Comparative Study of Removal of Cadmium Ions from Aqueous Solution Using *Dialium indum* and *Santalum album* Fruitshells as Adsorbents

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Sandal and velvet tamarind fruit shells were screened for their metal uptake capacities for Cd(II)ions, at various initial concentrations of 10, 20, 30 40 and 50 mg/ L at variable contact period of between 30 and 180 minutes and different adsorbent dosages of 0.2 – 1 g/l, pH(1 to 6) using batch adsorption mode. The adsorbents were characterized using standard methods. The amount of adsorbate adsorbed by the developed adsorbents for Cd^{2+} increased with increase in initial metal concentration, contact time, adsorbent dosage and pH until equilibrium point was reached. At equilibrium; the optimum contact time for this operation was 90 minutes for velvet tamarind and 120 minutes for sandal fruit, effective pH for both adsorbents is 5.5, the equilibrium initial metal concentrations are 42 and 41 mg/l for sandal fruit and velvet tamarind shell respectively. The data conformed to Freundlich isotherm with $r^2 > 0.95$ for both adsorbents and were also fit for second-order kinetics. The surface areas of the sandal fruit and velvet tamarind shell as determined were

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615 and 570 m^2/g. The results obtained from this study indicated a high adsorption ability of the adsorbents for Cd(II) with sandal fruit having better performance.

1. INTRODUCTION

The recent advances in industrial and technological advancements at the global level have brought about the introduction of different pollutants into water bodies. This tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment [1]. These metals are of special concern because of their persistency and health impacts. Industrial waste constitutes a major source of various kinds of metal pollution in natural water [2]. These toxic metals of interest include; Cd, Zn, Pb and Ni. These toxic heavy metals enter into the water bodies through waste waters from metal plating industries and industries of Cd Ni batteries, phosphate fertilizers, mining activities, pigments and stabilizer alloys etc Cd^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+} ions exist in the soil-water system as micronutrients for plants and animals' use. According to Dermibas [3], Cd^{2+} ion poisoning in humans are very serious, among which high blood pressures, kidney damage and destruction of testicular tissues and red blood vessels are prevalent [4]. US EPA standards for cadmium in drinking water is 0.005 mg/l.

A number of technologies have been developed over the years to remove toxic metals from water. The most important technologies include chemical precipitations, electro flotation, ion exchange, reverse osmosis, and adsorption on commercial activated carbon [5]. These methods are not cost effective and have prompted a search for cheaper substitutes. Low cost and non conventional adsorbents include the use of agricultural wastes like natural compost, Irish peanut, peanut shell, coconut shell, bone char and biomass such as *Aspergilus tereus* and *Mucus remanianus*, polymerized onion skin with formaldehyde and EDTA, modified cellulosic material, natural materials such as hair and cat tails (Thypha Plant) [6], waste wool [7], peanut skin [8], modified barks [9], barely straw [10], low rank coal [11], waste tyre rubber and tea leaves [12]. The present investigation attempts have been made to assess and compare the efficiency of low cost adsorbent materials prepared from sandal and velvet tamarind fruit shells for removal of Cd(II) from wastewater. The influence of various factors, such as adsorbent loadings, initial pH, temperature and initial metal ion concentration on the adsorption capacity were studied. The Langmuir and Freundlich models were used to analyze the adsorption equilibrium.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The sandal and velvet tamarind fruit shells biomasses were collected from agricultural wastes which are present in abundance for wastewater treatment and washed several times with distilled water, and then dried in an oven at 80°C for 24 h. The dried biomasses were ground with a mortar and pestle. The particles were separated by using a US standard testing sieve (No. 100). The material after sieving were soaked for twenty four hours in a solution prepared from sulphuric acid, then placed in a crucible and positioned at the center of a muffle furnace for 15 mins at 500°C, to produce the activated carbon (AC) which is cooled in desiccators [13].

2.2 Preparation of Adsorbate Stock Solution

Standard Cadmium stock solution (1000 mg/L) was prepared by dissolving 2.10 g of $Cd(NO_3)_2$ in deionized water then diluted to 1000 ml. pH adjustment of solution was made with dilute NaOH and HCl solutions. The reagent was of analytical grade and stored in polypropylene containers. Plastics were cleaned in dilute HNO_3 (10% v/v) and dried at 60°C after rinsing with deionized water.

2.3 Characterization of Adsorbents

The iodine number was determined based on [14] by using the sodium thiosulphate volumetric method. The specific surface area of the activated carbon was estimated using Sear's method [15,16]. Bulk density and Particle density were determined using method used by ([17]. Porosity was determined from the values of bulk density and particles density. Functional groups

presence in the adsorbents was determined by a Fourier-transform infrared spectrophotometer (FTIR; Shimadzu 8400s).The X-ray diffraction (XRD) of the adsorbents was determined in a Randi-con MD 10 model, while scanning electron microscopy (SEM; Hitachi S4800) was used to assess the morphology of the adsorbents.

2.4 Batch Adsorption Studies

The experiments were carried out in a batch mode for the measurements of adsorption capacities, and to generate adsorption kinetics [18]. The effect of pH (3, 4, 5, 6, 7and 8), contact time (30-180 mins), adsorbent dose (0.2-1g/l) and initial metal ion concentration (10-50mg/l) were determined at room temperature using stopper bottles. The initial pH of solution was adjusted by using 0.05 M HCl or 0.05 M NaOH without changing the volume of the sample. After agitating the sample for the required contact time, the contents were centrifuged and filtered through Whatman No.41 filter paper and unreacted cadmium in the filtrate was analyzed by atomic absorption spectrophotometer.

The adsorption capacity, q_e, was calculated as [19].

$$q_e = \frac{(C_0 - C_e)}{m} V \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium adsorbate concentrations in solution (mg/L), respectively, V is a known volume of synthetic wastewater (L), and m is a known mass of dry adsorbent (g).

2.5 Adsorption Isotherms

2.5.1 Freundlich adsorption isotherm

Freundlich Isotherm is represented by the following equation [20]:

$$q_e = K_F C_e^{1/n} \qquad (2)$$

Where;

qe = the amount of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent)
K_f = adsorption capacity
n = adsorption intensity are the empirical constants.
C_e = equilibrium concentration of adsorbate (mg/l)

2.5.2 Langmuir adsorption isotherm

Langmuir Isotherm is represented by the following equation [21]:

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \qquad (3)$$

q_{max} and b are Langmuir constants related to adsorption capacity (maximum specific uptake corresponding to the site saturation) and energy (intensity) of adsorption (L of adsorbent/mg of adsorbate) respectively.

2.5.3 Adsorption kinetics of Cd(II)

To describe the adsorption kinetics, the linear form of the pseudo-first order (Lagergern) equation reported in the literature was applied in the following form [22]:

$$log(q_e - q_t) = log\ q_e - \left(\frac{KI\ t}{2.303}\right) \qquad (4)$$

where K_l(min^{-1}) is the rate constant, and *qt* and *qe* are the amounts of metal ion adsorbed at time *t* and equilibrium, respectively.

To describe the adsorption kinetics, a pseudo-second order rate model reported in the literature was also applied in the following form [23];

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{1}{q_e}t \qquad (5)$$

Where,

h_o = the initial adsorption rate (mg/g min)
q_e = the amount of metal ion adsorbed at equilibrium (mg/g)
q_t = the mount a adsorbed at time t (mg/g)

The initial adsorption rate, h_o, as t'→ 0 is defined as:

$$h_o = K_2 q_e^2 \qquad (6)$$

Where,K_2 is the pseudo second order rate constant for the adsorption process (g/mg min).The initial adsorption rate h_o, the equilibrium adsorption capacity, and the rate constant K_2 were determined from the slope and intercept of the plot of t/q_t against t.

3. RESULTS AND DISCUSSION

The adsorbents characteristics were determined and the results are summarized, on Table 1.

Table 1. Physicochemical properties of adsorbents

Parameter	Adsorbents	
	SF	VT
Bulk density (g/cm^3)	0.92	0.151
Ash (%)	4.45	7.2
Iodine number (mg/g)	649.5	614.7
Surface area (m^2/g)	615	570
Particle density (g/cm^3)	1.25	0.72
Porosity (%)	26.4	79

3.1 XRD and SEM Analysis

The Figs. 1 and 2 represent the SEM images and XRD spectra showing the surface morphologies and XRD spectra peaks of Velvet tamarind and sandal fruit.

The surface morphology of the velvet tamarind and sandal fruit examined by SEM as shown in clearly revealed a fragmented and porous surface texture, which indicated the adsorbent was highly porous, with a high adsorption capacity [24]. The porous nature of adsorbent signifies sorption potential for metal ions, such as physical adsorption will play a major role in over all sorption process. The specific surface area of the adsorbents of 615 m^2/g for sandal fruit and 570 m^2/g for velvet tamarind further confirmed their porous nature. According to [25], an adsorbent with a surface area of 144 m^2/g and above can be classified as mesoporous. The XRD spectra of Sandal fruit and Velvet tamarind are shown in Fig. 3. XRD gave useful information about crystalline and amorphous changes of an adsorbent. The presence of sharp and weak peaks suggests an amorphous adsorbent [26] and the amorphous nature of the adsorbents indicates that Cd(II)ions in solution can easily penetrate its surface for efficient adsorption [27].

3.2 FTIR Analysis

Figs. 5, 6 shows the FTIR spectral of sandal fruit and velvet tamarind adsorbents.

The FTIR spectral of adsorbents sandal fruit and velvet tamarind were used to determine the vibration frequency changes in the functional groups on the surface which facilitates the adsorption of metal ions. The spectra of adsorbents were measured within the range of 400 – 4000 cm^{-1} wave number. The FTIR analysis results (Figs. 5 and 6) suggested the presence of such functional groups as the carboxylic acid or alcoholic O-H bond stretching which may overlap with amine (N-H) bond stretching at peaks between 3250-3400 cm^{-1}; possible C=O bond of carbonyl or amide groups within 1640-1670 cm^{-1}; C-O and O-H bond stretching of alcohol and ethers at 1000-1260 cm^{-1} of the finger-print region [28]. The FTIR spectroscopic analysis indicated broad bands at 3412 cm^{-1}, representing bonded –OH groups [29].

3.3 Effect of Contact Time

In adsorption system, the contact time plays a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. The effect of contact time on the adsorption of Cd(II) ions onto velvet tamarind and sandal fruit is shown in Fig. 7.

An initial increase in amount adsorbed with increased contact time was observed, and adsorption became fairly stable with time. Equilibrium removal was achieved around 90 min for velvet tamarind and 120 min for sandal fruit, after which further increases in contact time did not result in significant adsorption. These times were used in all experiments to ensure maximum removal. The rapid adsorption during the initial stages might be due to the presence of abundant active sites on the surface of both adsorbents which become saturated with time. Initially, sorption is controlled mainly by diffusion from the bulk to the surface of the adsorbents, whereas, later, sorption is probably an attachment-controlled process due to the presence of fewer active sites [30]. The adsorption began to slow down due to slow movement of Cd ions into the interior bulk of the biosorbent. Considering the effective adsorption time of 90 minutes for velvet tamarind which is lower than 120 minutes for sandal fruit, it can be said that it has less active sites which become saturated earlier than sandal fruit. Velvet tamarind has a surface area of 570 m^2/g and sandal fruit has the surface of 670 m^2/g which correspond to the rate of metal uptake by each of them. The trend observed for the metal ions in the two substrates under the same experimental conditions revealed that the pattern of adsorption is a function of the substrate [31].

3.4 Effect of PH

The effects of initial pH on adsorption process are presented at the Fig. 8. Importance of pH on heavy metal adsorption tests were undertaken with different initial pH values of the metal solutions, using a constant amount of sandal fruit and velvet tamarind adsorbents.
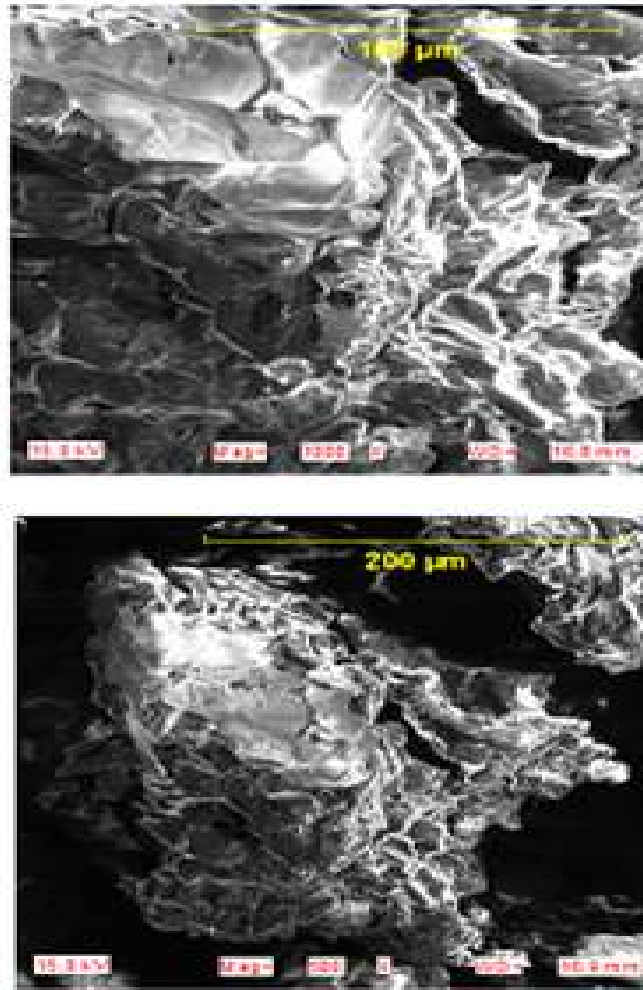
Fig. 1. Scanning electron microscopy (SEM) images of sandal fruit
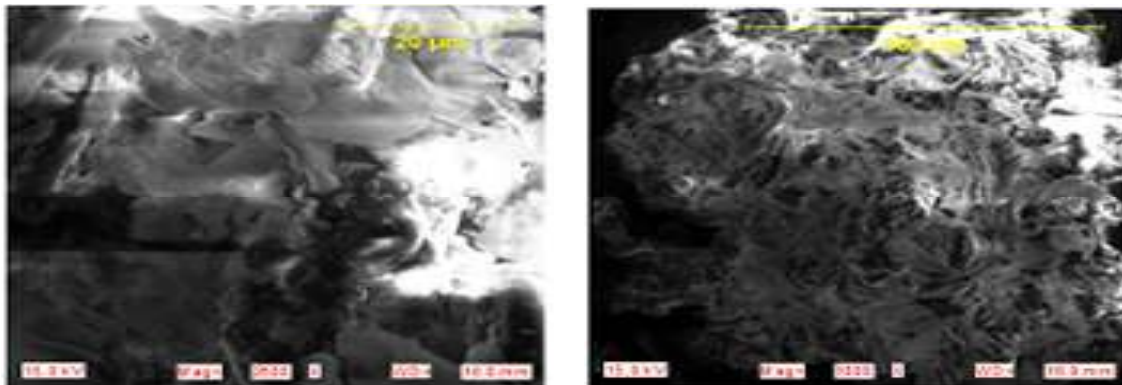

Fig. 2. Scanning electron microscopy (SEM) images of Velvet tamarind at 20 and 100 μm respectively

The adsorptive capacity of velvet tamarind and sandal fruit were dependent on pH of cadmium solution as the amount adsorbed varied with pH. At lower pH values, large number of H^+ ions

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neutralize the negatively charged adsorbent surfaces, thereby creating hindrance to the Cd(II) ions adsorption. At the high pH values, the reduction in adsorption may be due to the abundance of OH⁻ ions causing increased hindrance to diffusion of Cd (II) ions [32]. The adsorbents showed gradual increase in adsorption as the pH increases from 1 up to about 5.5. Both adsorbents performed optimally at pH of 5.5 and decreases with further increase in pH as shown in Fig. 10. The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution [33]. At low pH, the surface ligants are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force [34,35]. Furthermore, the effects of pH on the metal ions uptake by biomasses can also be justified by the association-dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present on the biomasses [36]. In fact, it is known that at low pH, most of the carboxylic groups is not dissociated and cannot bind the metal ions in solution, although they take part in complexation reactions [37]. The results obtained are in close agreement with previously reported studies [38,39].

3.5 Effect of Adsorbent Dose

Adsorbent dosage is a useful parameter for determining the capacity of an adsorbent for a given initial adsorbate concentration. The effect of modified velvet tamarind and sandal fruit dose on adsorption of Cd(II) ions from solution is shown in Fig. 9.

Adsorbent dose was varied between 0.2-1.2 g/l for adsorbents used. It is clearly seen that the amount of Cd(II)ions adsorbed increases as the adsorbent mass increases mainly due to an increase in the number of available active sites [40,41]. The adsorption of Cd (II) increases at a faster rate initially with increases in adsorbent dose. The result showed that further increase in the adsorbents dose could lead to increase in adsorption until the effective adsorption of 6.1 and 4.64 mg/g is attained for velvet tamarind and sandal fruit respectively. Increasing the dose of modified velvet tamarind from 1 to 1.2 g decreased the equilibrium adsorption capacity from 6.1 to 5.81 mg/g for Cd(II) and increasing

the dose of modified sandal fruit from 1 to 1.2 g decreased the equilibrium adsorption capacity from 4.64 to 4.42. This may be due to a decrease in the total adsorption surface area available, resulting from overlapping or aggregation of adsorption sites [42] or a higher adsorbent dose may provide more active adsorption sites, so that adsorption sites remain unsaturated during adsorption [43].

3.6 Effect of Initial Metal Ion Concentration

The amount of metal ions adsorbed is a function of the initial concentration of the adsorbate (metal ion), making it an important factor in effective adsorption. The effect of initial metal ion concentration (10 to 50 mg/l) on the adsorption of Cd(II) ions onto modified velvet tamarind and sandal fruit is shown in Fig. 10.

It shows that, as the concentration of Cd(II) in solution increases, the amount of Cd(II) adsorbed by the adsorbents increases. The amount of metal ions adsorbed by both adsorbents increased with the metal concentration, as the increasing concentration gradient overcomes the resistance to mass transfer of metal ions between the aqueous phase and the adsorbent [44]. A higher concentration in a solution implies a higher concentration of metal ion to be fixed on the surface of the adsorbent [45]. Modified sandal fruit had a higher adsorption capacity for metal ions than modified velvet tamarind as the initial ions concentration increases. At a concentration of 40 mg/L, 3.04 mg/g of Cd(II) ions were adsorbed by sandal fruit while velvet tamarind adsorbed 2.83 mg/g Cd(II). The higher adsorption by sandal fruit may be due to its larger surface area of 615 m²/g as compared with 570 m²/g for velvet tamarind. The equilibrium concentrations of ions during adsorption are 42 and 41 mg/l for sandal fruit and velvet tamarind respectively which are very close. The decrease in adsorption after that might be due to the agglomeration/ aggregation of the adsorbent particles at a higher concentration. Such aggregation can lead to decrease in the total surface area of the adsorbent available for adsorption and increase in diffusional path length [46]. Similar results were reported by many authors using different types of adsorbents [47,48].
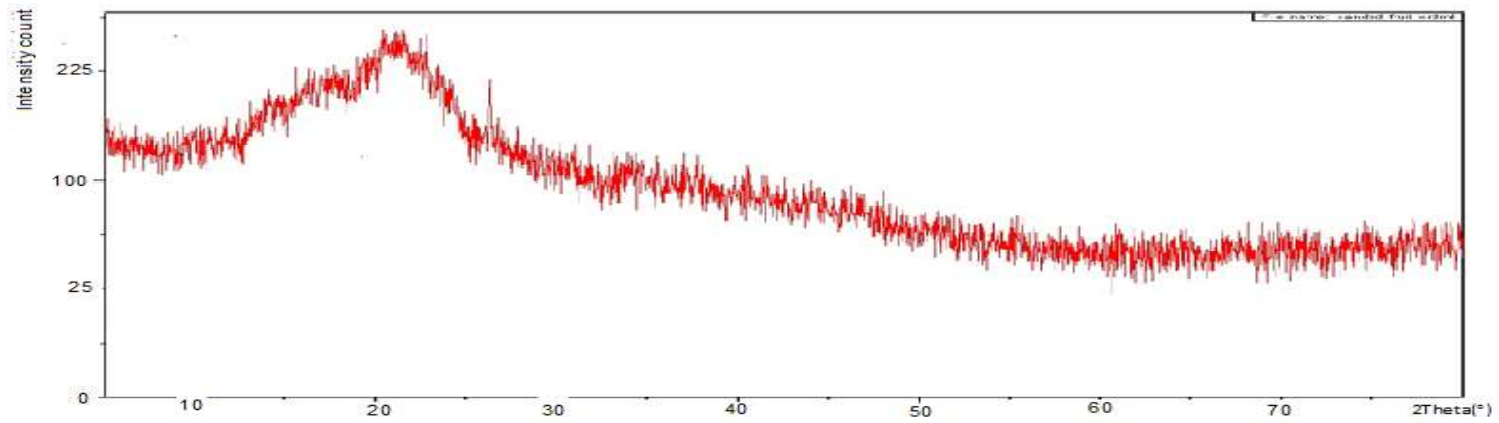
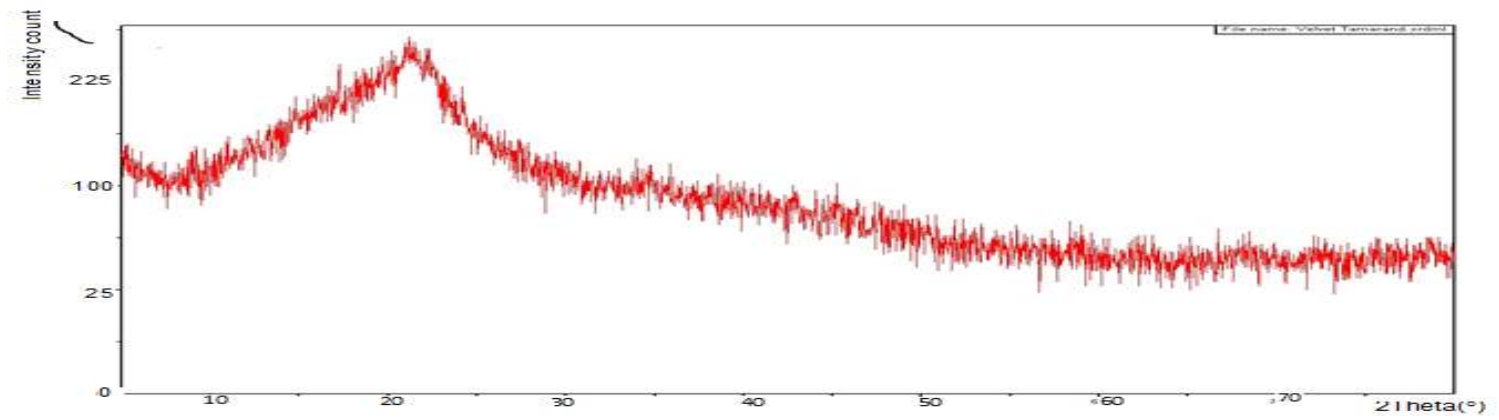**Fig. 3. X-ray diffraction spectrum of sandal fruit biomass**

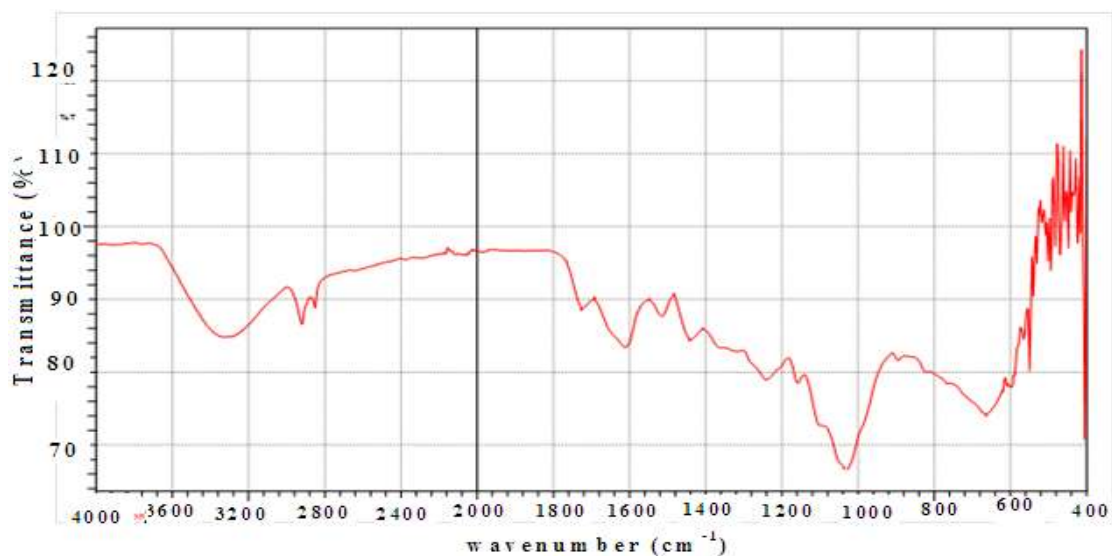**Fig. 4. X-ray diffraction spectrum of velvet tamarind biomass**

Fig. 5. Fourier transforms infrared (FTIR) spectra of Sandal fruit
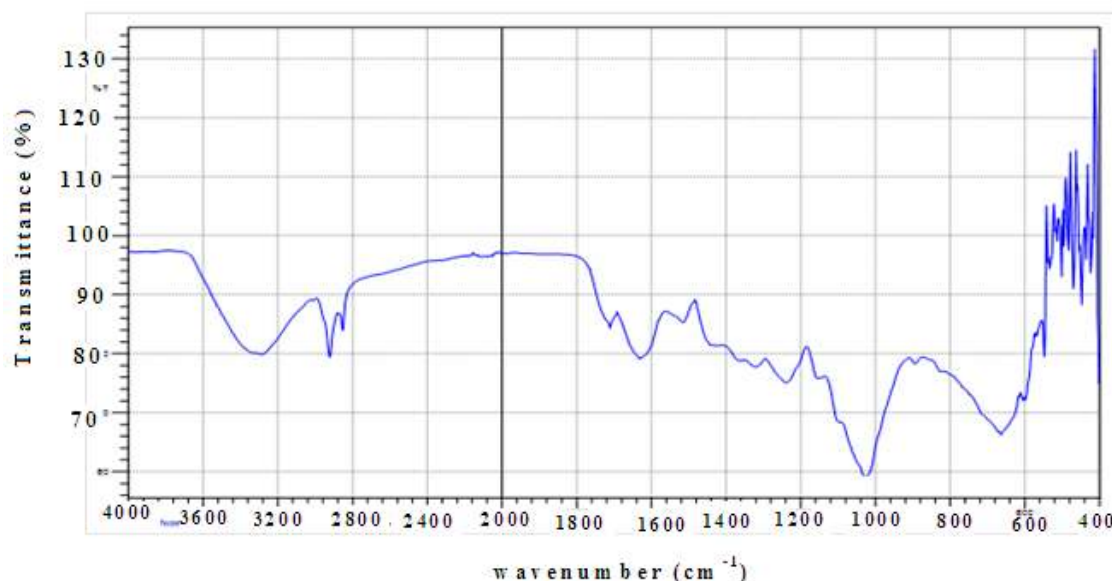

Fig. 6. Fourier transforms infrared (FTIR) spectra of velvet tamarind

3.7 Equilibrium Isotherm Modeling

Equilibrium adsorption isotherms are used to relate the adsorbate concentration in solution and the amount on the adsorbent at equilibrium [49]. These parameters often provide fundamental information on the sorption mechanism, surface properties and the affinity of adsorbents, which helps to determine the applicability of sorption as a unit operation. Therefore, it is important to establish the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems. The most frequently used isotherms, the Langmuir and Freundlich models, were therefore used to analyse the data (Table 2). The Langmuir isotherm is used to describe monolayer adsorption onto the surface of an adsorbent with a finite number of identical adsorption sites and no interaction between sites. The model is expressed as [50]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{6}$$

Where q_{max}(mg/g) is the monolayer adsorption capacity of the adsorbent, and b(L/mg) is the adsorption constant, which reflects the affinity between the adsorbent and adsorbate. Q_{max} and b were determined from the slope and intercept of the plots of Ce/qe versus Ce. Table 2 shows low correlation coefficients (r^2) for Cd(II)<0.95,

indicating that the adsorption does not follow the Langmuir isotherm closely. The Freundlich isotherm is based on the assumption that sorption takes place on a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially and can be expressed as [51]:
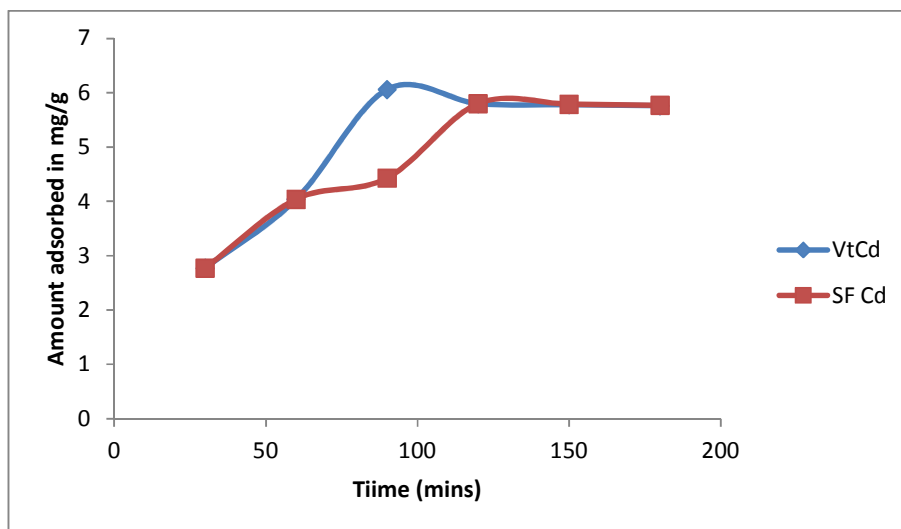

Fig. 7. Plot of amount of Cd(II) ions adsorbed versus Contact Time by Velvet tamarind and Sandal fruit (Temp. ±2℃; pH.5.5, Agitation 200 rpm , Initial concentration. 100 mg/l^{-1}, Adsorbent dosage: 1 g/50 ml)

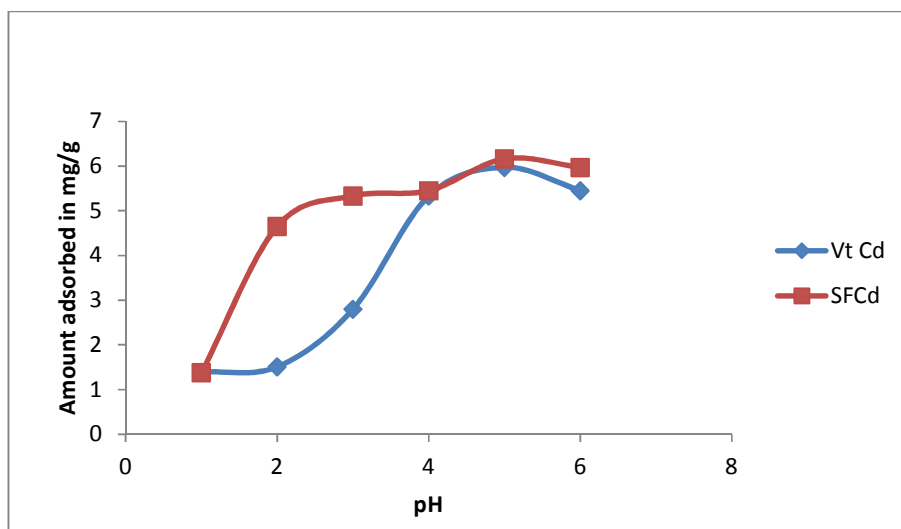**Fig. 8. Plot of amount of Cd adsorbed by Velvet tamarind and Sandal fruit versus pH (Temp.28±2℃; Agitation 200 rpm, Initial metal conc entration; 100 mg/l)**
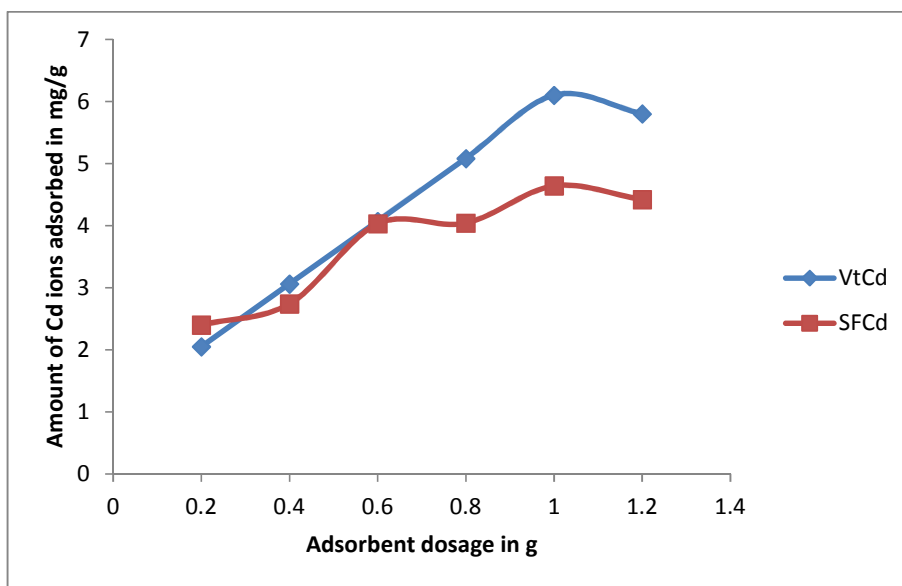
Fig. 9. Plot of amount of Cd ions adsorbed versus Adsorbent dosage by Velvet tamarind and Sandal fruit (Temp.28±2°C; pH.5.5, Agitation 20 0 rpm, Initial metal concentration; 100 mg/l)
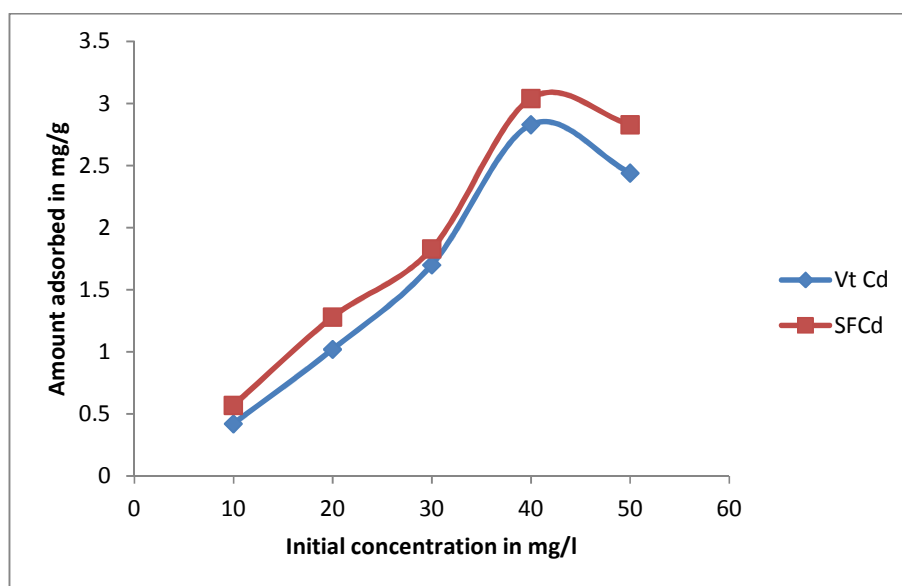

Fig. 10. Plot of amount of Cd(II) ions adsorbed in mg/g versus Initial concentration of Cd(II) ions by Velvet tamarind and Sandal fruit (Temp.28±2°C; pH.5.5, Agitation 200 rpm)

$$log\ q_e\ =\ logK_F\ +\ \left[\frac{1}{n}\right]logC_e \qquad (7)$$

Where KF (mg/g)(mg/L) and n are the constants for adsorption capacity and intensity, respectively. A plot of log qe versus log Ce gives a straight line of slope $1/n$ and intercepts log KF. As can be seen in Table 2, the r^2 values for both adsorbents for adsorption of Cd (II) were high (>0.95), indicating a good fit of the Freundlich model to the adsorption process. This suggests that the surfaces of the adsorbents are heterogeneous. Furthermore, the values of n obtained for both metal ions lie between 1 and 10, indicating favourable adsorption [52].

3.8 Kinetic Modeling

The mechanism controlling adsorption was investigated with pseudo-first order and pseudo-

second order. The kinetic parameters are shown in Table 3. The pseudo-first order or Lagergern equation is based on the assumption that the rate of adsorption site occupation is proportional to the number of unoccupied sites (Lagergren, 1898). The constant K_l and qe_{cal} were obtained from the slope and intercept of the plot of log(qe – qt) versus t from equation 4. The R^2 values (Table 3) obtained for the metal ions showed a poor fit.

The pseudo-second order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [53]. The plot of t/qt versus t yields a straight line therefore the pseudo-second order equation is applicable. K_2 and qe were calculated from the slope and intercept of the plot. This model provided a good fit to the experimental data for both metal ions, as seen from the r^2 values (Table 3):
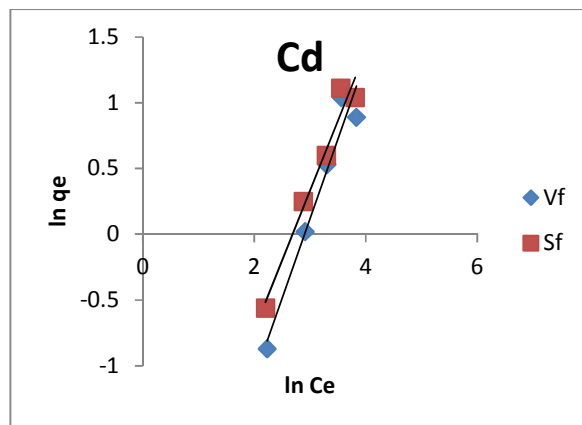

Fig. 11. Freundlich adsorption isotherm of Cadmium (II) ions by velvet tamarind and sandal fruit shells
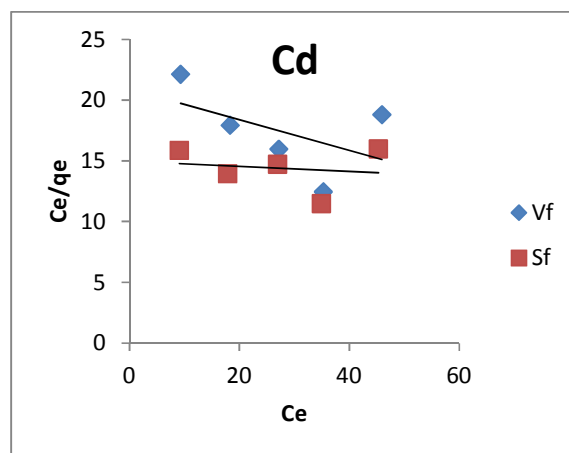

Fig. 12. Langmuir adsorption isotherm of Cadmium (II) ions by velvet tamarind and sandal fruit shells

Table 2. Values of langmuir and freundlich isotherm constants for adsorption of Cd(II)ions by velvet tamarind and sandal fruit

Heavy metal	Adsorbent	Freundlich			Langmuir		
		R^2	K_f	n	R^2	qmax	b
Cd	Vt	0.952	0.03	1.827	0.024	7.94	0.006
	S_f	0.964	0.058	1.943	0.253	50	0.001

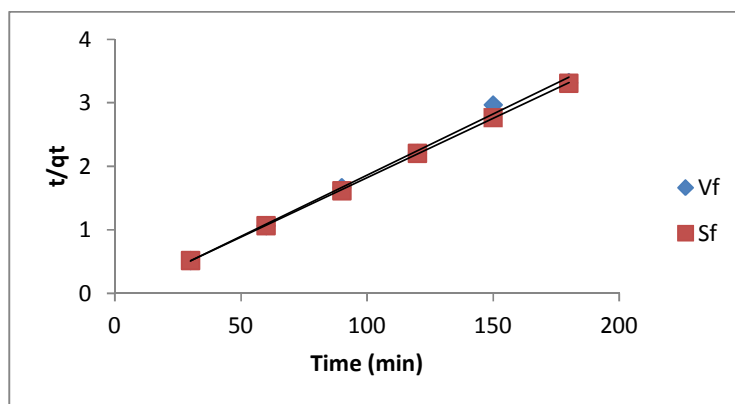*Vt : Velvet tamarind (Dialum indum); Sf: Sandal fruit (Santalum album)*

Fig. 13. Pseudo second order kinetic plot for Cadmium (II) ions adsorption by velvet tamarind and sandal fruits shell
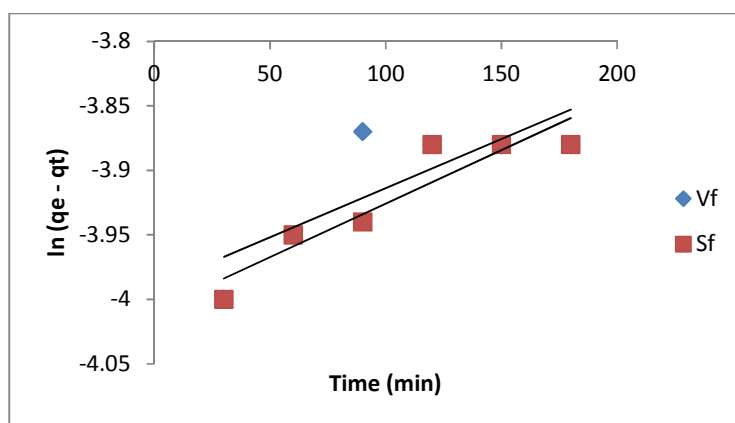

Fig. 14. Pseudo first order order kinetic plot for Cadmium (II) ions adsorption by velvet tamarind and sandal fruits shell

Table 3. The values of first- order and second order parameters obtained from the plot

Heavy metal	Adsorbent	First - order			Second-order		
		R^2	K_1	q_e	R^2	q_e	K_2
Cd	Vt	0.653	0.001	0.019	0.994	52.632	0.0004
	S_f	0.866	0.001	0.018	0.999	55.555	0.0003

4. CONCLUSION

Based upon the experimental results carried out in this work, the following conclusion can be drawn;

1. The FTIR spectra showed that certain functional groups OH, CO could be responsible for binding of metal ions from the solution by both adsorbents.
2. The heterogeneous natures of both adsorbents were revealed by the good fit of data to the Freundlich model indicating multilayer adsorption onto the adsorbents

3. Both adsorbents have a reasonably high surface area that can be used for adsorption
4. Extent of removal depends on the process parameters e,g Cd ion concentration, contact time, adsorbent dose and pH.
5. Both adsorbent can be applied as a cheap adsorbent for the removal of Cd(II) ions.
6. The adsorption capacity of treated sandal fruits for Cd(II) ions is more than that of velvet tamarind

ETHICAL APPROVAL

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. Each author confirms the manuscript represents honest work. All authors have approved the manuscript. Each author agrees with the order in which his name appears on the title page.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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