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(RESEARCH ARTICLE)

Investigation and optimization of cadmium ion adsorption from wastewater using raw and activated carbon of *Pterocarpus santalinoides* fruit

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Abstract

Treatment of heavy metal polluted water still remains a serious challenge for some developing countries without centralized wastewater systems. This study examined the potential of raw and activated carbon from *Pterocarpus santalinoides* fruit as an adsorbent for the removal of cadmium ions from contaminated water. Instrumental techniques such as fourier transform infra red spectrophotometer (FTIR), scanning electron microscopy (SEM), and atomic absorption spectrophotometer (AAS) were used to characterize the adsorbents. The study analyzed the effect of various factors, including adsorbent dosage (0.1 – 0.5 g), cadmium concentration (10 – 50 mg/l), contact time (20 – 100 min), and temperature (30 – 70 °C), respectively, on the adsorption of Cd^{2+} ions. The experimental findings revealed that the adsorbents have a high adsorption capacity for the removal of Cd^{2+} from aqueous solutions. Adsorption isotherms and kinetic models were applied to access the adsorption mechanism of cadmium removal. The Langmuir adsorption isotherm and pseudo-second-order model were found to fit the equilibrium data. Additionally, the adsorbents' efficiency were evaluated using central composite design (CCD) adapted from response surface methodology (RSM). Using adsorption percentage as a response, a 30 run experimental matrix was generated by the CCD based on the interaction effects of the four earlier stated variables. According to the results obtained, a linear model was generated, which indicated good predictability and results agreed with the experimental data. The contact time and adsorbent dosage were predicted to have a positive effect on the adsorption process. At optimal conditions of adsorbent dosage (0.5 g), contact time (100 min), cadmium concentration (46.93 mg/l), and temperature (70 °C), a desirability of 84 % was achieved by a numerical optimization approach demonstrating cadmium ion adsorption of 93 % for the raw and activated carbon from *Pterocarpus santalinoides* fruit.

Keywords: Cadmium ion; *Pterocarpus santalinoides* fruit; Wastewater; Adsorption; Response surface methodology

1. Introduction

Over the last decades, urbanization and industrialization have led to the introduction of high amounts of toxic metals into the environment [1]. These toxic metals are released to the ecosystem due to industrial activities arising from fuel production, electroplating, fertilizer industry, tanneries, the electrical appliance industry, leather, batteries, the paper industry and pesticides [2]. Water pollution has a great global effect on people's lives, especially in developing countries, arising from limitations in access to safe drinking water and increase in the risk of health challenges [3]. The industrial sector utilizes large amount of water and discharges the polluted water after usage, either to land drainage or rivers, which affects human health as well as aquatic plants and animals [4].

Cadmium (Cd) is a heavy metal that does not have any physiological function in the body and is highly toxic in nature [5]. Cadmium metal has been identified as a human carcinogen and teratogen affecting the liver, kidneys, and lungs [6].

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However, cadmium toxicity is linked to human body via the food chain and lead to many chronic and acute diseases, such as pulmonary oedema, hepatic dysfunction, damage to the adrenal glands, and haemotopoietic system [7].

Generally, the main objective of wastewater treatment before discharging into the ecosystems is the removal of pollutants like heavy metals. Several methods have been adopted to remove heavy metals from industrial wastewater, such as adsorption, chemical precipitation, reverse osmosis, sedimentation, ion exchange, membrane separation, chemical oxidation and reduction, electrochemical remediation, and solvent extraction. However, these methods have some limitation such as removal efficiency, operating costs and the generation of secondary sludge [8]. Therefore, adsorption technique is widely utilized in treatment of wastewater due to its low cost, environmentally friendly compatibility, high selectivity, flexibility, and high removal potential due to waste adsorbent availability, simple operation, reusability, high heavy metal removal uptake over a wide pH range, and remarkable ability to eliminate toxic metal ions from their complexes [4].

Agricultural materials are currently attracting attention, especially cellulosic materials, which show a high promise of adsorption capacity owing to their structures that contain lignin, lipids, promising adsorption capacity owing to their structures that contains lignin, lipids, proteins, starch, hemicelluloses, and water hydrocarbons [9]. The presence of amido, amino, carbonyl, alcoholic, sufhydryl, acetamido, and phenolic functional groups has contributed to the high adsorption efficiency of agricultural waste materials applied as adsorbents. The elimination of heavy metals from polluted water using biosorbents can be achieved through adsorption, fixation, and surface precipitation. The effectiveness of biosorption techniques in wastewater treatment is also affected by various physicochemical parameters of the adsorbent and adsorbate [4]. Several agricultural waste materials investigated are rice husk, peels of lime, orange, apple, banana, shells of groundnut, coconut, and walnut [10]. The agricultural waste materials have shown promising results in the removal of heavy metals from wastewater, either in their natural form or after physical or chemical modifications [10]. Agricultural waste materials are one of the major sources of low-cost adsorbents and they are readily available in large quantities [11]. The selection of carbon-rich adsorbent is very important in wastewater treatment, as heavy metals are removed by complexation or electrostatic interaction between the metal ions and adsorbent surface. *Pterocarpus santalinoides* fruit is a high carbonaceous agricultural waste material that is rich in phytochemicals [12].

The fruit of *Pterocarpus santalinoides* has been identified to contain high amount of polyphenols, alkaloids, flavonoids, saponnins, terpenes and glycosides [12,13]. The presence of these phytochemicals can provide binding sites for metal ions uptake via ion exchange, chelation, adsorption, micro-precipitation and complexation [14]. This research examines the application of *Pterocarpus santalinoides* fruit as an efficient biosorbent for the removal of Cd^{2+} ions from aqueous solutions. The present study focuses on the elimination of cadmium ions adsorption into raw and activated carbon of *Pterocarpus santalinoides* fruit as influenced by dosage, contact time, initial metal concentration and solution temperature. The results of the experiments were extended to the study of isotherm, kinetic, and thermodynamic parameters for the adsorption processes. The study also presents optimization of cadmium percentage removal from aqueous solutions on raw and activated carbon of the adsorbents by the central composite design (CCD) method in response surface methodology (RSM).

2. Material and methods

2.1. Chemical and Reagents

Analytical-grade reagents were used in this study. Stock solutions of 100 mg/l of Cd (II) ions were prepared using deionized water by dissolving the required amounts of $CdCl_2$ (a product of Loba Chemie PVT. Ltd., India). The corresponding dilutions used in the adsorption experiments were prepared from the stock solutions. The activated carbon was activated using 0.l M HCl (98%), a product of Sigma Aldrich with 98% purity.

2.2. Preparation of Adsorbent (Raw and Activated Carbon)

Pterocarpus santalinoides fruits were collected from the botanical farm of the Federal Polytechnic, Nekede Owerri, Imo State. The fruits were first washed thoroughly with running water, followed by distilled water to remove extraneous materials, and air dried for 14 days. The dried material had its seeds removed, leaving the shell. The shell was ground into powder. The powdered samples were separated into two portions, of which one was used to prepare activated carbon.

Activated carbon from *Pterocarpus santalinoides* shell was prepared by treating the ground-dried materials with 0.1 *M* HCl and putting them into a muffle furnace at 500 °C for 3 hours. Under vacuum, the muffle furnace was cooled to ambient temperature. Then, using distilled water, the produced products were rinsed until the pH of the filtrate reached

7. The activated carbon from *Pterocarpus santalinoides* shell was then dried at 100 °C. The ground raw and activated carbon were ground to a particle size of 53µm to obtain a fine powder. The powder of the individual adsorbents was labeled, kept in airtight plastic bottles, and stored in desiccator for further use.

2.3. Adsorbent Characterization

The mineral content of the adsorbents was determined following the guidelines of the ASTM E1755-01 standard [15]. The functional groups present on the surface of the raw adsorbent were determined using fourier transform infrared (FTIR) spectroscopy (Happ-Genzel). The surface morphology of the raw and activated carbon of the adsorbents was studied with the help of a scanning electron microscope (phenomProx).

2.4. Adsorption Study

2.4.1. Contact Time Effect

The adsorption studies were performed with each adsorbent and metal ion separately, using 100 ml of metal solution. The initial concentration of 40 mg/l was stirred with 0.1 g of adsorbents. After 60 min, the mixture was filtered, and the filtrate was analyzed for the unadsorbed Cd metal ions using an atomic absorption spectrophotometer (AAS).

2.4.2. Adsorbent Dose Effect

Batch studies on the effect of adsorbent dose on the removal efficiency of the adsorbents were also studied. The adsorbent was mixed with 40 mg/l of cadmium metal solution at various doses of 0.1, 0.2, 0.3, 0.4 and 0.5 g, respectively, in 100ml of metal solution and stirred for 60 min.

2.4.3. Initial Metal Concentration Effect

The effect of an initial metal concentration on the adsorption efficiency of adsorbents was examined in this experiment. The study was performed by preparing different concentrations of cadmium metal. The adsorbents were mixed with a synthetic aqueous solution of cadmium metal concentrations of 10, 20, 30, 40 and 50 mg/l, respectively, and were agitated continuously at a constant contact time of 60 min and adsorbent dose of 0.1 g. The volume of the synthetic aqueous solution was 100 ml.

2.4.4. Temperature Effect

Temperature is another variable that affect the metal adsorption process. The impact of temperature on the adsorption of Cd ions in the solution was demonstrated. Cadmium ions were removed from the aqueous solution at different temperature ranges of 30, 40, 50, 60, and 70 ℃ using a constant dosage of 0.1 g/100 ml of 40 mg/l Cd solution for 60min.

2.4.5. Determination of Metal Ion Content

The unadsorbed cadmium ion concentration was evaluated with atomic absorption spectrophotometer (AAS Model, Solar 950A).

2.4.6. Determination of Adsorption Efficiency and Capacity

The percentage adsorption efficiency (A %), and the adsorption capacity (qe) were calculated from the following equations:

$$A\,\% = \frac{C_o - C_e}{C_o} \times 100 \quad \ldots\ldots\ldots\ldots(1)$$

$$qe\ (mg/g) = \left(\frac{C_o - C_e}{m}\right) V \qquad \ldots\ldots\ldots\ldots(2)$$

Where C_o and C_e (mg/l) are the initial and final concentrations of Cd^{2+} ions in solution, respectively, V (L) is the volume of solution, and M (g) is the adsorbent mass.

2.5. Adsorption Isotherm Studies

The study applied Langmuir and Freundlich isotherm models to ascertain the adsorption capacity of the adsorbents. The adsorption isotherm models demonstrate a correlation between the amounts of Cd^{2+} ion in solution with the adsorbents. In the present study, Langmuir and Freundlich models were evaluated. The Langmuir isotherm explains single layer adsorption with adsorbent activated sites, whereas the Freundlich model is applied to heterogeneous surfaces with adsorption of multi-layer. The Langmuir and Freundlich adsorption isotherm equilibrium parameters were calculated following equation (3) and 4 respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \text{……….(3)}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \text{………(4)}$$

Where q_m and K_L are the Langmuir constants (mg/g), K_f are Freundlich equilibrium constant (mg/g), q_e is the metal dose adsorbed on a specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of the solution (mg/l) and q_m is the maximum dose of metal concentration required to form a monolayer (mg/g).

2.6. Adsorption Kinetic Modeling

The degree of adsorption as a function of contact time was utilized to study the kinetics of Pb^{2+} adsorption from an aqueous solution. The adsorption kinetic modeling data were analyzed for each adsorbent, using pseudo-first-order and pseudo-second-order models. The pseudo-first-order parameters were obtained following equation (5) while pseudo-second-order parameters were obtained following equation (6).

$$\text{In}\frac{C_t}{C_o} = -K_1 t \quad \text{………..(5)}$$

$$\frac{1}{C_t} = \frac{1}{C_o} + K_2 t \text{…………..(6)}$$

Where C_o is the initial concentration and C_t is the residual metal ion concentration of metal ion (mg/l) at a definite time t (min), K_1 is the pseudo-first order rate constant (min^{-1}), and K_2 is the pseudo-second order rate constant (g/mg.min).

2.7. Thermodynamic Studies

This study investigated the influence of solution temperature on the adsorption of Cd^{2+} ion by both adsorbent at different temperatures (303, 313, 323, 333 and 343 K). The thermodynamic parameters of entropy (ΔS^o), enthalpy (ΔH^o) and Gibb's energy (ΔG^o) were evaluated to determine the viability, exothermic or endothermic nature and spontaneity of the adsorption process using equation (7) and (8) respectively.

$$\Delta G^\circ = -RT\ln K_d \text{…………7}$$

Where K_d, T and R are the equilibrium rate constant (L/g), temperature (K) and gas constant (J/K.mol), respectively. The parameters of thermodynamic were calculated using equation (8).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{………………8}$$

2.8. Optimization Design

The adsorption efficiency of raw and activated carbon of *Pterocarpus santalinoides* was investigated based on the experimental design with the four operating factors (Table 1). This was carried out using central composite design (CCD) by Design – Expert software (Version 13.0.15) (Stat-Ease, Inc. USA). The independent variables in this study were adsorbent dosage, contact time, initial ion concentration and temperature, which generated 30 experimental runs.

Table 1 Central composite design matrix of independent variables for adsorption process

Factor	Low level (-1)	Medium (0)	High Level (+1)
A: Adsorbent dosage	20	60	100
B: Contact time (min)	0.1	0.3	0.5
C: Initial metal ion concentration	10	30	50
D: Temperature	303	323	343

The impact of the four independent variables such as A: adsorbent dosage (0.1-0.5 g) B: contact time (20-100 min), C: initial ion concentration (10-50 mg/l) and D: temperature (303-343 K) were examined on adsorption of Cd^{2+} by the two adsorbents with percentage removal efficiency as the responses.

3. Results and discussion

3.1. Characteristics of the Adsorbents

The surface morphology of raw and activated carbon *Pterocarpus santalinoides* fruit adsorbents was examined using scanning electron microscopy. Figure 1a-d displayed SEM image of the adsorbent before and after adsorption of Cd^{2+}. The SEM images show that the raw and activated carbon derived from the *Pterocarpus santalinoides* fruit adsorbent has pores and rough surfaces. These holes and fibrous surfaces were observed to cause the high adsorption of cadmium ions, which was seen after the adsorption of Cd^{2+}. The significant changes were seen on the surfaces of this adsorbent after adsorption of Cd^{2+} ions. These results revealed that raw and activated carbon derived from the *Pterocarpus santalinoides* fruit has enough active surface area and binding cavities to adsorb cadmium ions [16].

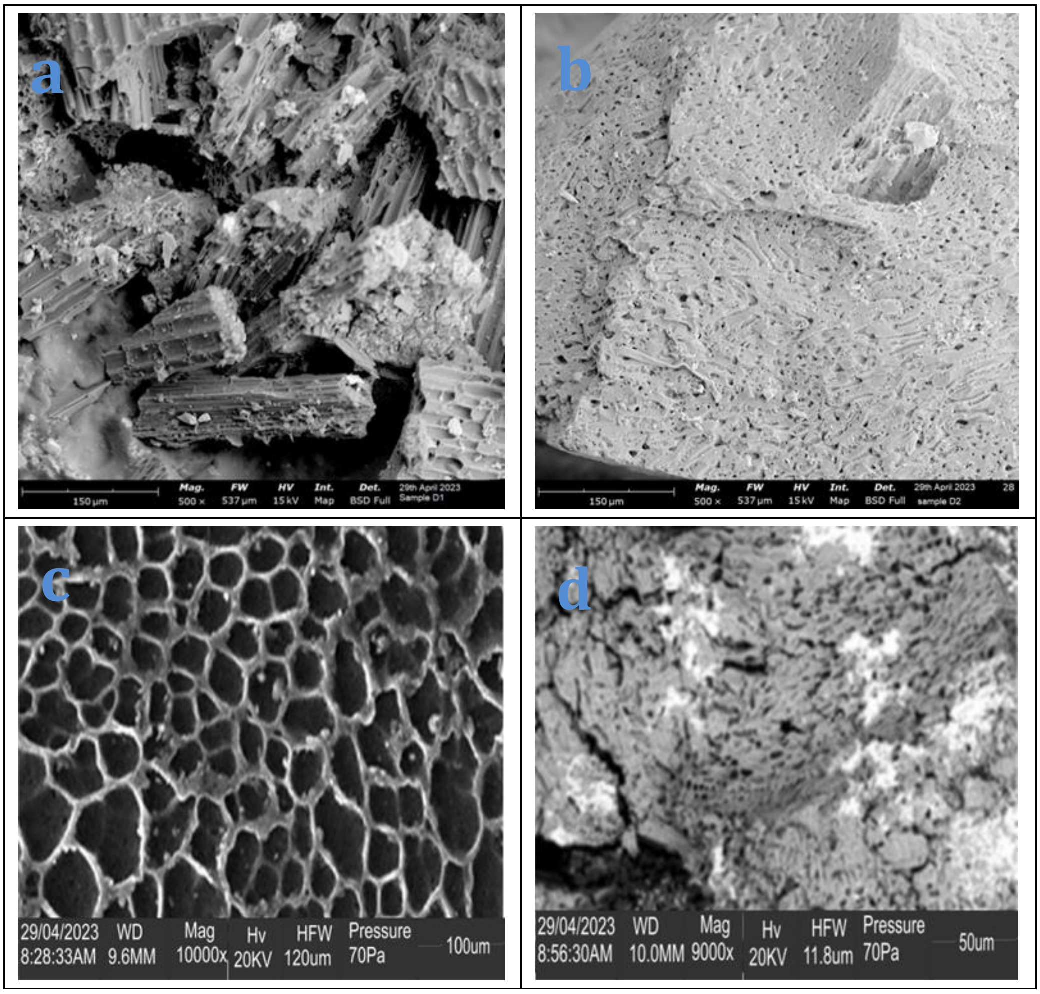

Figure 1 The SEM images of the adsorbent surface: (a) raw fruit before adsorption (b) raw fruit after cadmium (c) fruit activated carbon before adsorption (d)) after cadmium adsorption

The result of the mineral content of the raw and activated carbon of *Pterocarpus santalinoides* fruit shows that sodium recorded the highest amount in both the raw (0.2577 mg/g) and activated carbon derived from fruit (0.2819 mg/g) while magnesium recorded the least value in raw (0.1997mg/g) and activated carbon (0.1720mg/g) as tabulated in Table 1.

The presence of calcium, magnesium, potassium and sodium as the major element in agricultural waste materials correlates with previous reports in the literature [17].The presence of these minerals in adsorbent materials is necessary because of their ability to act as exchangeable cations in solution.

Table 2 Mineral composition of *Pterocarpus santalinoides* fruit adsorbent

Adsorbents	**Calcium (mg/g)**	**Magnesium (mg/g)**	**Potassium (mg/g)**	**Sodium (mg/g)**
Raw fruit	0.2218	0.1997	0.2300	0.2577
fruit activated carbon	0.2320	0.1720	0.1801	0.2819

The FTIR spectrum of raw *Pterocarpus santalinoides* fruit before adsorption is displayed in Figure 2. FTIR analysis of the raw adsorbent indicates the presence of various functional groups, including = C–H, –OH C–N, C=O, N=H, C≡C and C≡N groups. The polar –OH group is recognized by a broad peak at 3446.62 cm^{-1}, and the stretching vibrations of the carbonyl group can be linked in bands at 1726.72 cm^{-1}.The FTIR absorption bands stretching at 1171.49 cm^{-1} and 1450.62cm^{-1} indicate the presence of C–N and N–H bending of amines. The vibrations of C=O and N–H present in amides are identifiable at wave number of 1651.34cm^{-1} and 3818.06cm^{-1} respectively. The aromatic =C–H and phenolic –OH bands were also observed in the raw adsorbent at 718.71cm^{-1} and 3678.84cm^{-1} respectively. Polysaccharides can be recognized at wave numbers of 961.25cm^{-1} for =C–H bending 2191.91cm^{-1} for C≡C stretch, 2910.05cm^{-1} for C–H stretch and 3268.53 ≡C–H stretch. The presence of these functional groups indicates that groups are involved in the elimination of cadmium ions from polluted water through electrostatic attraction or complex formation between the adsorbent surface and metal ions [4,18].

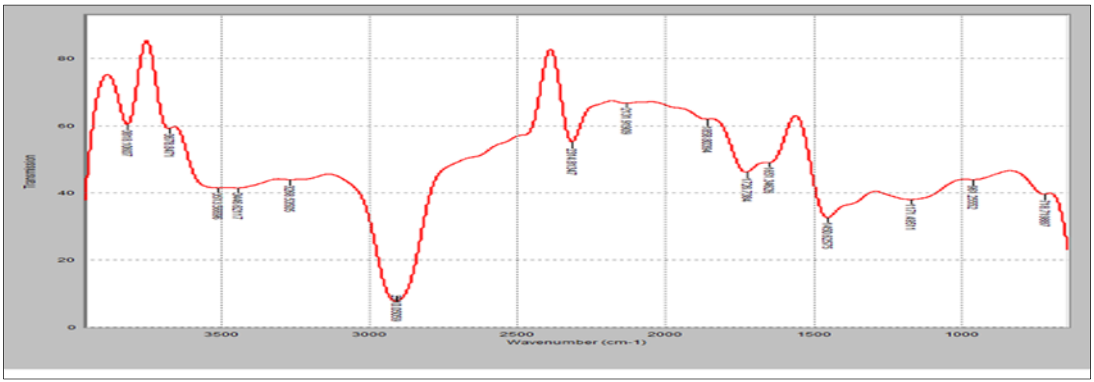

Figure 2 The FT-IR spectrum of *Pterocarpus santalinoides* fruit

3.2. Effect of adsorbent Dosage on Removal of cadmium

As shown in Figure 3, the increase in the adsorbent dosage from 0.1 to 0.5g in 100.ml of cadmium ion solution effectively increased the adsorption efficiency of Cd^{2+} by the raw and activated carbon of *Pterocarpus santalinoides* from 87.36 to 98.59% and 80.85 to 98.42%, respectively. The adsorption percentage increase with an adsorbent dosage increase is attributed to the availability of more adsorption sites and an increase in the adsorbent surface area [4,14].

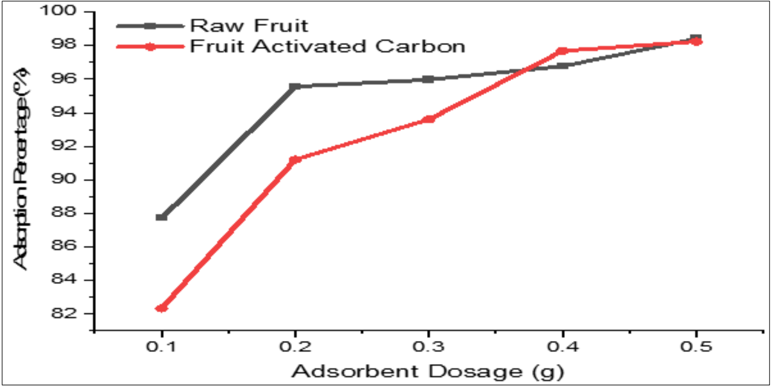

Figure 3 Effect of adsorbent dosage on the removal of Cd^{2+} ions by raw fruit and fruit activated carbon of *Pterocarpus santalinoides*

3.3. Effect of Contact Time

The elimination of cadmium ion was examined at different contact time ranging from 20–100 min. Figure 4 depicts that the percentage of cadmium adsorption increased with increasing contact time. The percentage of cadmium ion removal was rapidly higher initially but gradually increased with increasing contact time. It was observed that the raw fruit recorded 88.77% at 20 min and 99.28% at 100 min while the activated carbon derived from the fruit recorded 89.14% at 20 min and 99.37% at 100 min, respectively. The adsorption percentage increased with time because increasing the contact time of adsorption allows for more contact between the cadmium ion and the binding sites on the adsorbent surface. Therefore, more cadmium ion can be adsorbed by the adsorbent surface, resulting to higher adsorption percentages [17]. The adsorption percentage reached equilibrium capacity within 60 min for both adsorbents.

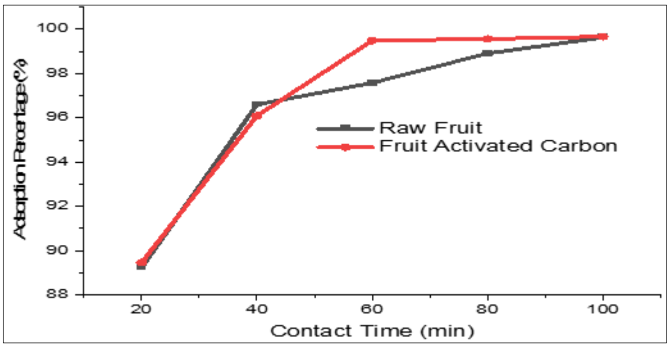

Figure 4 Effect of contact time on the removal of Cd^{2+} ions by raw fruit and fruit activated carbon of *Pterocarpus santalinoides*

3.4. Effect of Initial Metal Concentration

The impact of the initial metal concentration on cadmium ion adsorption percentage at constant dose of 0.1 g/100 ml for 60 min is displayed in Figure 5 and the result indicates that Cd^{2+} adsorption percentage was higher at lower initial metal concentrations in the solution [19]. The adsorption percentage of Cd^{2+} decreased from 99.79 to 80.57% and 99.40 to 81.76% for raw and activated carbon of *Pterocarpus santalinoides* fruit respectively. This trend is possible because the number of available adsorbent active sites is more when compared to the number of cadmium ion at lower concentration [16]. This result indicates that low adsorption percentage was recorded at high initial cadmium concentrations.

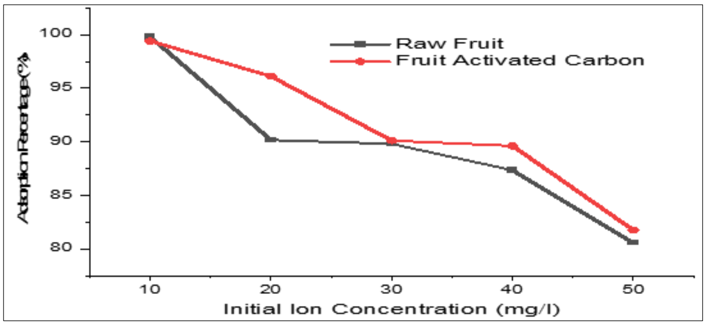

Figure 5 Effect of initial ion concentration on the removal of Cd^{2+} ions by raw fruit and fruit activated carbon of *Pterocarpus santalinoides*

3.5. Effect of Temperature

The adsorption of cadmium ion was investigated on five different temperatures: 30, 40, 50, 60 and 70 ^{0}C. The experimental results depicted in Figure 6 reveal that the percentage adsorption rate of Cd^{2+} ion depends on the solution temperature. The optimal temperature of 40 ^{0}C was found for raw adsorbent while 30 ^{0}C was obtained for activated carbon derived from *Pterocarpus santalinoides* for adsorption of cadmium ion. The adsorption rate was observed to decrease with increasing temperature. This phenomenon shows that the adsorption process is exothermic and no strong chemical bond was formed during adsorption [16].

Generally, *Pterocarpus santalinoides* fruit treated and untreated adsorbents shows a high adsorption uptake for cadmium ion over the wide range of temperature range studied, making it raw and modified form a potential adsorbent for removing cadmium ion from wastewater especially at low temperature.

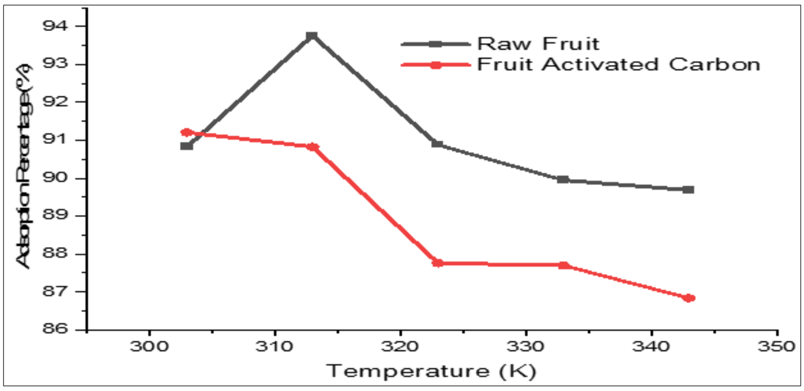

Figure 6 Effect of temperature on the removal of Cd^{2+} ions by raw fruit and fruit activated carbon of *Pterocarpus santalinoides*

3.6. Adsorption Isotherm Studies

The adsorption isotherms of the studied cadmium ion on *Pterocarpus santalinoides* (raw and activated carbon) were explained using the Langmuir and Freundlich isotherm models. The computed Langmuir and Freundlich isotherm parameters are shown in Table 3, along with their correlation coefficients for the adsorption experimental data. The experimental data shows that Langmuir isotherm was well fitted to both adsorbents for Cd^{2+} adsorption based on the R^2 values. The experimental results of Cd^{2+} adsorption on the adsorbents (raw and activated carbon) were similar in Langmuir model since the differences between R^2 values were negligible. The result reveals that cadmium adsorption occurred through monolayer adsorption [20,21].

Table 3 Isotherm model parameters for lead adsorption by raw and activated carbon of *Pterocarpus santalinoides* fruit

Adsorbents	**Freundlich Model**			**Langmuir Model**		
	$\frac{1}{n}$	K_f (mg/g)	R^2	q_L	K_f(mg/g)	R^2
Raw fruit	0.06	21.08	-0.9989	15.85	10.18	0.9999
Fruit activated carbon	0.03	20.59	-0.9447	19.31	15.33	0.9965

3.7. Adsorption Kinetic Modeling

Table 4 Kinetic adsorption model parameters for lead adsorption by raw and activated carbon of *Pterocarpus santalinoides* fruit

Adsorbents	**Pseudo first order**		**Pseudo second order**	
	K	R^2	K	R^2
Raw shell	$3.67X10^{-6}$	-0.0113	$4.72X10^{-2}$	0.9999
Shell activated carbon	$8.95X10^{-5}$	-0.1735	$4.68X10^{-2}$	0.9998

The pseudo-first order and pseudo-second-order models were fitted to the experimental data in order to estimate the adsorption rate of the adsorbents. The kinetic parameters calculated for the pseudo-first-order and pseudo-second order models for the adsorbents (raw and activated carbon) are depicts in Table 4. The experimental results revealed that the linear regression coefficient (R^2) of the pseudo-second order fitted well into the adsorption process than the pseudo-first-order kinetic model. The result predict that the overall adsorption rate of Cd^{2+} ions onto *Pterocarpus santalinoides* (Raw and activated carbon) is controlled by chemical adsorption [14,22]. Besides, there was no significant difference between the R^2value of pseudo-second-order for the two adsorbents studied. However, the closeness of R^2 value to 1 in pseudo-second-order confirms that the adsorption kinetics are controlled by this order and there is a strong interaction between adsorbent and adsorbate.

3.8. Thermodynamic studies

The thermodynamic parameters are important for determination of feasibility, nature of heat adsorption, and spontaneity of the adsorption process. The thermodynamic parameters obtained in this study are presented in Table 5, the standard (ΔS^o) was found to be positive for the temperatures tested, and the negative value of (ΔH^o) observed indicated that adsorption of Cd^{2+} ions by the adsorbents (raw and activated carbon) is exothermic. The Gibb's free energy demonstrated the spontaneity of the adsorption processes, and the negative value of (ΔG^o) illustrate that the adsorption of Cd by both adsorbents was spontaneous. The values of (ΔG^o) were observed to decrease as the solution temperature increased. The study shows that Cd^{2+} ion adsorptions were lower at high solution temperatures.

Table 5 Thermodynamic Parameters for cadmium adsorption onto raw and activated carbon of *Pterocarpus santalinoides* fruit

Adsorbents	ΔG° (KJ/mol)					ΔH° (K/mol)	ΔS° (KJ/mol)
	303 (K)	**313 (K)**	**323 (K)**	**333 (K)**	**343 (K)**		
Raw fruit	-5.85	-6.04	-6.23	-6.42	-6.62	-0.03	0.019
Fruit activated carbon	-6.88	-7.10	-7.33	-7.56	-7.78	-0.03	0.023

3.9. Design and Analysis by the CCD Method

Central composite model was chosen from response surface methodology from among the various methods provided by the design expert software for the study design. In this study, RSM was used to determine the optimal efficiency of cadmium removal and also determine the maximum conditions of the adsorption process variables such as contact time, adsorbent dosage, initial metal concentration, and solution temperature. The response for cadmium percentage removal by raw and activated carbon from *Pterocarpus santalinoides* fruit was obtained by a linear model. The actual response and predicted results obtained in the design of the experiment are shown in Table 6 and 7 respectively.

3.10. Model Assessment

Analysis of variance (ANOVA) as tabulated in Table 8 and 9 were used to analyze the statistical model for cadmium removal by the both adsorbents. The significance level of P-value was observed to be less than 0.05. according to the observations of ANOVA in Table 8 and 9, the adsorbent dosage (A), contact time (B), and initial metal concentration (C) were significant in both adsorbents. The solution temperature (D) was not significant and although temperature (D) had the lowest F-value and P-value was greater than 0.05, it shows that temperature has no proprietary effect on the adsorption process for both adsorbents.

The model equations (9) and (10) are expressed with the actual values of the input parameters (A, B, C, D) as a function of the responses (percentage adsorption). The positive sign represents the synergistic effect of the term on the responses, whereas the negative sign points out an antagonistic effect. In this view, the increasing order of the impact of the terms for the cadmium adsorption follows the same trends as A>B>D>C.

Percentage adsorption (Raw) = 92.74 +5.99A + 0.02B - 0.09C – 0.01D ………….(9)

Percentage adsorption (activated carbon) = 90.83 + 8.81A + 0.02B – 0.09C – 0.01D ………….(10)

The model equation shows that A and B with positive coefficients had direct effect on the cadmium removal efficiency, whereas C and D with negative coefficients had an inverse effect on the cadmium removal efficiency.

Table 6 Experimental and predicted values of cadmium adsorption by raw *Pterocarpus santalinoides* fruit

Run	**Factor 1 A:Adsorbent dosage (g)**	**Factor 2 B: Contact time (min)**	**Initial ion concentration (mg/l)**	**Temperature** °C	**Adsorption percentage Experimental (%)**	**Adsorption percentage Predicted (%)**
1	0.1	20	50	30	87.09	88.80
2	0.7	60	30	50	93.87	95.00
3	0.3	60	70	50	91.23	88.87
4	0.3	60	-10	50	95.75	96.34
5	0.3	60	30	50	93.26	92.60
6	0.5	100	50	30	92.37	93.15
7	0.5	20	50	70	89.47	90.72
8	0.3	60	30	50	93.26	92.60
9	0.1	100	10	30	94.50	94.49
10	0.5	100	50	70	92.07	92.67
11	0.3	60	30	50	93.26	92.60
12	0.5	20	10	70	94.28	94.46
13	0.3	60	30	50	93.26	92.60
14	0.3	140	30	50	93.77	94.55
15	0.3	60	30	50	93.26	92.60
16	0.1	20	10	70	91.60	92.06
17	0.5	20	10	30	94.57	94.93
18	0.3	60	30	90	93.26	92.13
19	0.1	100	50	30	89.70	90.75
20	0.5	20	50	30	92.37	91.20
21	0.5	100	10	70	96.88	96.41
22	0.1	100	10	70	94.20	94.01
23	0.3	-20	30	50	91.17	90.65
24	0.1	20	10	30	91.90	92.54
25	0.3	60	30	10	93.64	93.08
26	-0.1	60	30	50	91.49	90.21
27	0.1	100	50	70	89.40	90.27
28	0.3	60	30	50	93.26	92.60
29	0.5	100	10	30	97.16	96.88
30	0.1	20	50	70	86.80	88.32

Table 7 Experimental and predicted values of cadmium adsorption by activated carbon of *Pterocarpus santalinoides* fruit

Run	Factor 1 A:Adsorbent dosage (g)	Factor 2 B: Contact time (min)	Initial ion concentration (mg/l)	Temperature (°C)	Adsorption percentage Experimental (%)	Adsorption percentage Predicted(%)
1	0.1	20	50	30	86.19	87.57
2	0.7	60	30	50	93.90	95.40
3	0.3	60	70	50	90.65	88.37
4	0.3	60	-10	50	95.33	95.39
5	0.3	60	30	50	93.01	91.88
6	0.5	100	50	30	91.85	93.00
7	0.5	20	50	70	89.57	90.77
8	0.3	60	30	50	92.74	91.88
9	0.1	100	10	30	92.29	92.99
10	0.5	100	50	70	92.12	92.68
11	0.3	60	30	50	93.01	91.88
12	0.5	20	10	70	93.98	94.28
13	0.3	60	30	50	93.01	91.88
14	0.3	140	30	50	93.05	93.79
15	0.3	60	30	50	93.01	91.88
16	0.1	20	10	70	90.01	90.76
17	0.5	20	10	30	93.71	94.60
18	0.3	60	30	90	92.74	91.56
19	0.1	100	50	30	87.88	89.48
20	0.5	20	50	30	91.85	91.09
21	0.5	100	10	70	96.53	96.19
22	0.1	100	10	70	92.56	92.67
23	0.3	-20	30	50	90.50	89.97
24	0.1	20	10	30	89.74	91.07
25	0.3	60	30	10	93.59	92.20
26	-0.1	60	30	50	89.92	88.36
27	0.1	100	50	70	88.15	89.16
28	0.3	60	30	50	92.74	91.88
29	0.5	100	10	30	97.13	96.51
30	0.1	20	50	70	85.60	87.25

Table 8 Analysis of variance (ANOVA) results of linear model for cadmium adsorption by raw *Pterocarpus santalinoides* fruit

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-Value	
Model	142.45	4	35.61	34.17	< 0.0001	Significant
A-Adsorbate Dose	34.42	1	34.42	33.03	< 0.0001	Significant
B-Contact Time	22.82	1	22.82	21.89	< 0.0001	Significant
C-Initial ion Concentration	83.85	1	83.85	80.46	< 0.0001	Significant
D-Temperature	1.36	1	1.36	1.31	0.2636	Not significant
Residual	26.05	25	1.04			
Lack of Fit	26.05	20	1.30			
Pure error	0.0000	5	0.0000			
Cor Total	168.50	29				

Table 9 Analysis of variance (ANOVA) results of linear model cadmium adsorption by activated carbon of *Pterocarpus santalinoides* fruit

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-Value	
Model	170.91	4	42.73	29.08	< 0.0001	significant
A-Adsorbate Dose	74.48	1	74.48	50.70	< 0.0001	Significant
B-Contact Time	21.97	1	21.97	14.95	0.0007	Significant
C-Initial ion Concentration	73.85	1	73.85	50.27	< 0.0001	Significant
D-Temperature	0.6080	1	0.6080	0.4139	0.5259	Non significant
Residual	36.73	25	1.47			
Lack of Fit	36.63	20	1.83	94.22	< 0.0001	significant
Pure error	0.0972	5	0.0194			
Cor Total	207.63	29				

3.11. Model Validation

The model validation in this study was evaluated using both the coefficient of determination (R^2), adjusted coefficient (R^2) and predicted coefficient (R^2) with an estimated difference between the predicted and adjusted was less than 0.2 for both adsorbents (Table 10). The fit statistics, as tabulated in Table 10, show that the predicted R^2 of 0.7660 and 0.7393 were in reasonable agreement with the adjusted R^2 of 0.8206 and 0.7948 for raw and activated carbon of *Pterocarpus santalinoides* respectively. The difference between adjusted and predicted coefficient was noticed to be less than 0.2, indicating good predictability of the model for the adsorption process. The coefficient determination (R^2) of the model for both adsorbent surpasses the acceptable threshold value of R^2 being greater than or equal to 0.8, and the model becomes more relevant when it is closer to 1.0 [23].

The model has an adequate precision greater than 4.00, which indicates the desirability and implies an adequate signal. This also predicts that the model can be used to navigate the design space [24]. The coefficient of variation (CV %) was 1.10 % and 1.32 % for raw and activated carbon adsorbents, respectively, for the dependent variables, which depicted the accuracy of the measurements and reliability of the tests. The low standard deviation and PRESS values of 1.02 and 39.43 for raw and 1.21 and 54.14 for activated carbon respectively, indicated the suitability of the linear model selected for the experimental data [25].

Table 10 Model validation results for the response linear models for raw and activated carbon of *Pterocarpus santalinoides* fruit

Parameter	Raw adsorbent	Activated adsorbent
Standard deviation	1.02	1.21
Mean	96.60	91.88
Coefficient of variance (CV,%)	1.10	1.32
Coefficient of determination (R^2)	0.8454	0.8231
Adjusted R^2	0.8206	0.7948
Predicted R^2	0.7660	0.7393
Adequate precision	20.54	18.72
PRESS	39.43	54.14

3.12. Numerical Optimization Model

The Design–Expert software numerical optimization was carried out to maximize cadmium reduction by setting individual factor values within their respective range such as adsorbent dose (0.1-0.5 g), contact time (20-100 min), initial ion concentration (10-50 mg/g) and temperature (30-70 ºc), whereas the responses (adsorption percentage) for both adsorbents (raw and activated) were set at maximum with 95% confidence level. The desirability function approach was evaluated, and the optimized conditions obtained are presented in Figure 7. Thus, an optimum adsorbent dose of 0.5 g, contact time of 100 min, initial ion concentration of 46.93 mg and temperature of 70 ℃ resulted in percentage adsorption of 92.96% and 92.95% using raw and activated carbon from *Pterocarpus santalinoides* fruit, respectively, with a desirability 0.839. The control composite design model obtained from response surface methodology indicated a strong correlation between model prediction and actual conditions.

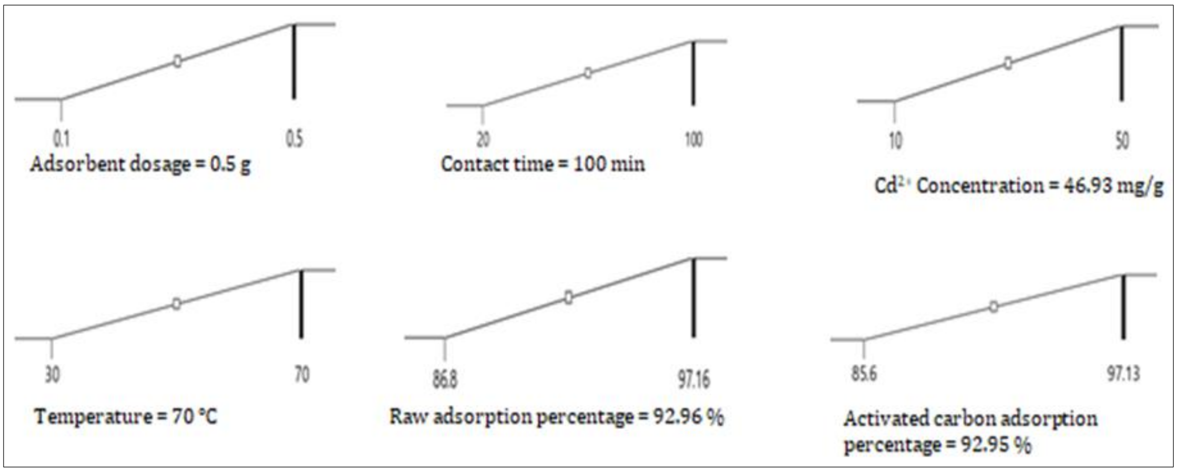

Figure 7 Numerical optimization model parameters for raw and activated carbon of *Pterocarpus santalinoides* fruit

4. Conclusion

In this study, the efficiency of the raw and activated carbon of *Pterocarpus santalinoides* fruit in the removal of cadmium ions from aqueous solutions as well as the impact of different variables were investigated. The studies showed that the raw and modified adsorbents can be considered effective adsorbents for the removal of cadmium metal ions from contaminated wastewater due to their various advantages, such as presence of functional groups, porosity, low cost, and natural origin. The removal efficiencies of cadmium metal were strongly dependent on their adsorbent dosage, contact time, initial ion concentration and temperature. The adsorption process was observed to be a single-layer process based on the Langmuir model, and the kinetic model of adsorption was well explained by the pseudo-second-order model, indicating chemisorption adsorption process. The thermodynamic study defined the adsorption process as endothermic, spontaneous, and feasible in nature. The CCD analysis via RSM was used to analyze and optimize the adsorption process. According to ANOVA, a linear model with high predictive power was applied to the experimental data ant the predicted results. Among the different variables studied, adsorbent dosage, contact time, and initial ion concentrations were identified as the parameters affecting the system's performance. The optimum system conditions for cadmium removal were obtained at Cd concentration = 46.93 mg/g, adsorbent dosage = 0.5 g, contact time =100 min and temperature = 70 °C, with the adsorption percentage of 92.96 % and 92.95 % for raw and activated carbon of the adsorbents, respectively. This study demonstrated that *Pterocarpus santalinoides* fruit has a relatively high potential for cadmium removal from aqueous solution and could be used as a low-cost adsorbent for treating wastewater with toxic heavy metals.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflict of interest.

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