



OPTIMIZATION OF THE CONDITIONS FOR ADSORPTION OF FLUORIDE IN AQUEOUS SOLUTION BY CARROT RESIDUE USING CENTRAL COMPOSITE DESIGN OF EXPERIMENT

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ABSTRACT

This study employs the use of carrot residue (CR) treated with dilute hydrochloric acid to remove fluoride ions in aqueous solution. The adsorption process parameters of pH, time of contact, adsorbent mass and initial ion concentration were optimized at ambient temperature by the use of central composite design of experiment. The CR adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Quadratic model was used to correlate the variables to the responses obtained from the design matrix in the laboratory and analysis of variance was used to test the significance of the independent variables and their interactions. Predicted values of % adsorption at optimum conditions for commercial activated carbon (AC) which served as control and CR were validated. From the results obtained, the optimum adsorption conditions were pH 5, time of contact 96 min, mass of adsorbent 1g and initial ion concentration of 10mg/L with desirability of 1. The design predicted values and experimental values obtained for AC were 85.63% and 87.59%, while those of CR were 87.67±0.02% and 90.25±0.02% respectively. From the results obtained, it was concluded that CR was as effective and a better adsorbent for removal of fluoride ions in aqueous solution than AC. Therefore, CR is a potential alternative to AC for fluoride adsorption in aqueous solution.

Keywords: Carrot Residue: Adsorption: fluoride: central composite design

INTRODUCTION

Water is essential for the survival of live on the earth. The increase in population and rapid industrial growth leads to high demands of fresh water to meet various needs especially for drinking and other domestic uses. More than 80% of Nigerians depend on groundwater for drinking and other domestic purposes (Tikki, 2014). Hence, there is the need to protect all sources of water from contamination. The consumption of contaminated water can impart severely on human health, resulting in portable water contamination related diseases. Fluoride is considered a toxic and harmful contaminant when present in drinking water at concentration greater than 1.5mg/l (Goswami, 2013; WHO, 2011). Fluoride has dual significance; it helps in the normal mineralization of bones and formation of dental enamel, when consumed in portable water in the concentration range of 0.5-1.5mg/l (SON, 2007). Concentrations below 0.5mg/l in drinking water will result in fluoride deficiency and can cause lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children (Vaish and

Vaish, 2000). Where fluoride is lacking in portable water fluoridation is required and if the concentration is above the required limit, excess fluoride must be removed.

Various treatment techniques such as ion exchange, chemical coagulation-precipitation process, electro coagulation, membrane processes, solar method adsorption has been reported to be used for removal of fluoride from water (Nemade *et al.*, 2002). Adsorption has been universally accepted as one of the most effective process for ion specie removal. For fluoride removal, adsorption techniques have more advantages because of their greater accessibility; do not require complicated hardware, inexpensive and capable of removing fluoride from water up to maximum extent (Gogoi and Baruah, 2008).

Central composite design (CCD) is used to study the individual and interactive effect of factors towards responses. CCD is a method that is suitable for fitting a quadratic model, helps to optimize the effective parameters with a minimum number of experimental runs and analyze interaction between the parameters (Auta and Hameed, 2011).

The use of natural, renewable, biodegradable and low-cost materials in place of conventional adsorbents like activated carbon, for the removal of ionic specie in aqueous solution is gaining grounds. This is because these materials are ecofriendly. In the present study, carrot residue (CR) treated with hydrochloric acid and commercial activated carbon (AC) as control were used as adsorbents for the removal of fluoride ion from aqueous solution. The conditions for the application of CR as adsorbent for the removal of fluoride ions in aqueous solution were optimized using central composite design of experiment.

MATERIALS AND METHODS

Preparation of Adsorbent Material

Carrot residue for these experiments was obtained from a carrot - juice processing factory in Ilorin, Kwara State, Nigeria. The CR was sun-dried for 48hours, grounded in a blender and sieved with a 2.5mm Endecott sieve. In order to eliminate soluble components such as tannin, resins reducing sugars and colouring substances, the residues were washed with 0.5M HCl, followed by washing with deionized water until a constant pH of 7 was achieved. The neutral material was dried for 48hours at 60° C in an oven and then allowed to cool before storing in clean plastic container.

Characterization of Carrot Residue

The surface chemistry of the adsorbent was determined using fourier transform infrared spectroscopy (FTIR). FTIR analysis was applied on carrot residue to determine the surface functional groups, by using FTIR-8400S spectrophotometer (SHIMADZU). The spectra were recorded from 4000 to 500 cm⁻¹. Scanning electron microscopy (SEM) analysis was performed on CR, to study its surface morphology. SEM Images were recorded using

JEOL JSM-6300F field emission SEM. A thin layer of platinum was sputter coated on the samples for charge dissipation during SEM imaging.

Preparation of Fluoride Stock Solution

Fluoride stock solution was prepared by dissolving 2.21g anhydrous sodium fluoride in 1L volumetric flask and made up to the mark with deionized water. Fluoride working standard solutions was prepared by diluting 100 ml stock solution to 1000 ml distilled water in volumetric flask. This means 1 ml solution contains 0.1 mg of fluoride.

Adsorption Studies

Batch adsorption experiments were performed at ambient temperature. Adsorbent dosage, pH, contact time and initial concentration were set as indicated in the experimental design. The mixture in a 250-ml Erlenmeyer flask was mounted on a shaking machine at a speed of 200 rpm. Fluoride ion in the aqueous samples was estimated using the standard method described by Dirisu *et al.*, (2016). The amount of fluoride ion adsorbed was determined by using equation (1).

$$\text{Percentage adsorbed (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where C_o= initial fluoride concentration (mg/L) and C_e= equilibrium fluoride concentration after adsorption (mg/L). The equilibrium amounts q_e (mg/g) adsorbed per unit mass of adsorbent was determined using equation (2)

$$\text{Equilibrium amount (q}_e\text{)} = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where q_e is the equilibrium amount of metal ions absorbed per unit mass of adsorbent (mg/g); V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Design of Experiments

Central composite design (CCD) of experimental in Design Expert Software 6.0.6 version computer programme was used in this study.

Table 1: Different variables and coded level for central composite design (CCD)

Variables	Code	Unit	Coded Variable Levels		
			Low-level (-1)	Mid-level (0)	High-level (+1)
pH	X ₁	-	2	4	6
Contact time	X ₂	min	60	120	180
Mass of adsorbent	X ₃	g	0.5	1.0	1.5
Ion concentration	X ₄	mg/l	5	10	15

The CCD used is characterized by three operations namely: 2ⁿ factorial runs, 2n axial runs and six Centre runs, for four factors it translated into 16 factorial points, 8 axial

points and 6 replicates at the center which gives a total of 30 experiments. The number of runs can be determined using equation (3).

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Total number of experiments (N) = $2^n + 2n + n_c$
 (3) (Garba and Rahim, 2014)

where n is the number of factors, n_c is the number of center points (six replicates). The two level independent variables (Table 1) were coded as +1 and -1 for high and low values respectively and were used to represent the eight factorial points. The six axial points were located at $(\pm\alpha, 0, 0)$, $(0, \pm\alpha, 0)$, $(0, 0, \pm\alpha)$, and the six replicates were at the center $(0, 0, 0)$. Alpha α , the distance of the axial point from the center which makes the design rotatable had its value fixed at $\alpha = 1.682$. These variables (Table 1) with their respective ranges were chosen based on literature and preliminary studies. Rotatability value (α) which depends on the number of points in the factorial portion of the design was determined using equation (4) as report by Ahmad and Alrozi, (2010).

$$\alpha = N^{1/4} \quad (4)$$

Where $N = 2n$ which is the number of points, n is the number of factors.

This optimization process include three major steps; performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model.

$$Y = f(X_1, X_2, X_3, X_4, \dots, X_n) \quad (5)$$

Where Y is the response of the system, and X_i is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surface. Optimal conditions for the responses (% adsorbed by AC and CR) were determined using the optimal predictor quadratic model in the equation (6).

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} x_i \right)^2 + \sum_{i=1}^n \sum_{j=i+1}^n b_{ij} x_i x_j \quad (6)$$

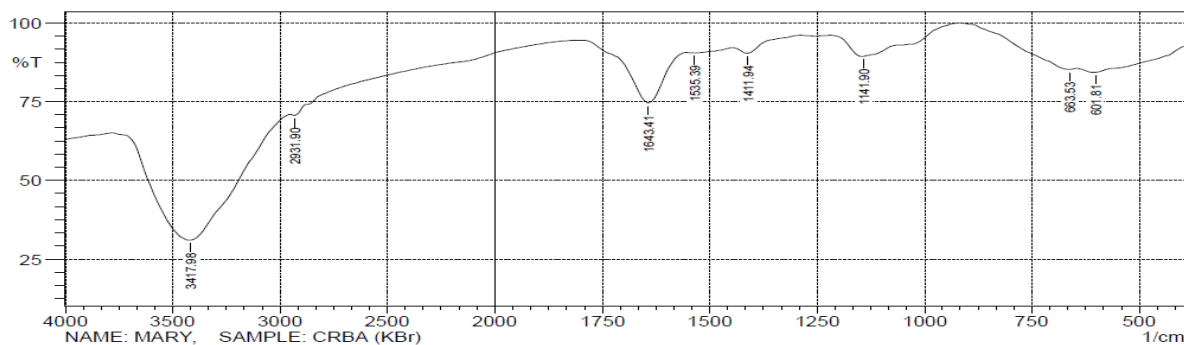
Where Y is the predicted response, b_0 is the constant coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients and $x_i x_j x_k x_l$ are the coded values of the adsorption variables considered. The quality of the fit of polynomial model was expressed by the correlation coefficient (R^2). The significance and adequacy of the used model was further explained using F-value (Fisher variation ratio), probability value (Prob > F) (Kumar *et al.*, 2009).

RESULTS AND DISCUSSION

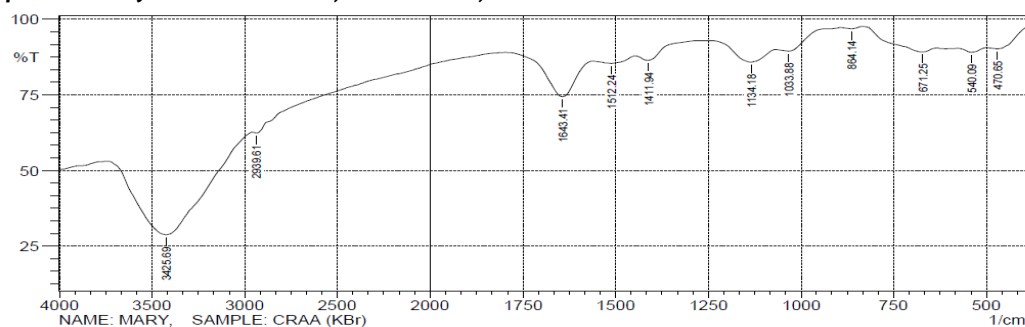
Characterization of the Adsorbent

Result in Figure 1 is the FTIR spectra before adsorption (a) and after adsorption (b) for the adsorption of fluoride ions unto CR adsorbent. The broad bands in the region of 3425 and 1141 cm^{-1} indicate the presence of surface hydroxyl (OH), 2931 and 663 cm^{-1} C-H groups respectively, the peak at 1535 cm^{-1} indicate the presence of carbonyl group, other researchers have found these functional groups in carbonaceous materials (Naushad *et al.*, 2015; Alqadami *et al.*, 2016). After adsorption the FTIR spectra show that there was a change in position and intensity of these groups which indicates their participation in the adsorption process. It was noted that a new peak was formed at 1033 cm^{-1} (Figure 1b) which showed the adsorption of fluoride onto the carrot residue (CR).

Figure 2 is the SEM image of the adsorbent describing the surface morphology of the carrot residue before and after fluoride adsorption. It can be seen in (a) before adsorption that the adsorbent has a well-developed and uniform surface with orderly pore structure and (b) after adsorption; the pore on the surface of the adsorbent was covered by a white thread-like layer which confirms the adsorption of fluoride ions onto the surface of the CR.

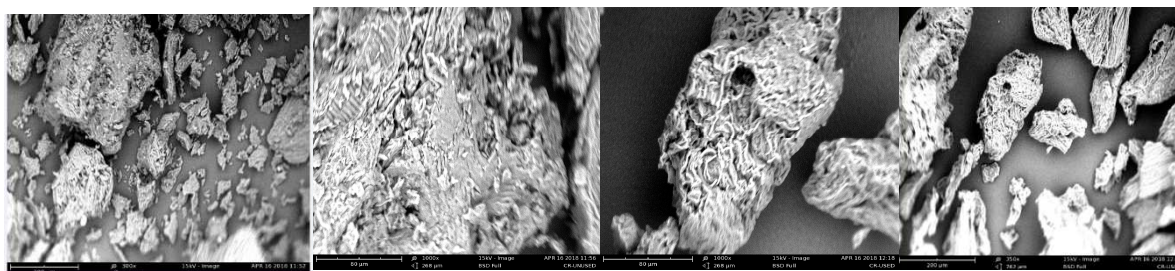


(a) Before Adsorption



(b) After Adsorption

Figure 1: FTIR Spectrum of CR before adsorption and after adsorption



(i) Before Adsorption

(ii)

(i) After Adsorption

(ii)

Figure 2: SEM micrograph (i) at 1000 and (ii) 300 magnification of CR before adsorption and after adsorption

STATISTICAL ANALYSIS

Table 2: Experimental Responses obtained using CCD

Run	Level (Coded)				Factors					% Adsorbed	
					pH (X ₁)	Time (X ₂) (min)	Mass of adsorbent (X ₃) (g)	Ion con. (X ₄) (mg/L)	AC	CR	
1	0	0	0	0	4.00	120.00	1.00	10.00	83.43	86.13	
2	1	-1	1	-1	6.00	60.00	1.50	5.00	66.40	69.23	
3	-1	-1	-1	-1	2.00	60.00	0.50	5.00	63.84	66.56	
4	-1	1	1	1	2.00	180.00	1.50	15.00	74.95	80.99	
5	1	1	1	1	6.00	180.00	1.50	15.00	83.48	81.36	
6	-1	1	-1	-1	2.00	180.00	0.50	5.00	71.45	72.42	
7	1	1	-1	-1	6.00	180.00	0.50	5.00	64.43	67.45	
8	-1	-1	-1	1	2.00	60.00	0.50	15.00	85.24	86.27	
9	1	-1	-1	-1	6.00	60.00	0.50	5.00	61.83	66.83	
10	0	0	0	0	4.00	120.00	1.00	10.00	84.01	86.26	
11	1	-1	-1	1	6.00	60.00	0.50	15.00	87.15	85.10	
12	0	0	0	0	4.00	120.00	1.00	10.00	83.59	86.12	
13	-1	-1	1	-1	2.00	60.00	1.50	5.00	60.89	65.05	
14	1	1	-1	1	6.00	180.00	0.50	15.00	81.59	85.20	
15	-1	1	-1	1	2.00	180.00	0.50	15.00	86.30	88.00	
16	1	-1	1	1	6.00	60.00	1.50	15.00	87.35	86.11	
17	-1	-1	1	1	2.00	60.00	1.50	15.00	82.80	80.95	
18	-1	1	1	-1	2.00	180.00	1.50	5.00	63.42	68.87	
19	1	1	1	-1	6.00	180.00	1.50	5.00	85.70	65.96	
20	0	0	0	0	4.00	120.00	1.00	10.00	82.79	86.62	
21	0	0	0	-1	4.00	120.00	1.00	5.00	71.98	72.34	
22	0	0	-1	0	4.00	120.00	0.50	10.00	78.05	88.39	
23	0	-1	0	0	4.00	60.00	1.00	10.00	81.70	86.20	
24	0	1	0	0	4.00	180.00	1.00	10.00	82.47	76.34	
25	1	0	0	0	6.00	120.00	1.00	10.00	87.68	89.27	
26	0	0	1	0	4.00	120.00	1.50	10.00	79.73	79.01	
27	0	0	0	0	4.00	120.00	1.00	10.00	85.10	84.15	
28	-1	-1	0	0	2.00	120.00	1.00	10.00	86.21	88.40	
29	0	0	0	1	4.00	120.00	1.00	15.00	86.90	89.37	
30	0	0	0	0	4.00	120.00	1.00	10.00	85.70	84.23	

From the results in Table 2 the percentage removal of fluoride ions using CR adsorbent is between 65.05 - 88.39% and that of AC 60.89 - 87.68%. The model expression was selected in accordance with sequential model sum of square that is based on the polynomial highest order where the model was not aliased and the additional terms were significant. Quadratic model was selected for CR adsorption using the computer software. The response (% adsorbed) for CR was selected and a regression analysis performed. The R^2 value of the model indicates the correlation between experimental and predicted data, R^2 value of CR is 0.9429 which are within desirable range as presented in Figures 3. The R^2 value is close to unity this implies that there is a good agreement between the experimental and predicted value of the model. The final model empirical equation for

the adsorption capacity CR for fluoride is given as equation 7.

Regression Equation the Responses Generated using CR as Adsorbent

$$Y_{CR} = 86.06 - 0.056X_1 - 0.32X_2 - 1.76X_3 + 8.26X_4 + 2.30X_1^2 - 5.26X_2^2 - 1.33X_3^2 + 5.68X_4^2 - 1.17X_1X_2 + 0.97X_1X_3 + 0.31X_1X_4 - 0.78X_2X_3 - 0.62X_2X_4 - 0.69X_3X_4 \quad (7)$$

In the equation above the factors take their coded form, represented as % adsorbed by carrot residue (Y_{CR}), pH (X_1), Time (X_2), Mass of adsorbent (X_3), and Fluoride ion concentration (X_4). The positive sign before the terms indicates synergetic effect while the negative sign antagonistic effect (Garba and Rahim, 2014). The appearance of a single variable in a term signified a single factor effect; two variables imply a double factor effect and a second order term indicate the quadratic effect (Ahmad and Alrozi, 2010).

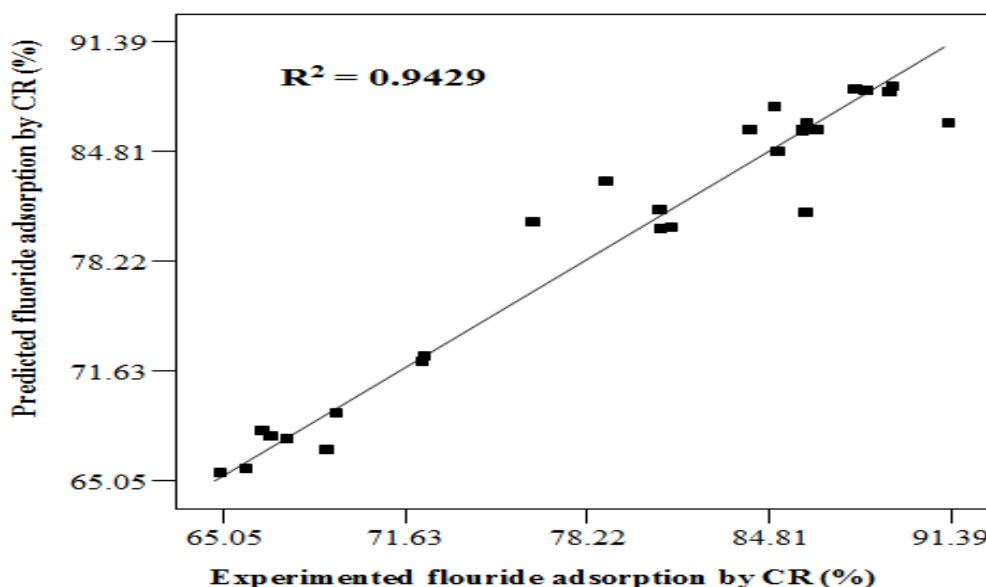


Figure 3: Relationship between the predicted and experimental data for fluoride adsorption by CR

Analysis of Variance

Analysis of variance (ANOVA) result of adsorption of fluoride by CR is presented in Table 3. This was used to validate the adequacy and importance of the models terms. The model terms having value of Prob. > F less than 0.05 are considered as significant. The F-value is 16.50 and > 0.0001 for Prob. > F value also having the significant model terms as X_3 , X_4 ,

X_2^2 , X_4^2 with X_1 , X_2 , X_1^2 , X_3^2 , X_1X_2 , X_1X_3 , X_1X_4 , X_2X_3 , X_2X_4 , and X_3X_4 been insignificant to the response. This is due to the F-value high F-value shows significance while low F-value shows insignificance. This statistical analysis obtained from the result shows that the model is suitable for predicting the adsorption of fluoride using carrot residue.

Table 3: The ANOVA for response surface quadratic model of adsorption of fluoride by Carrot residue

Source	Sum of Squares	Degree of freedom	Mean of Square	F-Value	Prob. > F	Remarks
Model	1759.21	14	125.66	16.50	< 0.0001	significant
X ₁	0.056	1	0.056	7.297x10 ⁻³	0.9331	
X ₂	1.81	1	1.81	0.24	0.6333	
X ₃	55.79	1	55.79	7.33	0.0170	
X ₄	1227.44	1	1227.44	161.22	< 0.0001	
X ₁ ²	13.46	1	13.46	1.77	0.2048	
X ₂ ²	70.29	1	70.29	9.23	0.0089	
X ₃ ²	4.50	1	4.50	0.59	0.4546	
X ₄ ²	81.81	1	81.81	10.75	0.0055	
X ₁ X ₂	21.97	1	21.97	2.89	0.1115	
X ₁ X ₃	14.96	1	14.96	1.96	0.1828	
X ₁ X ₄	1.56	1	1.56	0.20	0.6581	
X ₂ X ₃	9.72	1	9.72	1.28	0.2775	
X ₂ X ₄	6.14	1	6.14	0.81	0.3844	
X ₃ X ₄	7.58	1	7.58	1.00	0.3354	
Residual	106.59	14	7.61			
Lack of fit	106.42	10	10.64	254.48	< 0.0001	Significant
Pure Error	0.17	4	0.042			
Correlation Total	2105.48	29				

Effects of interaction between Variables

From Table 2 and Table 3, it can be deduced that the adsorption of fluoride onto the control adsorbent AC and CR, was highly influenced by the initial ion concentration. Other factors followed in this order pH > time > mass of adsorbent. These deductions were based on the F-value of (114.09) for initial ion concentration, (4.99) pH, (1.48) time and (0.13) mass of adsorbent. For the quadratic effect, mass of adsorbent (6.14 F-value) was the highest followed by that of initial ion concentration (4.86), pH (2.28) with time (0.80). The interaction of the factors with each other have high F-values for pH and mass of adsorbent was 16.76, time and initial ion concentration (14.06) and (4.26) mass of adsorbent and initial ion concentration and low F-values for are pH and time (0.50), pH and ion concentration

(0.43), with time and mass of adsorbent (0.12) which was the least value.

The three dimensional response surfaces plot for the adsorption of fluoride onto CR is presented in Figure 4. From Figure 4 the combine effect of initial ion concentration and pH at fixed time (120min) and mass of adsorbent (1g), the highest % adsorbed value of 91.52 can be achieved. For the combined effect of initial ion concentration and time of contact 89.07% fluoride uptake can be obtained at fixed values of pH 4 and CR mass of 1g. The interaction effect of initial ion concentration and mass of adsorbent revealed a 90.03% fluoride ion removal at constant value of pH 4 and contact time of 120min. The surface plots showed clearly the influence of initial ion concentration on the responses for CR.

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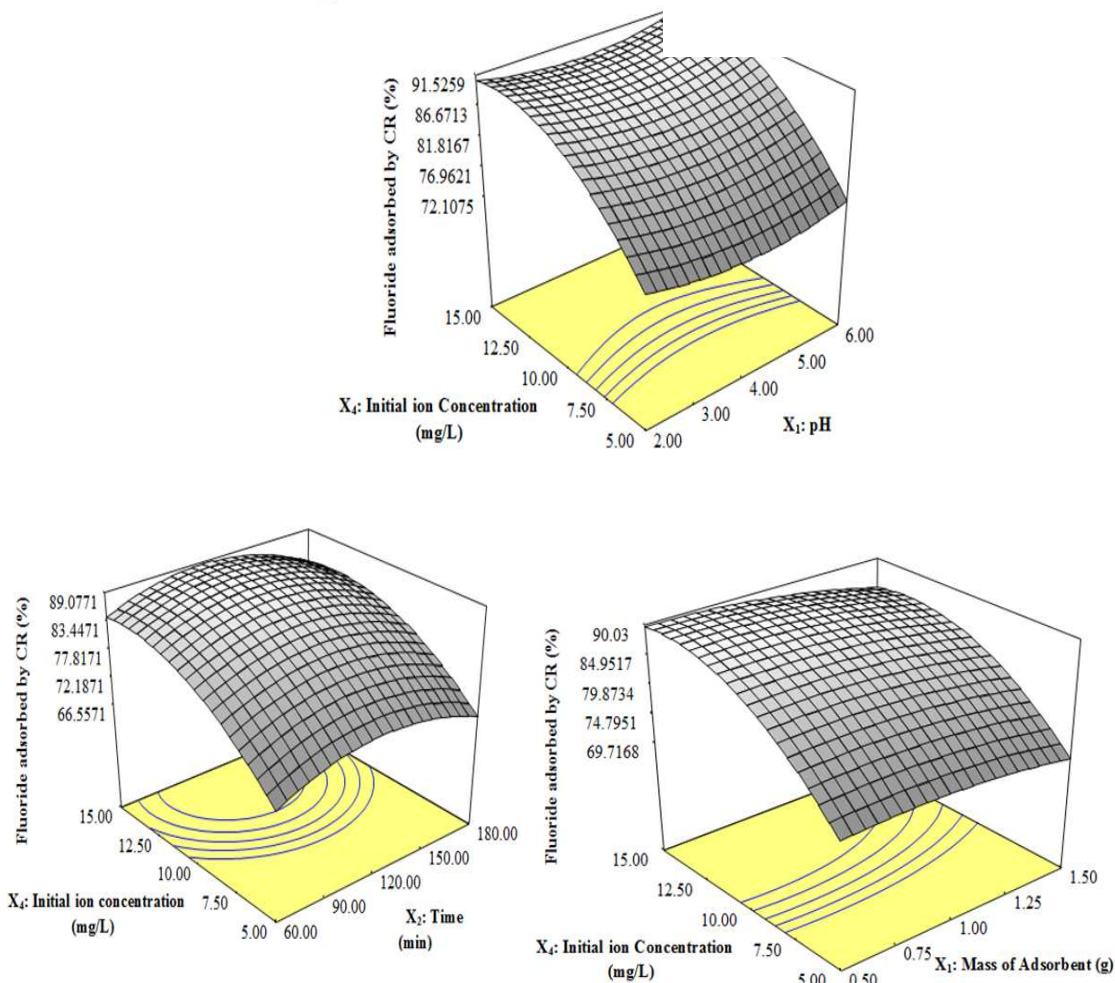


Figure 4: Three dimensional response surface plot for Adsorption of Fluoride unto CR

Process Optimization Model Validation

Optimum conditions for adsorption is very vital for batch adsorption processes, therefore the optimum values (Figure 5) of fluoride

adsorption processes by AC and CR for the process variables investigated were pH 5, time 96min, mass of adsorbent: 1g, initial ion concentration 10mg/l and desirability of 1.

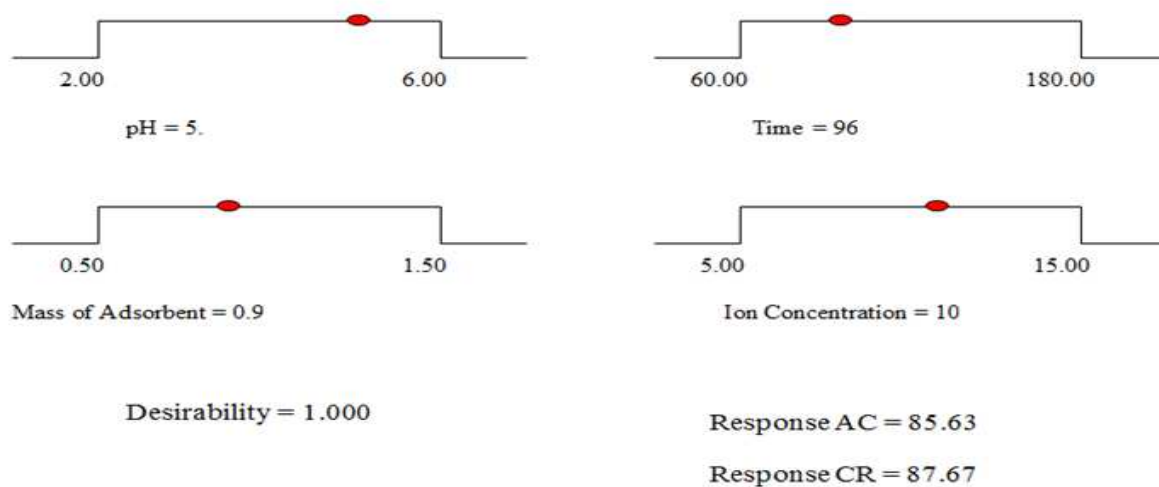


Figure 5: Optimal process conditions for adsorption of fluoride by AC and CR

The model validation results (Table 4) indicate that at the optimum conditions the experimental (actual) % adsorbed values obtained in the laboratory were only slightly higher than those predicted at the same condition. This is a strong indication that the model is valid and can be used to select process conditions before actual experimental in the

laboratory. The use of the model will save time because fewer experimental runs will be required in the laboratory. The model predicted a higher % adsorbed value for CR against AC, which was confirmed in the actual values of 87.59% (AC) and 90.25% (CR) obtained in the laboratory.

Table 4: Model validation parameters and percentage removal by AC and CR

Model validation parameters				% Removal			
pH	Time (min)	Mass of adsorbent (g)	Initial ion concentration (mg/L)	Predicted		Actual	
				AC	CR	AC	CR
5.0	96.0	1.0	10.0	85.63	87.67	87.59±0.02	90.25±0.02

CONCLUSION

In this study, it was established that the optimum adsorption conditions for the removal of fluoride ions in aqueous solution by carrot residue were pH 5.0, time 96.0 min, and 1.0 g adsorbent dose and 10.0mg/L initial concentration. The treated CR can remove up

to 90.25±0.02% fluoride ions in solution. CR performed better than AC with a value of 87.59±0.02%. Therefore, the treated CR is a viable local alternative to the imported and expensive AC for the removal of fluoride ions in solution.

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