
Response Surface Methodology Approach to Optimization of Uptake Capacity of Metal Ions from Ternary Aqueous Solution with Activated Carbon from *Acacia senegal* (L.) Willd Pods

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ABSTRACT

H₃PO₄ was used to prepare activated carbon from Acacia senegal pods. The prepared carbon was used to adsorb ions of Cd, Cr and Pb from a ternary solution. Design of Experiment was carried out using Central Composite Design (CCD) and adsorption experiment was carried out as arranged in a design matrix obtained from Design Expert software. The factors considered were, pH, adsorbent dose, contact time and initial concentration of Cd, Pb and Cr. Uptake capacities of respective metal ions were taken as the response of the design. The optimum factor levels which were responsible for uptake capacities 87.82mg/g, 79.44mg/g and 73.66mg/g for Cd, Cr and Pb respectively predicted by the model were 144.25mg/L, 135.02mg/L, 132.46mg/L, 6.5, 0.01g and 10min as initial concentrations of Cd, Cr, Pb, pH, dosage and contact time respectively. A model was predicted for the experiment and it was further validated with coefficient of determination (R^2) = 0.8989, 0.8869 and 0.859 for uptake of Cd, Pb and Cr respectively. Revealing that the predicted values agree reasonably with the experimental values. Activated carbon from Acacia senegal pods has demonstrated to be effective in metal ions adsorption from aqueous solution.

Keywords: *Acacia senegal*; Ternary; CCD; uptake capacity

INTRODUCTION

“Water is Life” as the saying goes, it has various uses from domestic to industrial aspect of human endeavors, and it is also a very critical component needed for day to day activities of all living things (USGS, 2018). The quality of fresh water is under continuous stress due to anthropogenic activities (WHO, 2018). The resultant effects of heavy metal pollution can never be over emphasized. Some heavy metals have been reported to have carcinogenic and teratogenic effects on mammals, exposure to some of them can also cause neurological damages as well as cardiovascular disorder (Janus and Krajnc, 1990; Cadmium^a, 2018; Lead, 2018).

Conventional methods for removal of heavy metal ions from water include, electro-floatation, reverse osmosis, ion exchange, adsorption on activated carbon and so on (Lofrano *et al.*, 2012). Green chemistry which is an emerging concept encourages minimization of biological or chemical sludge, possibility of metal recovery, regeneration of adsorbent, all can be achieved by adsorption of heavy metals from wastewater by activated carbon (Lofrano *et al.*, 2012).

Optimization is the discipline of changing a procedure so as to get the best combination of factor settings of some interested set of factors to give a maximum response or goal without exceeding set

constraint (David, 2000). The main objective of optimization is to cut or eliminate time and resource wastage, costs, bottlenecks, and mistakes while achieving the procedure goal (*Process optimization*, 2018).

Response surface methodologies (RSM) are multivariate techniques where response functions are used to fit domain of experiment studied in the theoretical design (Myers, 1971; Box *et al.*, 1987). The major aim of this method is to change all significant variables at a time and then fit the experimental data to a predicted mathematical model (Krowiak *et al.*, 2014). Thus, the number of experiments in RSM is less than the conventional methods. Central Composite Design (CCD) is a branch of RSM, it composes a 2^k factorial design, which provides data for estimating the first-order effects of each variable and interactions between the variables, and a “star” design comprising of $2k + 1$ points, which provides data for approximating second-order effect (David, 2000). Where k is the number of factors considered during the course of the experiment.

MATERIALS AND METHODS

Materials

The following reagents were used during the course of this research work; they were used as purchased without further purification; $\text{Pb}(\text{NO}_3)_2$ 99% purity (by KIMIE laboratories, Mumbai India), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 98% purity, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 98% purity, H_3PO_4 , 99% purity (by British Drug House (BDH), England), distilled water (from Chemistry department of Ahmadu Bello University, Zaria), Nitrogen gas 97% purity (from BOC gas ltd, Kaduna).

Acacia senegal pods were sourced from Ahmadu Bello University Botanical garden and environs.

Preparation of Activated Carbon

The pods were sun-dried for six days to dehydrate it completely. Size reduction was carried out on the dried sample using mortar and pestle. The precursor was impregnated with 85% w/v H_3PO_4 , with impregnation ratio of 1:1. The resulting mixture was kept in an oven at 85°C for 24 hours, after which it was loaded into a tube furnace. Heating was carried out at 600°C for 2 hours in a nitrogen atmosphere. The nitrogen was passed through furnace at rate of 150mL/min from the time heating started till furnace cooled down. The AC was washed with distilled water until pH was attained, dried, crushed, sieved with a 0.25mm mesh and stored in an air tight container for further characterization and experiments. (Garba *et al.*, 2014, Abdulrazak *et al.*, 2017).

The expression for calculating impregnation ratio is shown below:

$$I_1 \quad r = \frac{D}{D} \frac{w}{w} \frac{h_0}{h_0} \frac{H_3P_4}{p} \quad (1)$$

Preparation of metal stock solutions

Stock solutions of 1000mg/L of Cadmium, Chromium and Lead were prepared by dissolving 2.7543g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 5.7308g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.5985g of $\text{Pb}(\text{NO}_3)_2$ into separate 1L distilled-deionised water.

Design of Experiment using RSM

Design-Expert software version 11.0.3 (Stat-Ease, Inc., Minneapolis, MN 55413, USA) was used to carry out the design of experiment. In the design process, six factors were considered viz;

Initial concentrations of Cadmium, Lead, Chromium, pH, adsorbent dosage and shaking time. Three responses were noted as the objectives of the design, these; uptake capacities of Cadmium, Lead and Chromium. The factors employed in the design are shown in table 1 below.

Table 1: Factors and their corresponding levels (un-coded and coded)

Coded level	Initial Cr(mg/L)	Initial Cd(mg/L)	Initial Pb(mg/L)	pH	Adsorbent dose(g)	Contact time(min)
	A	B	C	D	E	F
-1	56	56	56	4	0.15	8
+1	149	149	149	8	0.4	20
0	102.5	102.5	102.5	6	0.275	14
- α	29.7	29.7	29.7	2.9	0.08	4.6
+ α	175.3	175.3	175.3	9.1	0.47	23.4

The various stock solutions were diluted appropriately to get the working solution; these solutions were mixed as shown in the design matrix and made up to 50mL using distilled water. The pH of the metals solutions were adjusted to the required value using 0.01M HCl or 0.01M NaOH, the needed mass of the AC was added to the solutions after which the mixture is loaded on a mechanical shaker and shaken for the required time at constant speed of 250rpm and room temperature of 27°C (Garba *et al.*, 2016). After shaking, the mixture was then filtered with a filter paper and the residual concentrations of the metals in the mixture were determined using a Flame Atomic Absorption Spectrophotometer.

The uptake capacity, q of individual metal was calculated using the expression below:

$$q_t, (m/g) = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where: C_0 = Initial concentration

C_t = Concentration after shaking for time, t

V = Volume of solution

W = mass of adsorbent

A quadratic model in form of expression below was developed for the adsorption of the metal as it was influenced by the parameters considered during the experiments;

$$Y = b_0 + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^n b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j + \epsilon \quad (3)$$

Where: Y = Predicted response, b_0 = Constant coefficient, b_i = Linear coefficient, b_{ii} = Quadratic coefficient, b_{ij} = Interaction coefficient, x_i & x_j = Factors considered and ϵ = Random error

Coefficient of Determination (R^2) was used to determine the quality of the model as it compared the data from predicted model with data gotten from experimental runs (Anilkumar *et al.*, 2016).

RESULTS AND DISCUSSION

Model and Statistics

Table 2 below showed the design matrix consisting of each factor combination and their respective response, uptake of Cd was found to be in range of 4.53 to 60.96mg/g, Cr was 4.07 to 53.4 and Pb was 4.97 to 55.44mg/g. The models (in actual form) for respective metal ion uptake are

presented in equations 4, 5 and 6, with positive term indicating the term affecting uptake positively while negative term points to the uptake been affected negatively by the term in the model equations.

Results of the significance of the model are displayed in table 3, the p-value of all the models are less than 0.05 indicating that they are significant. These were further confirmed by the high R^2 of the model (*Design expert, 2018*). The first six solutions of the optimum variables predicted by the software for maximum uptake of the three metals were presented in table 4 below. These were further validated by comparing experimental results to the predicted results. Strong coefficients of determination (R^2) ranging from 0.859 to 0.8989 as shown in table 5 were obtained, signifying less variation between the predicted and actual values (*Design expert, 2018*).

Table 6 showed some previous works reported in literatures and how the present study compared to them favorably by having total uptake of 240.92mg/g for all the three metals combined in an aqueous solution.

Table 2: Experimental runs with coded variables and responses

Run	A	B	C	D	E	F	Cd uptake (mg/g)	Cr uptake (mg/g)	Pb uptake (mg/g)	Total uptake (mg/g)
1	- α	0	0	0	0	0	4.53	17.42	18.02	39.97
2	1	-1	-1	1	-1	-1	48.16	18.44	18.50	85.10
3	0	0	- α	0	0	0	17.44	16.04	4.97	38.45
4	0	0	0	0	- α	0	60.96	53.40	55.44	169.80
5	0	0	0	0	0	0	17.15	15.67	17.95	50.77
6	1	1	-1	-1	-1	-1	47.03	41.35	8.67	97.04
7	0	0	0	0	0	0	17.40	15.79	18.22	51.42
8	1	1	-1	1	1	-1	18.61	18.59	6.99	44.20
9	-1	1	1	-1	1	-1	6.23	14.70	13.25	34.18
10	1	-1	1	-1	1	-1	17.69	4.78	14.21	36.68
11	-1	1	-1	-1	1	1	6.23	15.01	5.01	26.25
12	α	0	0	0	0	0	30.48	15.62	17.96	64.05
13	-1	1	-1	1	-1	-1	18.60	49.59	18.49	86.67
14	0	0	0	0	0	0	17.33	15.73	17.59	50.65
15	-1	-1	-1	-1	1	-1	6.25	5.55	5.12	16.93
16	-1	1	1	-1	-1	1	16.58	41.21	28.88	86.67
17	0	0	0	0	0	α	17.43	15.72	17.91	51.06
18	0	0	0	0	0	- α	17.40	15.65	17.84	50.90
19	0	0	0	0	0	0	17.61	15.64	18.16	51.41
20	0	- α	0	0	0	0	17.45	4.07	18.50	40.01
21	0	0	0	α	0	0	18.64	18.64	18.55	55.82
22	0	0	0	- α	0	0	17.38	14.27	10.38	42.03
23	-1	-1	-1	1	1	1	7.00	7.00	6.91	20.91

Run	A	B	C	D	E	F	Cd uptake (mg/g)	Cr uptake (mg/g)	Pb uptake (mg/g)	Total uptake (mg/g)
24	-1	1	1	1	1	1	7.00	18.63	18.44	44.06
25	1	1	-1	1	-1	1	48.81	49.67	18.61	117.09
26	-1	-1	1	1	-1	1	18.25	18.67	49.54	86.46
27	1	1	1	-1	1	1	17.73	15.65	15.47	48.84
28	1	-1	1	-1	-1	1	47.17	13.47	35.81	96.45
29	-1	-1	1	1	1	-1	7.00	7.00	18.60	32.60
30	0	0	α	0	0	0	17.44	14.71	30.65	62.81
31	0	0	0	0	α	0	10.24	9.13	10.77	30.14
32	0	α	0	0	0	0	17.43	26.32	18.13	61.87
33	0	0	0	0	0	0	16.96	14.72	18.14	49.82
34	-1	-1	-1	-1	-1	1	16.64	13.75	9.57	39.96
35	1	-1	-1	-1	1	1	17.72	5.13	5.71	28.55
36	1	-1	1	1	1	1	18.38	7.00	18.61	43.99
37	1	1	-1	1	-1	-1	49.56	49.67	18.66	117.88
38	1	1	1	1	-1	-1	48.98	49.67	49.51	148.16
39	0	0	0	0	0	0	17.52	15.72	18.13	51.37
40	-1	-1	1	-1	-1	-1	16.66	14.93	38.68	70.28

Table 3: Model significance table

Response	Source	Sum of Squares	Df	Mean Square	F-value	p-value	Verdict
Cd removal Model		7862.53	4	1965.63	329.20	< 0.0001	Significant
	A-Initial Cd	2720.07	1	2720.07	455.55	< 0.0001	R ² =0.9796
	E-Dosage	3457.44	1	3457.44	579.04	< 0.0001	
	AE	508.05	1	508.05	85.09	< 0.0001	
	E ²	642.50	1	642.50	107.60	< 0.0001	
	Residual		208.98	35	5.97		
Cr removal Model		7408.64	5	1481.73	322.02	< 0.0001	Significant
	B-Initial Cr	2435.82	1	2435.82	529.37	< 0.0001	R ² =0.9847
	D-pH	111.22	1	111.22	24.17	< 0.0001	
	E-Dosage	3038.22	1	3038.22	660.29	< 0.0001	
	BE	478.39	1	478.39	103.97	< 0.0001	
	E ²	575.44	1	575.44	125.06	< 0.0001	
Residual		156.45	34	4.60			
Pb removal Model		5171.38	6	861.90	72.50	< 0.0001	Significant
	C-Initial Pb	2194.68	1	2194.68	184.61	< 0.0001	R ² =0.9727

Response	Source	Sum of Squares	Df	Mean Square	F-value	p-value	Verdict
	D-pH	305.19	1	305.19	25.67	< 0.0001	
	E-Dosage	2258.95	1	2258.95	190.01	< 0.0001	
	CE	399.75	1	399.75	33.62	< 0.0001	
	D ²	99.00	1	99.00	8.33	0.0068	
	E ²	379.07	1	379.07	31.89	< 0.0001	
	Residual	392.32	33	11.89			

$$C_u \quad (m/g) = +27.09666 + 0.444874A - 229.78146E - 0.829152A + 406.94443E^2 \quad (4)$$

$$C_u \quad (m/g) = +17.88569 + 0.430086B + 1.03633D - 213.66239E - 0.815875BE + 385.12882E^2 \quad (5)$$

$$P_u \quad (m/g) = -28.89674 + 0.416523C + 12.02479D - 117.43715E - 0.779127C - 8.60059D - 0.659779D^2 + 318.25644E^2 \quad (6)$$

Table 4: Optimization solutions

Solution	Initial Cd (mg/L)	Initial Cr(mg/L)	Initial Pb(mg/L)	pH	Dosage (g)	Time (min)	Cd uptake (mg/g)	Cr uptake (mg/g)	Pb uptake (mg/g)	Desirability
1	89.07	121.30	83.48	7.95	0.010	17.95	63.73	75.20	57.29	1.00
2	144.25	135.02	132.46	6.5	0.010	10.06	87.82	79.44	73.66	1.00
3	103.68	81.02	96.08	6.6	0.010	16.80	70.10	56.84	59.37	1.00
4	113.64	75.71	82.10	7.9	0.010	8.43	74.45	55.87	56.58	1.00
5	84.27	91.87	148.03	6.2	0.010	8.00	61.63	61.01	79.26	1.00
6	86.21	133.80	138.77	7.1	0.010	19.22	62.48	79.63	78.27	1.00

Table 5: Validation results

Solution	Cd uptake (mg/g)		Cr uptake (mg/g)		Pb uptake (mg/g)	
	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	62.05	63.73	75.5	75.20	59.43	57.29
2	88	87.82	77.57	79.44	68.5	73.66
3	63.55	70.10	60.11	56.84	51.55	59.37
4	68	74.45	48.76	55.87	57.76	56.58
5	46.5	61.63	62.3	61.01	79.44	79.26
6	46	62.48	75.02	79.63	73.34	78.27
R²	0.8989		0.8869		0.859	

Table 6: Previous literatures on adsorption uptake capacities

Adsorbent	Adsorbate	Q _{max} (mg/g)	References
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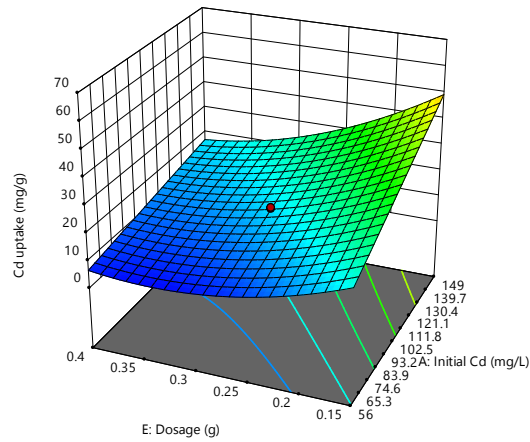


Fig 3 Interactive effects of dosage and initial concentration of Cd on Cd uptake

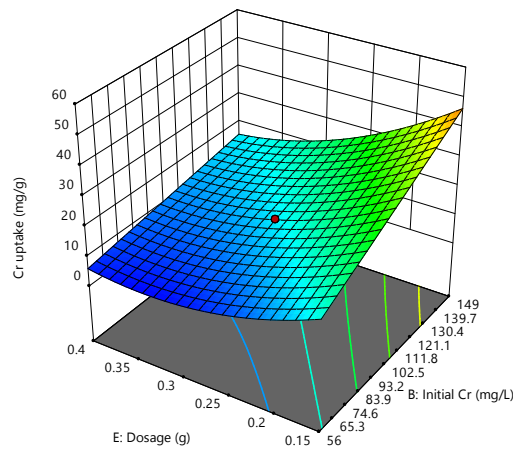


Fig 4 Interactive effects of dosage and initial concentration of Cr on Cr uptake

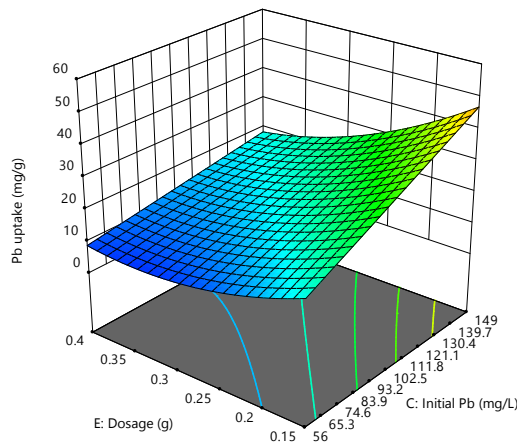


Fig 5 Interactive effects of dosage and initial concentration of Pb on Pb uptake

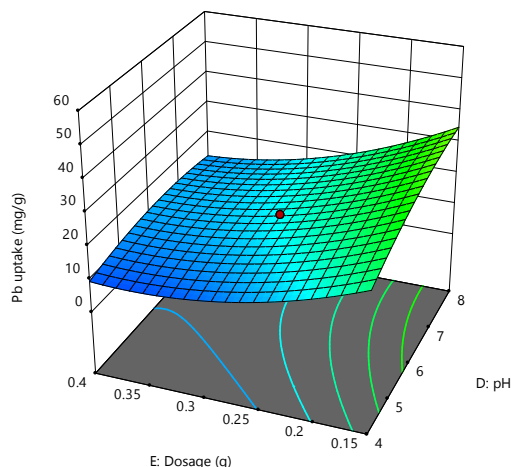


Fig 6 Interactive effects of dosage and pH on Pb uptake

CONCLUSION

The activated carbon prepared from *Acacia senegal* has demonstrated high effectiveness in adsorption Cd, Cr and Pb, so it can be employed in water treatment processes. Optimization of application of the activated carbon was also successfully executed, resulting to using the minimum amount of the carbon for maximum uptake of the metal ions.

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