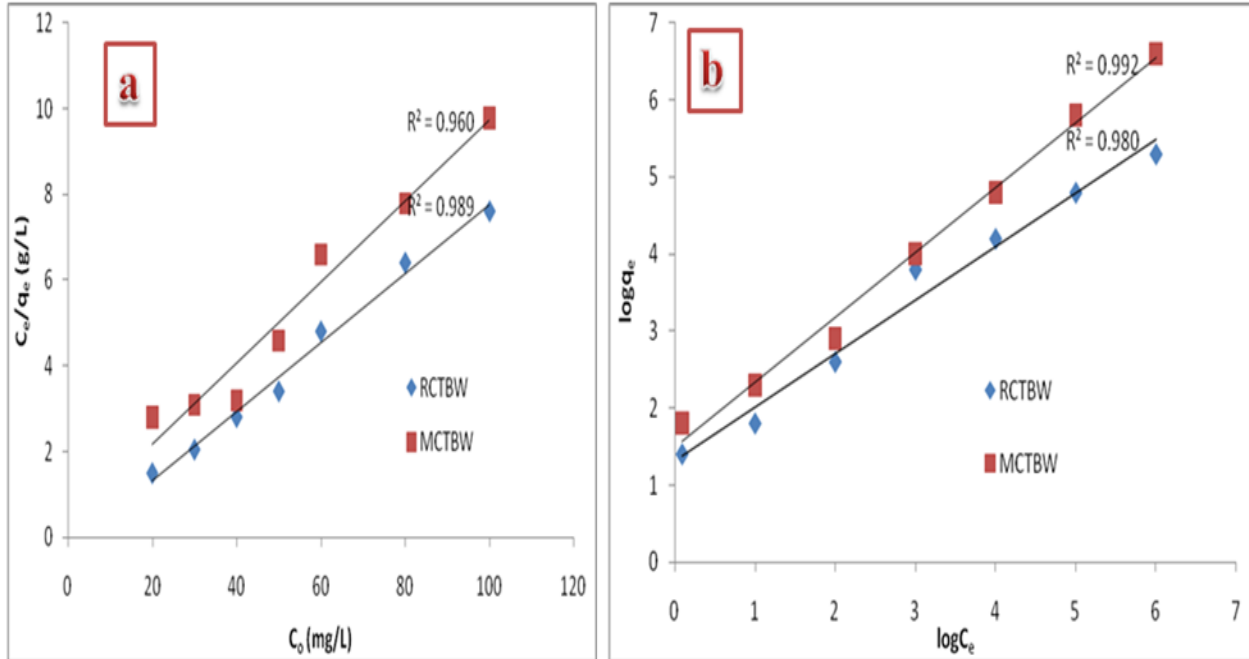


Fig.5: (a) Langmuir and (b) Freundlich Adsorption Isotherm Plots for the Uptake of Cd(II) by Raw and Acid-Modified Cassava Tuber Bark Waste while the Concentrations were varied.

The values of the correlation coefficients, R^2 for the sorption of Cd(II) ions by RCTBW and MCTBW are 0.960 and 0.989 respectively. This suggests that the Langmuir model fits the sorption process. Also, the values of the adsorption intensity (R_L) of the Langmuir model was found to be between 0 and 1 which suggests a favourable sorption process for both biomasses tested. The Freundlich isotherm suggests a monolayer adsorption on heterogeneous active sites in which there is interactions between the adsorbed molecules. The linearized form of the Freundlich equation is given as [24]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where q_e is the amount of Cd(II) ions adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration (mg/L), K_F is the adsorbent capacity and n is the adsorption intensity. The plot of $\log q_e$ against $\log C_e$ with a slope and intercept which correspond to $1/n$ and $\log K_F$ is shown in Fig. 5b and the physical parameters are presented in Table 1. The values of the correlation coefficients, R^2 for the sorption of Cd(II) ions by RCTBW and MCTBW are 0.980 and 0.992 respectively for the Freundlich isotherm. This suggests that the sorption data for the removal of Cd(II) ions fit the Freundlich isotherm. As illustrated in Table 1, the sorption parameters obtained from the sorption of Cd(II) ions by raw and acid-modified cassava tuber

bark waste fit better with the Freundlich isotherm than the Langmuir isotherm. Upon treatment with nitric acid, the sorption parameters showed better correlations than the raw sorbent.

Table 1: Langmuir and Freundlich Isotherms Parameters for the Sorption of Cd(II) ions on Raw and Modified Cassava Tuber Bark Waste.

		RCTBW	MCTBW
Langmuir	q_m	33.4	73.2
	b	0.830	2.121
	R²	0.960	0.989
	R_L	0.721	0.540
Freundlich	n	0.163	0.191
	K_F	10.241	18.235
	R²	0.980	0.992

Table 2: Maximum Adsorption Capacities for Cadmium Sorption by Different Biomasses.

Biomass	q _m (mg/g)	References
Cassava tuber bark waste	26.3	[11]
Corn cob	5.09	[14]
Grape stalk	27.88	[16]
Hazelnut shell	5.42	[17]
Peanut hulls	5.96	[18]
Rice husk	103.09	[19]
Sawdust	73.62	[21]
RCTBW	33.4	Present study
MCTBW	73.2	Present study

Kinetic Studies

The kinetic studies were evaluated using three kinetic models namely: Lagergren-pseudo-first-order model, Ho-pseudo-second-order and the intra-particle diffusion models. The linearized representations of the equations of these models are shown in equations 6 - 10 [32].

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

This can be rearranged as:

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad (7)$$

$$t/Q_t = 1/k_2 Q_e^2 + (1/Q_e)t \quad (8)$$

This can be rearranged as:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (9)$$

$$Q_t = K_{id} t^{0.5} + C_i \quad (10)$$

The plots of Q_t against t from the least square fit method were used to estimate the values of Q_e and k_1 as presented in Fig. 6 with physical parameters listed in Table 3. Where k_2 is the equilibrium rate constant of the pseudo-second-order model in g/mg/ mins, Q_e is the amount of Cd (II) ions adsorbed at equilibrium in mg/g, Q_t is the amount of Cd (II) ions adsorbed at time t in mg/g. The corresponding values of Q_e and k_2 were evaluated from the plots of Q_t against t of the least square fit method as shown in Fig. 7, while the physical parameters are presented in Table 3. The values of the correlation coefficients (R^2) for first and second-order models are high for the two biomasses. However, on comparison of the values of experimental adsorption capacity ($q_{e,exp.}$) with calculated adsorption capacity ($q_{e,cal.}$) showed better relationship or closeness for the first-order

model than second-order model. Thus, it can be deduced that the uptake of Cd(II) ions by RCTBW and MCTBW is governed by Lagergren- pseudo-first-order kinetic model. Also, the values of the correlation coefficients (R^2) obtained from the intra-particle diffusion model are found to be closed to unity, which indicates the application of this model.

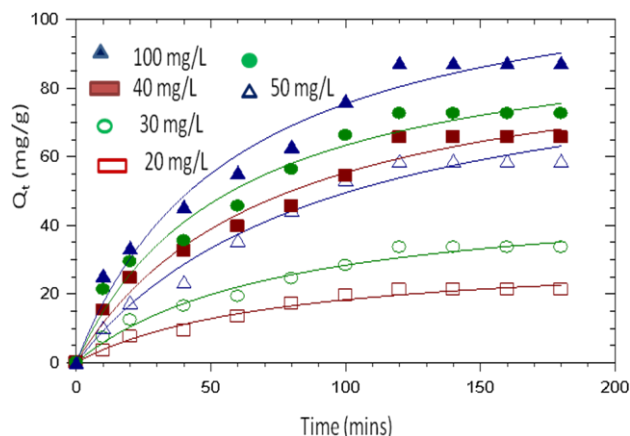


Fig.6: Lagergren-pseudo-first-order Model of Raw and Acid-Modified Cassava Tuber Bark Waste.

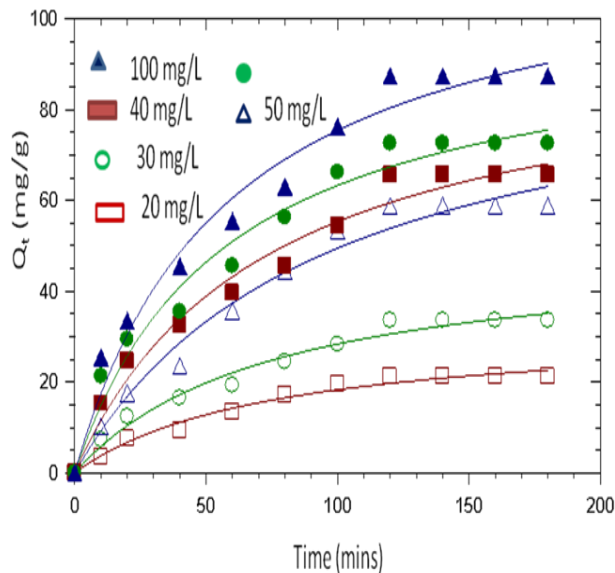


Fig. 7: Ho's second-order Model of Raw and Acid-Modified Cassava Tuber Bark Waste.

Table 3: Kinetic Model Parameters for the Adsorption of Cd(II) ion by RCTBW and MCTBW

		RCTBW	MCTBW
First-order model	q_{eexp} (mg/g)	33.2	73.2
	k_1 (mins)	0.071	0.091
	q_{ecal} (mg/L)	20.32	71.22
Second-order model	R^2	0.96	0.98
	k_2 (mins)	0.048	0.036
	q_{cal} (mg/g)	27.76	66.77
Intra-particle	k	1.23	0.94
	R^2	0.94	0.96

Conclusion

This study justify the potency of raw and acid-modified cassava tuber bark waste as effective sorbents for Cd(II) ions from aqueous solution in a batch process. The results revealed that the percentage removal of Cd(II) ions by both biomasses depends on factors such as temperature, initial metal concentrations, solution pH, adsorbent dosage and temperature. Maximum uptake of Cd(II) ions was attained at a pH of 6 and 5 for RCTBW and MCTBW respectively. The adsorption data were tested with both Langmuir and Freundlich isotherm models, while the kinetic process is governed by Lagergren-pseudo-first-order model. Thus, the ability of raw and modified cassava tuber bark waste as cheap biosorbents for the removal of Cd(II) ions from aqueous solutions had been successfully demonstrated.

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