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Central composite design analysis and optimization of cadmium adsorption from synthetic wastewater by avocado seed activated carbon

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Abstract

This study examines the adsorptive removal of cadmium from aqueous solutions using chemically modified avocado seed activated carbon (ASAC). The prepared adsorbent was characterized using FTIR, Boehm titration, iodine number, pHpzc, proximate analysis and surface area, respectively. A two-level, four-factor central composite design (CCD) in response surface methodology (RSM) was utilized to optimize the effect of the four process variables namely initial concentration (100-200 mgL^{-1}), adsorbent dosage (0.10-1.0 g), pH (3-8) and contact time (10-180 min) on cadmium removal from aqueous solution. Based on the design, a total of 30 adsorption experiments were performed and a quadratic model was developed linking the process factors to the response. Analysis of variance (ANOVA) was applied to assess the adequacy of the model. From the analysis, the model's coefficient of determination (R^2) of 0.9730 and F-value of 38.55 are indicative that the model is adequate and can be used to navigate the design space. The optimum conditions of initial concentration (200 mgL^{-1}), adsorbent dose (0.1 g), pH (3.37) and contact time (100 min) were obtained from the desirability function. The adsorption equilibrium data were best described by the Jovanovic model. Finally, the pseudo second order kinetic model described the cadmium adsorption process best.

Keywords: adsorption, cadmium, central composite design, optimization, response, statistical analysis

Introduction

Metals and their compounds are very important and indispensable part of any country's technological and industrial advancement. The presence of these heavy metals in waste streams and groundwater pose a very serious environmental problem since these metal ions are reported to be noxious to human beings as well as other living organisms [1, 2], causing serious fatality especially if their concentration is more than the accepted limit [3]. The annual toxicity resulting from heavy metal discharged into the environment is believed to exceed the total toxicity of organic and radioactive waste [4]. Heavy metals are elements whose densities are relatively high (> 5 g/cm^3) and could be toxic even at low concentration [5]. These metals are usually not biodegradable, when released into the environment, they can persist for decades and if ingested beyond tolerable levels can have adverse effects on humans.

Heavy metals such as cadmium, lead, mercury, nickel, silver, chromium, and cobalt are of concern since they are toxic to human health. Cadmium occurs naturally in soil, rocks, coal and in mineral fertilizers. It has also been found in several industrial wastes. Cadmium is widely used in metal plating, pigments and metal coatings, as stabilizers in PVC products, rechargeable nickel-cadmium batteries and as anticorrosive agents [5].

Natural and man-made sources of cadmium which include the application of sewage sludge, industrial discharge, and fertilizers on farmland have increased soil and water contamination. Ingestion and accumulation of high dosage of cadmium in the human body cause high blood-pressures, liver disease, nerve or brain damage, even cancer [6]. Low-level exposure over a long period may cause skeletal damage, the build-up of cadmium in the kidney, kidney disease, fragile bones and damage to the lungs [7]. In plants, the accumulation of cadmium in plant tissues can lead to a decrease in seed germination, lipid content and plant growth [8]. Hence, there is need to remove this toxic pollutant from wastewater effluents.

The main technologies used for cadmium ion removal from wastewater include precipitation, ion-exchange, membrane processes, solvent extraction, electrocoagulation, coagulation-flocculation and electrolytic recovery [9]. However, these conventional physicochemical treatment methods for removing heavy metals from waste streams are very expensive, thus, there is a need for cheaper methods for waste effluent treatment.

Adsorption, which is a process that utilizes biological materials and activated carbon as adsorbents have been studied by several researchers as an alternative technique to conventional methods for heavy metal sequestration from wastewater [10]. Various functional groups on the surface of these adsorbents can bind heavy metals. The major advantages of adsorption technology are its effectiveness in reducing the concentration of heavy metal ions even at low concentrations of the metal and the use of cheap and readily available agricultural materials for activated carbon production.

To optimize the process variables for the adsorption process, the combined effect of initial metal ion concentration, adsorbent dose, pH and contact time, a central composite design in response surface methodology (RSM) using Design Expert Software Version 7.0.0 (Stat-Ease) is used. Thus, the main purposes of this study are to model and optimize the adsorption of cadmium using avocado seed activated carbon

(ASAC) by response surface methodology. Besides, isotherm and kinetic studies of the adsorption process will be studied.

Material and method

Sample Collection and Pretreatment

A collection of 20 fresh ripe avocados (*Persea Americana)* was bought from the Bamenda food market in the North-West Region of Cameroon. The avocados were all washed and the flesh removed to get the seeds. The seeds were cut into small pieces using a knife then washed thoroughly with distilled water and sundry for ten days. The dried samples were crushed into powder using a high power electric blender and screened through a set of sieves to obtain a particle size of 100 µm. The resulting powder was oven dried for 24 hours at 105 ^oC.

Preparation of Activated Carbon

500 g of raw avocado seed powder was impregnated using H_3PO_4 at a 1:1 (W:V) impregnation ratio. The impregnation was carried out at 105 ^oC in a hot air oven for 24h to achieve good penetration of the chemical into the interior of the precursor material. The impregnated sample was then dried at 105 ^oC in an oven for 12h. The dried impregnated sample was transferred into a porcelain crucible with lid. The crucible was placed inside an electric Muffle furnace and the sample carbonized at 400 ^oC for 1h, in the absence of air. The carbonized sample was then cooled to room temperature and washed with distilled water until the pH value of the rinsed water was neutral. The washed activated carbon was then dried in the oven at 105 ^oC for 5 hours. The sample was further pulverized and packed in cellulose paper packets for experimental work. The adsorbent prepared by H_3PO_4 was denoted as ASAC throughout this study.

Characterization of ASAC.

The Fourier Transform Infrared (FTIR) spectra of the ASAC was obtained using a Brüker alpha –p Spectrometer in the scanning range 4000–400 cm^{-1}. The other physicochemical properties of the adsorbent were reported in earlier investigations [11].

Preparation of Cd (II) Stock solution

All the chemicals and reagents used in this work were of analytical grade and were used without further purification. The Cd (II) ion stock solutions with a concentration of 1000 mg/L was prepared by dissolving 2.1930 g of $CdSO_4.8/3H_2O$ inside a 1L volumetric flask with freshly prepared distilled water. Solutions of various concentrations used in the adsorption studies were obtained by diluting portions of the stock solution with distilled water. A pH meter (WTM VARIO) was utilized for pH measurement and the pH of the solution was adjusted to the desired value by adding a small amount of 0.1 M HCl and 0.1 M NaOH.

Response Surface Methodology (RSM) and Experimental Design

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effect of several independent parameters on the response and fitting empirical models to the experimental data. The main objective of RSM is to determine the relationship between a set of experimental factors and observed results. RSM is essentially made up of three major steps: performing statistically designed experiments, estimating coefficients in a mathematical model and predicting the response and checking the adequacy of the model [12]. The RSM approach has extensively been applied in important process design and optimization, chemical engineering and as well as in adsorption process optimization [13].

In this study, a standard RSM design called the face-centered central composite design (CCD) which is appropriate for fitting second-degree polynomial equations was applied to study the factors for the removal of Cd^{2+} from aqueous solution. A CCD has three groups of design points [14].

a) Two-level factorial (2k), consisting of possible combinations of +1 and -1 levels of factors.
b) 2k axial points (sometimes called star points) fixed axially at a distance say α from the center to generate quadratic terms. The axial points make the design rotatable.
c) Center points which represent replicate terms. Center points provide a good and independent estimate of the experimental error and the reproducibility of the data.

By considering these points, the number of experiments designed using CCD will be

$$N = k^2 + 2k + n = \qquad (1)$$

Where N is the total number of experiments, k is the number of factors studied and n is the number of replicates. In CCD, the value for α which determine the location of the axial points is calculated as

$$\alpha = (2k)^{0.25} \qquad (2)$$

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The response (the removal efficiency of Cd^{2+} ion) was used to develop an empirical model which correlated the response to the studied factors, using a second-degree polynomial equation as given by equation 3.

$$Y(\%) = b_o + \sum_{i=1}^{n} b_i x_i + (\sum_{i=1}^{n} b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (3)$$

Where Y (%) is the predicted response (the removal efficiency), b_o the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i and x_j are the coded values of the factors studied.

For a design of four independent factors (k = 4), each with two different levels, the total number of experiments (N) was calculated using equation (1); $N = 4^2 + (2 \times 4) + 6 = 30$. After having specified the range of each of the process factors, they are coded to lie at ± 1 for the factorial points, 0 for the center points and ±α for the axial points. The chosen process factors with their limits, units, and notations are presented in Table 1.

Table 1: Process factors and their levels considered for the removal of Cd^{2+} ions.

Factors	Units	code	levels				
			-α	-1	0	+1	+α
Initial Concentration	mg/L	A	100	100	150	200	200
Adsorbent Dose	g	B	0.1	0.1	0.55	1	1
pH		C	3	3	5.5	8	8
Contact Time	min	D	10	10	95	180	180

Batch adsorption experiments

The batch experiments were carried out with variations of the four process factors including contact time (10-180 min), adsorbent dosage (0.1-1 g), pH (3-8), and initial metal ion concentration (100-200 mg/L) were analyzed using the central composite design (CCD). The 30 experimental runs with the various combinations of the different factors were randomly performed according to Table 2, by mechanical agitation at room temperature. A known mass of adsorbent was added to each, 100 mL solution of cadmium (II) ions of known pH and known initial metal ion concentration. After agitation, the solution was filtered using a What man No. 1 filter paper and the residual Cd^{2+} ions in the filtrate were analyzed by complexometric titration using standardized 0.1 M EDTA (Ethylenediaminetetraacetic acid) buffered at pH 5 using acetic acid/sodium acetate buffer with methyl blue used as an indicator [15]. Typically, 100 mL of each Cd^{2+} ion solution was pipetted into a 250-mL conical flask, 4mL of buffer solution and 2-3 drops of methyl blue were added, and the mixture was titrated with 0.1 M EDTA solution until the colour changed from blue to yellow. The amount of Cd^{2+} ions adsorbed at equilibrium (Qe) and the removal efficiency (Y%) were calculated using the following expressions:

$$Q_e = \frac{(C_o - C_e)\,V}{M} \tag{4}$$

$$Y(\%) = \frac{C_o \text{ - } C_e}{C_o} \text{ x } 100 \tag{5}$$

Table 2: Design matrix for the adsorption of cadmium by ASAC.

Run	Initial Concentration (mg/L) (A)	Adsorbent Doage (g) (B)	pH (C)	Contact Time (min) (D)	Removal Efficiency (%)
1	150	0.55	5.5	95	77.69
2	150	0.55	5.5	95	77.69
3	150	0.55	5.5	10	89.31
4	200	0.1	8	10	72.27
5	100	1	3	180	84.61
6	150	0.1	5.5	95	74.71
7	200	1	8	180	78
8	100	0.1	3	10	80.62
9	200	1	3	10	74.31
10	150	0.55	5.5	95	76.63
11	150	0.55	5.5	95	77.69
12	200	1	8	10	73.12
13	100	0.1	8	10	63.82
14	100	0.1	8	180	50.68
15	150	0.55	5.5	95	80.22
16	150	0.55	3	95	80.02
17	100	0.55	5.5	95	77.07
18	200	1	3	180	84.9
19	200	0.1	3	180	90.21
20	100	1	3	10	73.75
21	200	0.1	3	10	97.89
22	150	0.55	5.5	180	89.08
23	100	0.1	3	180	73.21
24	200	0.55	5.5	95	85.81
25	150	0.55	5.5	95	77.69
26	200	0.1	8	180	58.87
27	100	1	8	10	81.39
28	150	1	5.5	95	72.21
29	150	0.55	8	95	69.38
30	100	1	8	180	86.53

Adsorption Equilibrium and Kinetic Studies

Adsorption isotherm and kinetic models are usually employed to represent the interaction between the adsorbent and adsorbate at equilibrium and to establish the mechanism of the adsorption process. In order to find the most appropriate isotherm and kinetic model for the adsorption of cadmium, the results obtained were analyzed with the following isotherm models, Langmuir [16], Freundlich [17], Jovanovic [18], and Harkins-Jura isotherms [19]. While the kinetics of the adsorption process was analyzed with the pseudo-first order [20], pseudo-second order [21], intraparticle diffusion [22], and Boyd [23] models. For both equilibrium and kinetic studies, the adsorption experiments were performed at predetermined time intervals for analyzing the residual dye concentration using optimized conditions previously obtained from the CCD analysis. The equations for the kinetics and isotherm models employed in this study are presented in Table 3.

Table 3: Isotherms and Kinetics model equations for Cd^{2+} adsorption.

Model	**Linear equation**	**plot**	**Symbol representation**
Isotherm models			
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	C_e/q_e vs C_e	where q_e (mg/g) and q_m (mg/g) are the equilibrium and maximum adsorption capacity of DR81 dye, respectively, C_e (mg/L) is the concentration of DR81 dye at equilibrium, k_1 (L/mg) is the Langmuir constant.
Freundlich isotherm	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	Log q_e vs log C_e	Where K_F (L/g) and n are Freundlich isotherm constants which are related to the adsorption capacity and the adsorption intensity, respectively.
Jovanovic isotherm	$Inq_e = Inq_{max} - K_J C_e$	Inq_e vs C_e	Where K_J (L/g) is the Jovanovic constant. q_{max} (mg/g) is the maximum cadmium (II) uptake.
Harkins-Jura isotherm	$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e$	$1/q_e^2$ vs log C_e	Where A (g^2/L) and B (mg^2/L) are isotherm constants.
Kinetic models			
Pseudo-first order model	$\log(q_e - q_t) = \log q_e + \frac{k_1}{2.303}t$	Log (q_e-q_t) vs t	Where q_t is the adsorption capacity at time t (mg/g); k_1 is the rate constant of first-order (min^{-1}).
Pseudo-second order model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	t/q_t vs t	Where k_2 is the second-order adsorption rate constant (g/mg min).
Intraparticle diffusion model	$q_t = k_{id}t^{1/2} + I$	q_t vs $t^{1/2}$	Where K_{id} is the intraparticle diffusion rate constant (mg/g $min^{1/2}$) and I is the intercept.
Boyd model	$\ln\left[\frac{1}{1-F(t)}\right] = \frac{\pi^2 D_e t}{r^2}$	Ln [1/(1-F(t))] vs t	where $F(t) = q_t/q_e$ is the fractional attainment of equilibrium at time t, D_e is the effective diffusion coefficient of phenol in the adsorbent phase (cm^2/s), r is the radius of the adsorbent particles assume to be spherical

Results and Discussion

Characterization

Fourier transform infrared spectra analysis

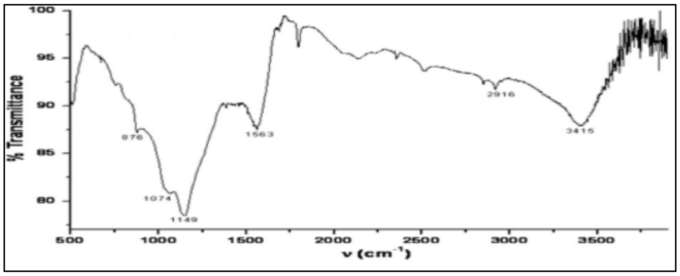

Fig 1: Fourier Transform Infrared spectrum of ASAC

The Fourier transform infrared spectrum of ASAC is given in Figure 1. it can be observed that the functional groups responsible for adsorption on the surface of the adsorbent are, a hydroxyl group at 3415 cm^{-1}, unsymmetrical aliphatic C–H stretching at 2916 cm^{-1} and C=C stretching of aromatic rings at 1563 cm^{-1}. The band at 1149 cm^{-1} on the surface of ASAC can be attributed to C–O stretching in alcohol or ether and the band at 876 cm^{-1} can be ascribed to symmetrical vibration in a chain of P-O-P and to P-C phosphorus-containing compound.

Physicochemical/Proximate Analysis

The physicochemical properties and proximate analysis of ASAC were reported in earlier investigations [11], and are summarized in Table 4.

Table 4: Physicochemical and proximate analysis of ASAC.

pH_{pzc}	**Proximate Analysis**				**Boehm titration (mmol/g)**				**Iodine number (m^2/g)**	**S_{BET} (m^2/g)**
	Moisture content	**Volatile matter**	**Ash content**	**Fixed carbon**	**Carboxylic**	**Lactonic**	**phenolic**	**Total basic**		
6.5	9.45	8.09	5.38	77.08	0.36	0.59	0.29	0.34	645	641.55

Development of model equation

The design matrix containing the studied factors, their ranges and the response which is the removal efficiency (%) of Cd (II) (Y_{Cd}) is presented in Table 2. The results obtained were then evaluated with CCD in RSM for the development of the model's regression equation. A quadratic second order polynomial expression as suggested by the software (Table 5) fitted the data suitably. The model equation was selected in conformity with the sequential model sum of the square that is based on the highest order polynomial where the additional terms of the model are significant and the model is not aliased [1, 24].

Both the regression coefficients (R^2) and adjusted R^2 are used to validate the quality of the proposed models; values closer to 1.0 confirm a good agreement between the predicted and experimental data [25]. Thus, the correlation between experimental and predicted response is evident as indicated by the model's R^2 and adjusted R^2 values of 0.9730 and 0.9477, which are within the desirability range. The final model's equation for the removal efficiency of Cd (II) (Y_{Cd}) is given by equation (6).

$$\text{Removal Efficiency} = 79.13 + 2.43A + 2.59B - 5.86C - 0.58D - 4.18AB - 2.20AC - 0.066AD + 6.11BC + 4.57BD - 1.43CD + 1.13A2 - 6.86B2 - 5.62C2 + 8.88D2 \qquad (6)$$

The cooperative and counter effects of the studied factors were elucidated by the negative and positive coefficients before the terms in the model equation. A negative coefficient value implies that the term negatively affects Cd (II) adsorption (i.e. the removal efficiency decreases), whereas a positive coefficient values mean that the term increase Cd (II) adsorption in the tested range [26].

Table 5: Model summary statistics.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	180867.04	1	180867.04	-	-	
Linear vs Mean	850.30	4	212.58	3.05	0.0353	
2FI vs Linear	1321.26	6	220.21	9.99	< 0.0001	
Quadratic vs 2FI	348.87	4	87.22	18.67	< 0.0001	Suggested
Cubic vs Quadratic	42.72	8	5.34	1.37	0.3466	Aliased
Residual	27.34	7	3.91			
Total	183457.54	30	6115.25			

Statistical analysis

The fitness of the model was investigated using the analysis of variance (ANOVA) at 95% confidence interval. The ANOVA of Cd (II) removal efficiency is presented in Table 6. The significance and insignificance of each term in the model were determined by the Fisher's F-test and P-value. A term is significant if the F-value is large and the P-value is less than 0.05. The F-value for a model or term is the ratio of mean square for the individual term to the mean square for the residual [26]. Based on the P-values presented in Table 6, the significant model terms were A, B, C, AB, AC, BC, BD, CD, B^2, C^2, and D^2 with D, AD, and A^2 insignificant to the response. In order to simplify the model, the insignificant terms (D, AB, A^2) can be eliminated.

The lack of fits test was further used to justify the model's adequacy. The lack of fit F-value of 4.39 with $P > 0.05$ suggests that the lack of fit was not significant. A non-significant lack of fit is considered good and is desired for the model to fit.

Adequate precision (AP) is basically a measure of signal to noise ratio. Ratios greater than 4 indicate that the model is adequate and can be used to navigate the design space [27]. In this study, the AP ratio of 31.04 indicates an adequate signal and thus the model can be used to predict the response.

The coefficient of variation (CV) is the ratio of the standard deviation of the mean expressed as a percentage. For a model to be considered reliable and reproducible it must have a CV less than 10% [28]. In this investigation, the CV value of 2.78% reflects a good precision and reliability of the experiments.

Table 6: Analysis of variance (ANOVA) and test of significance for cadmium uptake by ASAC.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2520.44	14	180.03	38.55	< 0.0001	significant
A-Initial Concentration	106.09	1	106.09	22.71	0.0003	
B-Adsorbent Dose	120.33	1	120.33	25.76	0.0001	
C-pH	617.88	1	617.88	132.28	< 0.0001	
D-Contact time	6.00	1	6.00	1.28	0.2750	
AB	279.39	1	279.39	59.81	< 0.0001	
AC	77.79	1	77.79	16.65	0.0010	
AD	0.07	1	0.07	0.02	0.9040	
BC	597.31	1	597.31	127.87	< 0.0001	
BD	333.98	1	333.98	71.50	< 0.0001	
CD	32.72	1	32.72	7.00	0.0183	
A^2	3.28	1	3.28	0.70	0.4153	
B^2	121.75	1	121.75	26.06	0.0001	
C^2	81.69	1	81.69	17.49	0.0008	
D^2	204.30	1	204.30	43.74	< 0.0001	
Residual	70.07	15	4.67			
Lack of Fit	62.90	10	6.29	4.39	0.0581	not significant
Std. Dev.	2.16		R-Squared		0.9730	
Mean	77.65		Adj R-Squared		0.9477	
C.V. %	2.78		Pred R-Squared		0.9038	
PRESS	249.13		Adeq Precision		31.04	

Effects of individual variables and their interactions

It can be inferred from Table 6 that the individual effects of factors (initial concentration, adsorbent dose, and pH) on cadmium uptake by ASAC were more dominant than the effect of contact time, based on their high F-values of 22.71 (initial concentration), 25.76 (adsorbent dose), 132.28 (pH), and 1.28 (contact time). The two factor interaction effects of initial concentration and adsorbent dose (F-value of 59.81), initial concentration and pH (16.65), adsorbent dose and pH (127.87) and adsorbent dose and contact time (71.50) are more pronounced than the interaction effects of initial concentration and contact time (0.02) and pH and contact time (7.00). The quadratic effects of adsorbent dosage (F-value of 26.06), pH (17.49) and contact time (43.74) were most noticeable than the quadratic effect of initial concentration (0.70). From these results, it can be concluded that the adsorption of cadmium from aqueous solution by avocado seed activated carbon is highly dependent on pH and the combined effects of the mass of adsorbent and pH, due to their very high F-values. Figure 2 depicts the three-dimensional response surfaces of the interaction effects of the process variables on the adsorption of cadmium. From the plots in Figure 2, it can be noticed that an increase in the removal efficiency of Cd (II) by ASAC can be observed with increase in initial concentration, the mass of adsorbent and increase in pH to a maximum of about 6. The interaction effect of adsorbent dose and pH can be observed to show a lopsided effect on cadmium removal efficiency.

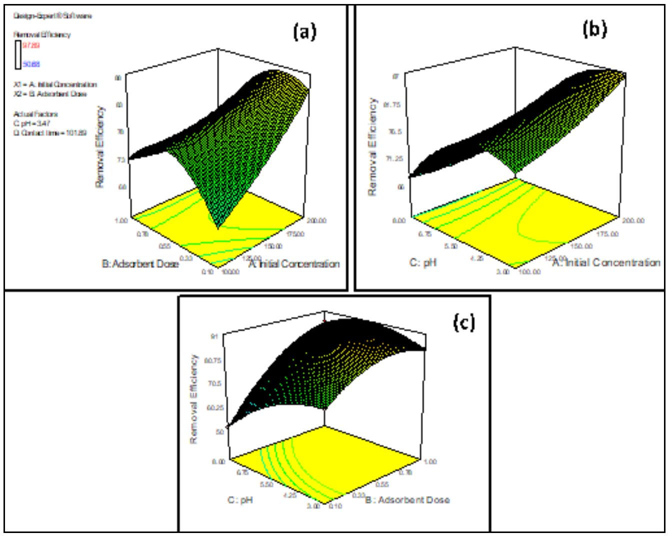

Fig 2: 3D response surface plots of interaction effects of the adsorption of cadmium by ASAC: (a) initial concentration and adsorbent dose, (b) initial concentration and pH and (c) adsorbent dose and pH.

Process optimisation/validation

The numerical optimisation of Cd (II) adsorption onto ASAC was done using the desirability function in design expert software, were the desired goals and weights for each factor and the response was chosen. The target criterion in the optimisation analysis was set as a maximum for the response and initial concentration of Cd^{2+} ions in solution, minimum for adsorbent dosage and contact time and within the range of pH. The optimum conditions for adsorption obtained were initial concentration of 200 mg/L, the adsorbent dosage of 0.10 g, pH of 3.37 and contact time of 100 min. At this condition, cadmium removal by ASAC predicted using the model was 98.28% and a desirability of 1.0. These optimum conditions were verified experimentally which resulted in a 98.03% removal efficiency of cadmium by ASAC. The result obtained portray a good agreement between the experimental value and that predicted by the model.

Adsorption Isotherm Studies

Adsorption isotherms are useful in determining the nature of the interaction between the adsorbate and the adsorbent. In order to determine the most befitting isotherm model for the sorption of Cadmium, the equilibrium data obtained using optimized values for the studied parameters were fitted to the Langmuir, Freundlich, Jovanovic, and Harkins-Jura isotherm models. From the plots in Figure 3 and the results of the isotherm parameters listed in Table 7, it is evident that the Jovanovic isotherm model (Figure 3c) which is essentially the same as the Langmuir model appeared to be much more relevant in fitting the experimental data than the other models studied. Since it has the highest coefficient of determination for the concentration range studied. The fitness of the Jovanovic model implies that the adsorption of Cd^{2+} ions from bulk solution formed a monolayer at specific homogeneous sites within the adsorbent, with monolayer adsorption capacities of 37.60 mg/g, 40.86 mg/g, 47.61 mg/g, 52.22 mg/g, and 58.87 mg/g for 100 mg/L, 125 mg/L, 150 mg/L, 175 mg/L, and 200 mg/L Cd^{2+} ion concentration respectively. As can be observed from Table 7, all the R_L (dimensionless separation factor) values from the Langmuir plot lie between 0 and 1 indicating the adsorption process is favourable understudied conditions. The n values gotten from the Freundlich plot were observed to be greater than unity for the studied concentration range, further suggesting favourable adsorption conditions.

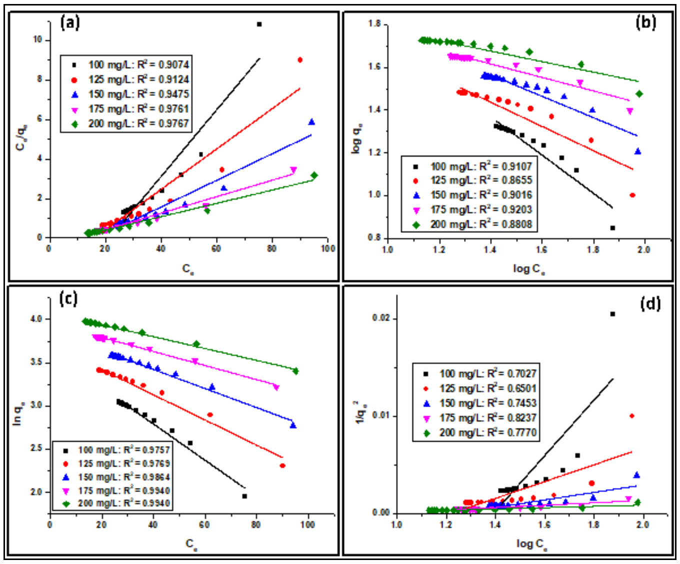

Fig 3: (a) Langmuir, (b) Freundlich, (c) Jovanovic and (d) Harkins-Jura adsorption isotherm plots for the sorption of cadmium onto ASAC.

Table 7: Adsorption isotherm parameters for the different models studied.

Models	Parameters	Concentration (mg/L)				
		100	125	150	175	200
Langmuir	q_{max} (mg/g)	5.91	9.76	14.79	23.92	29.50
	K_l (L/mg)	0.0465	0.0632	0.0601	0.1034	0.1257
	R_L	0.1770	0.1124	0.0999	0.0524	0.0383
	R^2	0.9074	0.9124	0.9475	0.9761	0.9767
Freundlich	n	1.1207	1.7671	2.0096	3.1776	4.0733
	K_f	414.095	169.395	182.138	113.815	104.544
	R^2	0.9107	0.8655	0.9016	0.9203	0.8808
Jovanovic	q_{max} (mg/g)	37.60	40.86	47.61	52.22	58.87
	K_j	0.0209	0.0146	0.011	0.0081	0.0069
	R^2	0.9757	0.9769	0.9864	0.9940	0.9940
Harkins-Jura	A_h	35.211	116.279	256.410	833.333	1428.571
	B_h	1.3908	1.2209	1.2051	0.9167	0.7143
	R^2	0.7027	0.6501	0.7453	0.8237	0.7770

Adsorption Kinetic Studies

In this study, the pseudo-first-order, pseudo-second order, intraparticle diffusion and Boyd kinetic models were examined to explore the rate and the controlling mechanism of adsorption of Cd^{2+} on ASAC. The linear plots obtained for the different kinetic models is presented in Figure 4 and all the kinetic parameters and coefficients of determination values obtained are summarized in Table 8. It can be inferred from the results that the adsorption of Cd^{2+} onto avocado seed activated carbon followed the pseudo-second-order kinetic model since the plot exhibit excellent linearity with high coefficients of determination ($R^2 > 0.99$) for all the studied concentrations in comparison to the pseudo-first-order model. In addition, the theoretical q_e values obtained from the pseudo-second-order model are in perfect agreement with the experimental q_e values. The mechanism of the adsorption process was assessed using the intraparticle diffusion and Boyd models. From the intraparticle diffusion plot (Figure 4c), it can be noticed that the plots showed two linear portions suggesting that two mechanisms are simultaneously occurring during the adsorption process and this deviation might be due to the difference in the mass transfer rate in the initial and final stage of adsorption [29]. The kinetic data were further analyzed with Boyd's model (Figure 4d) to affirm the actual adsorption mechanism of cadmium onto ASAC. It can be observed from the plots that the linear plots do not pass through the origin, this is indicative that the adsorption process is controlled by both intraparticle diffusion and film diffusion. From Table 8, values of the effective diffusion coefficient (D_i) which lie in the range (10^{-6} to 10^{-8} cm^2/s) provide a confirmation that film diffusion predominates over intraparticle diffusion in the uptake of cadmium from aqueous solution by ASAC. Similar results were reported by [11, 30].

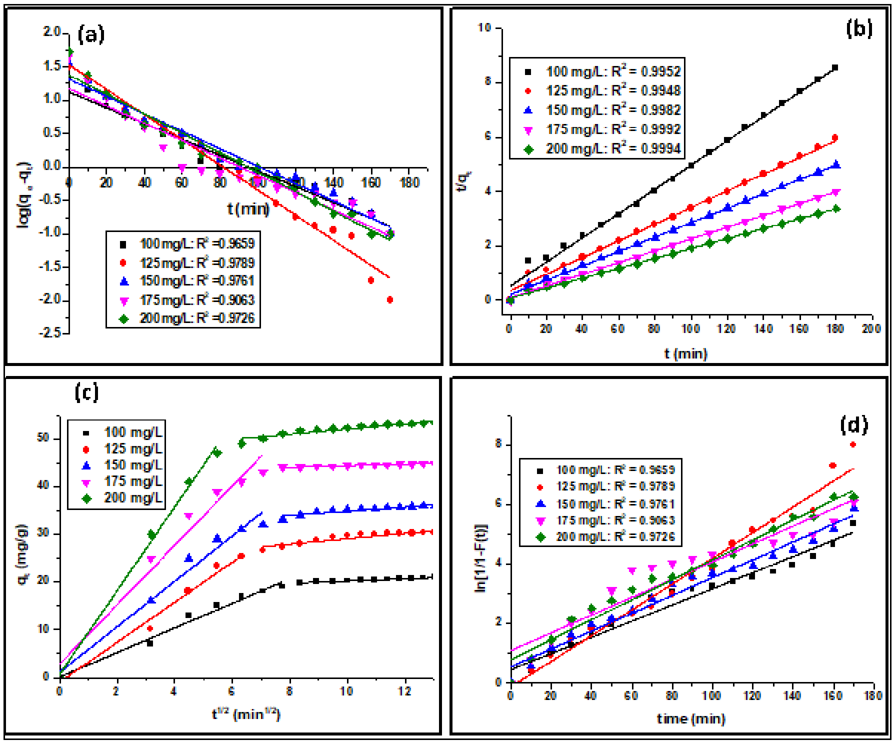

Fig 4: (a) Pseudo first order (b) Pseudo second order (c) Intraparticle diffusion (d) Boyd model

Table 8: Summary of parameters for kinetic models.

Kinetic Models	Parameters		Concentration (mg/L)				
			100	**125**	**150**	**175**	**200**
	$q_{e, exp}$ (mg/g)		21	30.28	36.1	45	53.3
Pseudo-first order model	$q_{e, cal}$ (mg/g)		13.33	34.40	20.78	15.0	24.01
	K_1 (1/min)		0.0272	0.0433	0.0299	0.0299	0.0336
	R_1^2		0.9659	0.9789	0.9761	0.9063	0.9726
Pseudo-second order model	$q_{e, cal}$ (mg/g)		22.37	32.57	37.74	46.08	54.64
	K_2 (mg/g.min)		0.00384	0.00268	0.00333	0.00491	0.00393
	R_2^2		0.9952	0.9948	.09982	0.9992	0.9994
Intraparticle diffusion model	First line segment	K_{id} (mg/g.min)	2.569	4.1818	4.7424	6.2026	8.7457
		I	0.1431	0.9158	1.2154	2.9309	0.8325
		R^2	0.9801	0.9817	0.9750	0.9651	0.9946
	Second line segment	K_{id} (mg/g.min)	0.2277	0.5570	0.4396	0.1683	0.5376
		I	17.9208	23.4839	30.4693	42.7037	46.6289
		R^2	0.9972	0.8286	0.8339	0.9900	0.8785
Boyd model	B(slope)		0.0272	0.0433	0.03	0.0299	0.0335
	Intercept		0.4543	0.1276	0.5519	1.0987	0.7972
	D_i (cm^2/s)		6.89 x 10^{-8}	1.10 x 10^{-7}	7.60 x 10^{-8}	7.57 x 10^{-8}	8.49 x 10^{-8}
	R^2		0.9659	0.9789	0.9761	0.9063	0.9726

Comparison of avocado seed activated carbon (ASAC) with other adsorbents

A comparative study of the maximum cadmium adsorption capacity of ASAC has been done with other adsorbents reported in the literature and are presented in Table 9. From the values in Table 9, it can be observed that the maximum adsorption capacity of avocado seed activated carbon for cadmium is comparable and reasonably higher than that of many corresponding adsorbent materials. The low cost and ready availability of ASAC are some extra advantages, which make avocado seed activated carbon a better adsorbent for the uptake of cadmium from aqueous solution.

Table 9: Comparison of Cd^{2+} ion adsorption capacity onto ASAC with other adsorbents.

Adsorbent	Concentration (mg/L)	q_e(mg/g)	references
ASAC	100	37.6	This work
	125	40.86	
	150	47.61	
	175	52.22	
	200	58.87	
Rhizopus arrhizus		26.8	[31]
Calocybe indica		24.09	[32]
Agaricus bisporus		29.67	[32]
Amanita rubescens		27.3	[33]
Phanerochaeta chrysosporium		23.0	[34]
Mucor rouxii (NaOH treated)		20.3	[35]
Mucor heimalis		85.47	[36]

Conclusion

In this study, avocado seed activated carbon was tried and assessed as a potential adsorbent for the abstraction of cadmium from aqueous solution using batch adsorption method. During the adsorption process, four factors (initial concentration, adsorbent dosage, pH and contact time) were optimized with the help of CCD with the removal efficiency (%) of cadmium as the analyzed response. Based on the results of the analysis, the removal efficiency of Cd (II) by ASAC increased with increase in initial concentration, adsorbent dose, and pH up to a certain level while contact time had little significance on the sorption process. The highest removal efficiency of Cd (II) was obtained at the optimum conditions of initial concentration of 200 mg/L, the adsorbent dosage of 0.10 g, pH of 3.37 and contact time of 100 min with a desirability of 1.0. Equilibrium data analysis showed the Jovanovic isotherm model to be the best-fitted model. The pseudo-second-order kinetic model was the most appropriate model that described the adsorption process and both intraparticle diffusion and liquid film diffusion mechanisms were both involved in the adsorption of cadmium onto avocado seed activated carbon. Finally, the reported results in this study portrayed the feasibility of utilizing the central composite design model to optimize the experiments for cadmium removal by adsorption using avocado seed activated carbon as a low-cost adsorbent.

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