Original Research Article

Optimization and modeling of cyanide removal from cassava waste water using calcined and activated adsorbent mixtures of oyster shell and periwinkle shell ash

ABSTRACT

Cyanide, a toxic compound found in cassava wastewater which on frequent basis is discharged to the environment poses danger to the ecosystem; this research work aims to curb this menace. Temperature, pH, dosage, contact time, adsorbent mixture ratio and initial concentration were optimized using CCD on periwinkle-oyster shells composite mixtures for activated and also, calcined adsorbents on the cyanide adsorption from cassava wastewater. Three RSM models (linear, 2FI and quadratic) were applied to study, optimize and predict this adsorption process. ANOVA showed that quadratic model best predicted the processes for both the activated and calcined adsorbents having R^2 values of 0.9678, CV% of 15.51% for the activated and R^2 values of 0.9550, CV% of 18.54% for the calcined composite adsorbent. Surface and contour plots were generated to study the interaction between the adsorption parameters and cyanide adsorption. Results from this study also show that pH and initial cyanide concentration were the most determining factors of the adsorption process for both adsorbent samples with the highest adsorption capacity of 96.648% and 96.112% obtained for the activated and calcined composite adsorbent respectively. Numerical optimization was carried out and the confirmation test on the analyzed best-fit quadratic models yielded actual adsorption efficiency of 90.174% as against the predicted adsorption efficiency of 89.83% for the activated and actual adsorption efficiency of 82.274% as against the predicted adsorption efficiency of 83.475% for the calcined composite adsorbent hence, confirms that both activated and calcined adsorbents of oyster-periwinkle shells composite mixture is effective for cyanide adsorption from cassava wastewater and the RSM models were effective to optimize and predict the process.

Keywords: cyanide, periwinkle-oyster shell composite adsorbent, cassava wastewater, adsorption.

1. INTRODUCTION

Cassava a tuberous, woody perennial plant of the spurge family had become a staple food in most developing African sub-Saharan countriesand most Asian countries [18] and during the production of cassava into various products not only solid wastes but also liquid wastes hazardous to the environment is generated [13].The wastewater from washing of the tubers during processing contains large amount of inert materials with low chemical oxygen demand (COD) while that obtained from the de-watering of the grated paste has high contaminating load of biological oxygen demand (BOD), COD and high cyanide content [27] and when discharged untreated to the environment, poses grave danger to the ecosystem[18].

Cyanide (C-N) is a chemical compound consisting of one atom of carbon connected to one atom of nitrogen by three molecular bonds (C≡N) and cyanides are compounds (substances formed by the joining of two or more atoms) that contain a cyanide group [1].There are two cyanogenicglucosides present in cassava roots, namely linamarin that accounts for 95% of total cyanogen content and lotaustralin[32]. These cyanogens are distributed widely throughout the plants with large amounts in the leaves and root cortex [11]. When the roots are completely disrupted, all linamarin will come out in contact with its hydrolytic enzyme (linamarase), resulting in hydrolysis and subsequent removal of the breakdown products during washing.

Cyanides can both occur naturally or be man-made and most cyanides are powerful and rapid-acting poisons. A short-term exposure to cyanide causes rapid breathing, tremors, other neurological effects and long-term exposure causes weight loss, thyroid effects, nerve damage and death [30].

Large quantities of oyster shells are found in the coastal area of Niger delta region of Nigeria as waste with no further use after the edible part had been stripped off. However, a small amount is used instead of aggregates for temporary and remedial measures to cover up muddy areas for easy road access. Therefore, piles of oyster shells which are common in regions of oyster production, thus constitute nuisance to the environment [8].

Periwinkles are marine mollusks (gastropods) with dense spiral shells, found mostly in the Niger Delta lagoons and mudflats between East Calabar and West Nigerian Badagry[25]. People in this region eat the edible portion as seafood and few individuals use the shell as a coarse aggregate in concrete in fields where there are no stones or granite for purposes such as paving water-logged regions. A large quantity of periwinkle shell is therefore still being disposed-off as waste and has accumulated over the years in many places [8].

According to [22], adsorption is a phenomenon that collects gas or liquid matter in molecules, atoms or ions on the surface of another solid substance. Adsorption can also include removal of dissolved solids in a solution or solvent by a solid surface or recovery of dissolved solvents by that surface, a process called desorption [29].Studies on the use of seafood waste had been carried out to develop low cost adsorbent for the treatment of wastewater, and these include oyster shell [3], [33],[26], [12], land snail shell [19] and periwinkle shell [15], [14], [2], [9], [10], [28].

The primary purpose of embarking on this study is to model and optimize the adsorption of cyanide from cassava wastewater with a measured dosage of a mixture of periwinkle shell and oyster shell ash in calcinated and activated forms.Response surface methodology (RSM) models were studied to predict the cyanide adsorption from cassava

wastewater.Temperature, pH, dosage, contact time, adsorbent mixture ratio and initial concentration as adsorption parameters were utilized to study the adsorption process.

2. MATERIAL AND METHODS

2.1 Materials

Bitter cassava variety (TMS98/0581) was obtained from the Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria. Periwinkle and oyster shells were gotten from a market dumpsite in Uyo, AkwaIbom State of Nigeria. In this study analytical grade chemicals were used and the following computer software was utilized during this study:

i. Microsoft excel
ii. Design expert (version 11)

2.2 Methods

2.2.1 Calcination and activation of the oyster shell and periwinkle shell

The oyster shells and periwinkle shells were separately washed with warm water to remove dirt and other impurities, first rinsed with clean water and finally rinsed with distilled water. They were separately sun dried afterwards to further dehydrate them before they were separately pulverized into powder using a hammer mill and sieved with a 106 µm Tyler sieve. The methods of [16], [23], [31] with slight modifications were used to calcinate and activate the oyster shells and periwinkle shells separately.The resulting powdered precursor was calcinated using Gallenkamp muffle furnace (serial number 1B2613B) at limited supply of air operated at a temperature of 600^{o}C for 2 hours and allowed to cool to room temperature afterwards.Chemical activation was done using ortho-phosphoric acid (H_3PO_4). The calcined sample (100g) was soaked in 200 ml of 0.5 M of H_3PO_4 for 12 hours in order to allow sufficient time for the surface pores to be properly activated. The sample was then heated to form a paste. The paste was re-introduced into the muffle furnace (serial number 1B2613B) at a temperature of 700^{o}C for 2 hours and allowed to cool to room temperature again. The resulting activated sample was washed with distilled water to remove excess acid, oven-dried at 100^{o}C for 12 hours and finally stored in an air-tight container.

2.2.2 Preparation of cassava wastewater

The method of [14] was used to prepare the cassava wastewater. The cassava was peeled, washed and crushed to a pulp. 2kg of the cassava pulp was soaked in 20L of water overnight. The cassava pulp was then squeezed and sieved out leaving the remaining filtrate added to the water used to wash the peeled tubers. The sample was stored in a container and refrigerated in order to slow down microbial activity.

2.2.3 Experimental Design

2.2.3.1 Central composite design (CCD)

The CCD of the RSM was used to generate the experimental data and the range of adsorption parameters values utilized is shown in Table 1.The CCD had 8 center points, 12 axial points and 32 factorial points making a total of 52 runs (for each set of all 6 adsorption parameters combined) each for the mixture of activated oyster and periwinkle shell ash (MASA), then a mixture of calcined oyster and periwinkle shell ash (MCSA) making a total of 104 runs for both adsorbents.

Table1: Range of factors of experiment

Factors	Range
A; pH	4 to 12
B; contact time (minutes)	80 to 100
C; adsorbent dosage (g)	2 to 6
D; adsorbent mixture ratio	0.5 to 0.9
E; temperature (^{o}C)	25 to 45
F; Initial C-N concentration (mg/l)	60 to 140

2.2.4 Experiment procedure for cyanide adsorption

Batch process technique was employed in the determination of amount of cyanide concentration adsorbed by the adsorbents. The varying factors presented in Table 1 was used simultaneously to carry out the batch adsorption experiment in 250 ml conical flask. The conical flask and its content was agitated at a stirring speed of 150 rpm using an orbital shaker (Optima, Model 05-752). Drop-wise addition of HCl and/or NaOH solutions was used to control the pH, varying temperature (tempt.) was controlled by a water bath shaker. Distilled water was used to control the concentration (conc.) of cyanide, amount of dosage used was dependent on the ratio of the mixture. The adsorbent mixture ratio is expressed as ratio of oyster shell to periwinkle shell (that is, oyster shell : periwinkle shell). For example, a run of adsorbent dosage of 4g and adsorbent mixture ratio of 1 implies that 2g of oyster shell ash and 2g of periwinkle shell ash was mixed, a run of adsorbent dosage of 4g and adsorbent mixture ratio of 0.7 implies that 1.65g approximately of oyster shell ash and 2.35g approximately of periwinkle shell ash was mixed.A constant volume of 100ml of cassava wastewater (mixture of distill water and cyanide concentration) was used per batch (or run). The initial concentration and final concentration of the cyanide was determined using a UVSpectrophotometer (Model T60) at wavelength of 490 nm. The percentage cyanide adsorbed (adsorption rate efficiency, R) by MASA, then MCSA was calculated using Equation[21], [24]:

$$R(\%) = \frac{Co-Ce}{Co} X\ 100 \qquad \text{Equation 1}$$

Co = Initial cyanide concentration in wastewater (mg/l),
Ce = Final cyanide concentration in wastewater (mg/l)

2.2.5 Experiment procedure for cyanide adsorption

On completing the laboratory experiment, the data obtained was utilized in the generation of response surface methodology (RSM) models. The 3 RSM models applied for the analysis of response 1 and response 2 are:

i. Linear model

$$R = a_0 + a_1A + a_2B + a_3C + a_4D + a_5E + a_6F \qquad \text{Equation 2}$$

ii. Two-factor interaction (2FI)

$$R = a_0 + a_1A + a_2B + a_3C + a_4D + a_5E + a_6F + a_7AB + a_8AC + a_9AD + a_{10}AE + a_{11}AF + a_{12}BC + a_{13}BD + a_{14}BE + a_{15}BF + a_{16}CD + a_{17}CE + a_{18}CF + a_{19}DE + a_{20}DF + a_{21}EF \qquad \text{Equation 3}$$

iii. Quadratic model

$$R = a_0 + a_1A + a_2B + a_3C + a_4D + a_5E + a_6F + a_7AB + a_8AC + a_9AD + a_{10}AE + a_{11}AF + a_{12}BC + a_{13}BD + a_{14}BE + a_{15}BF + a_{16}CD + a_{17}CE + a_{18}CF + a_{19}DE + a_{20}DF + a_{21}EF + a_{22}A^2 + a_{23}B^2 + a_{24}C^2 + a_{25}D^2 + a_{26}E^2 + a_{27}F^2$$

Equation 4

Where R is the response (quantity of the adsorbate adsorbed = final concentration of adsorbate at equilibrium, Ce), A to F represent each of the factors and a_0 to a_{27} are the regression coefficients to be obtained.

Each of the RSM model proposed was subjected to analysis of variance (ANOVA) in order to determine the prediction performance of each RSM model and the model with the best prediction performance was utilized for the optimization of the responsesdone using the Design Expert 11 by applying the numerical optimization technique for the minimization of final cyanide concentration at equilibrium, Ce for response 1, R1 (MASA) and response 2, R2 (MCSA). The confirmation test was performed afterwards to check and verify the models.

3. RESULTS AND DISCUSSION

3.1 Characterization of cassava wastewater

The results for the characterization of the cassava wastewater shown in Table 2 indicates that the cassava wastewater is acidic and the cyanide content is highly above the stipulated standard of 0.2mg/l set by the Environmental Protection Agency (EPA) for the safe discharge of cyanide bearing wastewater into the environment [1], [14], [3], [20]. Table 2 showed a pH of 4.65 which was within the expected acidic range of 3.8 – 5.7 as reported by other researchers [1], [14], [3], [20].

Table 2: Characterization of the cassava wastewater sample

Property parameters	Values
pH	4.65
Cyanide Concentration (mg/l)	106

3.2 Characterization of the calcined and activated oyster and periwinkle shell ash

The physico-chemical properties of the prepared calcined oyster shell ash (COSA), activated oyster shell ash (AOSA), calcined periwinkle shell ash (CPSA) and activated periwinkle shell ash (APSA) and the methods used to obtain them are listed in Table 3.

Table 3: Physico-chemical properties of APSA, AOSA, CPSA and COSA

Parameters	APSA	AOSA	CPSA	COSA	Method
Bulk density (g/cm^3)	0.75	0.73	0.70	0.69	[4], [19]
Ash content (%)	2.38	2.52	2.49	2.61	[5]
Moisture content (%)	5.9	5.0	5.7	4.9	[6]
pH	6.8	6.7	6.4	5.6	[7]
Surface area (m^2/g)	915	909.4	891.33	874.67	Sear's method [4]

3.3 Amount of cyanide adsorbed by MASA and MCSA

The comparative plot of the amount of cyanide adsorbed using MASA and MCSA is shown in Figure 1.

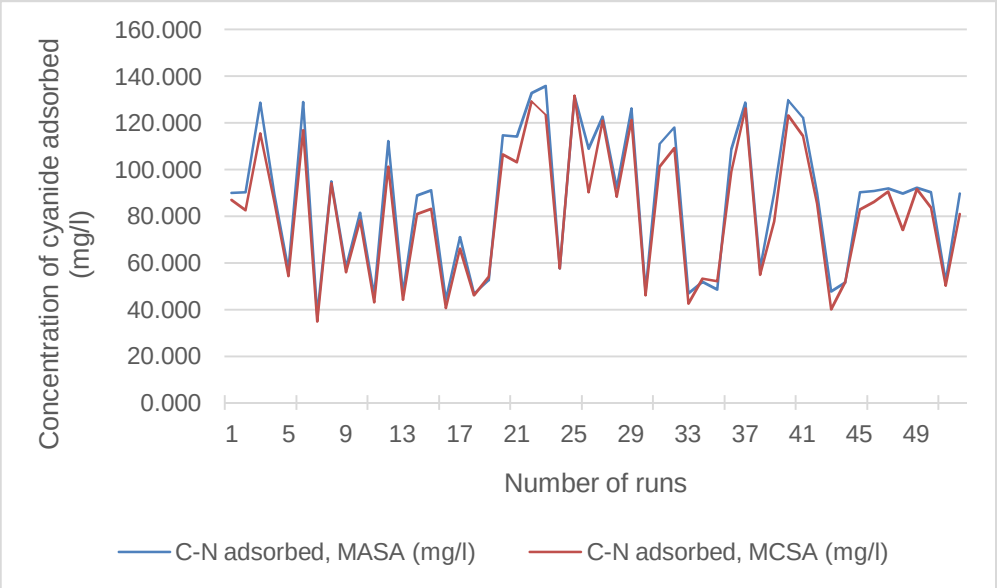


Fig. 1: Comparative plot of the amount of cyanide (C-N) adsorbed by MASA and MCSA

Figure 1shows that MASA had a better adsorption capacity than the MCSA and this affirms with the characterization performance of activated shell ash having a better adsorption performance than the calcined shell ash because of its higher bulk density [14], [3], lower ash content [17] and higher surface area [17].The higher the ash content, the lower the exposed specific surface area resulting in lower available active sites which in turn reduces the strength and adsorptive capacity of the adsorbent and a good adsorbent should have a low ash content as possible of less than 15% [17].Though moisture content of the adsorbent does not really affect the adsorptive capacity, it is important to note that it dilutes the carbon which demands the use of additional weight of carbon during treatment process and a low moisture content indicates that the adsorbent material had been properly prepared, handled and stored. [14]. Also, the higher the surface area, the more the available active sites for adsorption resulting in higher adsorptive capacity of the adsorbent and these were the case in this study.

3.4 Response obtained for all 3 RSM models (Linear, 2FI and Quadratic) using MASA (Response 1, R1)

The response is the final concentration of cyanide at equilibrium, Ce (mg/l).The comparative of the prediction of R1 for all three RSM models studied (linear, 2FI and quadratic models) is shown in Figure 2.

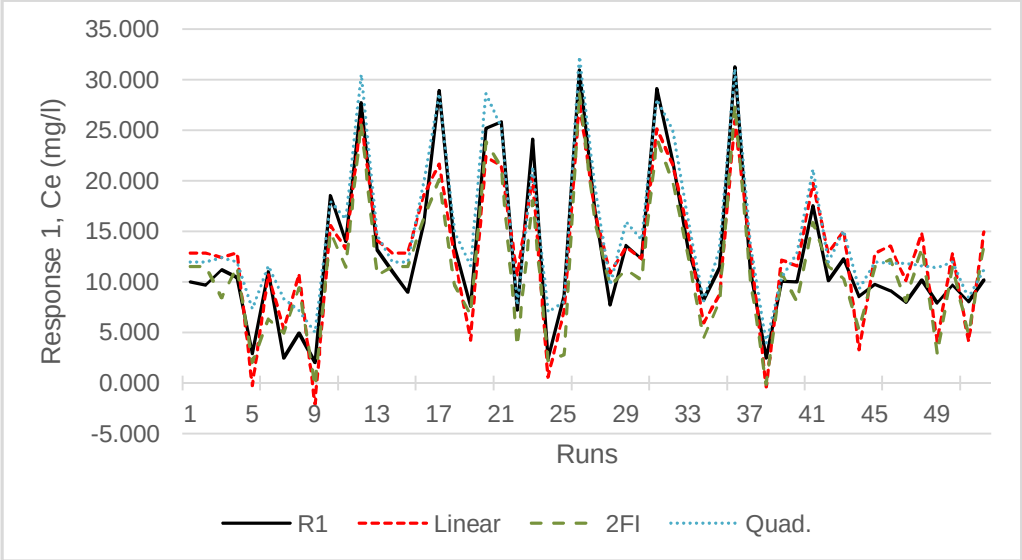
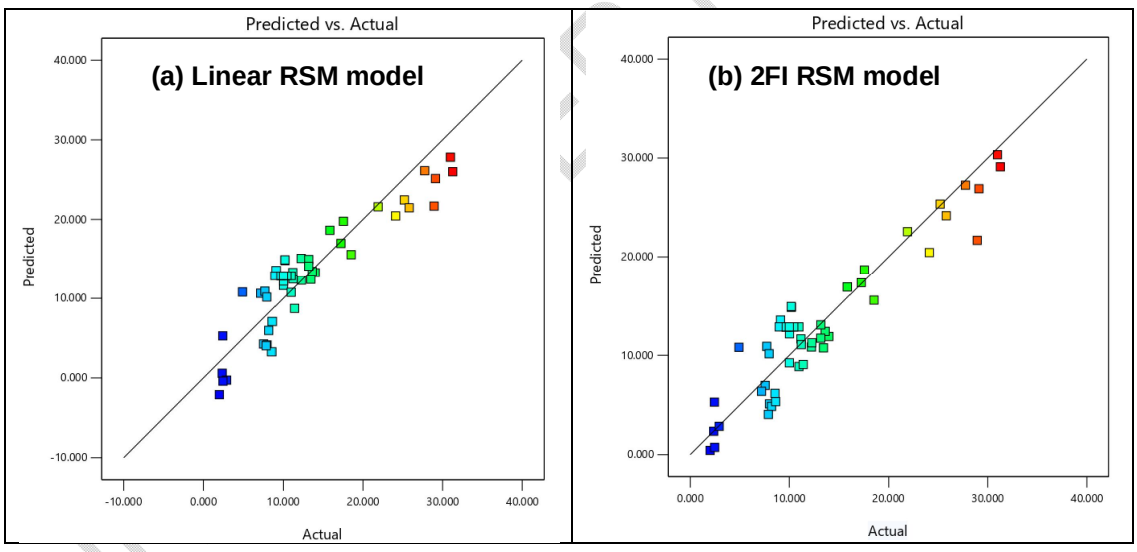


Fig. 2: Comparative plot of predicted R1 of all 3 RSM models studied and actual R1

Figure 3shows the Design Expert software plot of actual values versus predicted values for R1.



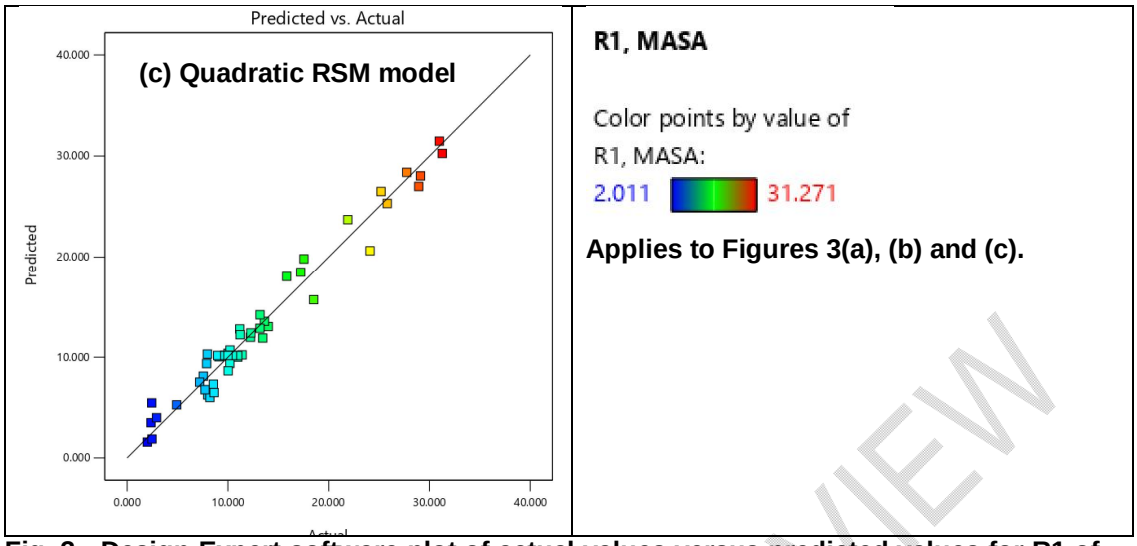


Fig. 3: Design Expert software plot of actual values versus predicted values for R1 of all three RSM models studied

The summary of all three RSM models studied for R1 is shown in Table 4.

Table 4: Model summary statistics for R1

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	
Linear	3.41	0.8245	0.8011	0.7704	
2FI	3.52	0.8747	0.7869	0.6468	
Quadratic	**2.00**	**0.9678**	**0.9316**	**0.7939**	**Suggested**

Table 5 shows the generated equations for all three RSM models studied for R1.

Table 5: Generated RSM model equations for R1

Model	RSM Model equation	
Linear	R1 = 34.467 - 1.469A - 0.131B - 0.687C - 2.320D - 0.180E + 0.126F	
2FI	R1 = 36.532 - 0.951A - 0.246B - 0.825C - 28.401D - 0.182E + 0.336F + 0.010AB - 0.057AC - 0.140AD + 0.001AE - 0.011AF + 0.006BC + 0.129BD + 0.000679BE - 0.000985BF + 1.105CD - 0.009CE - 0.004CF + 0.173DE + 0.051DF - 0.002EF	
Quadratic	**R1 = 10.632 - 4.513A + 0.896B + 1.697C - 15.556D - 1.068E + 0.176F + 0.010AB - 0.057AC - 0.140AD + 0.001AE - 0.011AF + 0.006BC + 0.129BD + 0.000679BE - 0.000985BF + 1.105CD - 0.009CE - 0.004CF + 0.173DE + 0.051DF - 0.002EF + 0.223A^2 - 0.006B^2 - 0.315C^2 - 9.175D^2 + 0.013E^2 + 0.000798F^2**	**Suggested**

3.4 Response obtained for all 3 RSM models (Linear, 2FI and Quadratic) using MCSA (Response 2, R2)

The comparative of the prediction of response 2 for all three RSM models studied is shown in Figure 4.

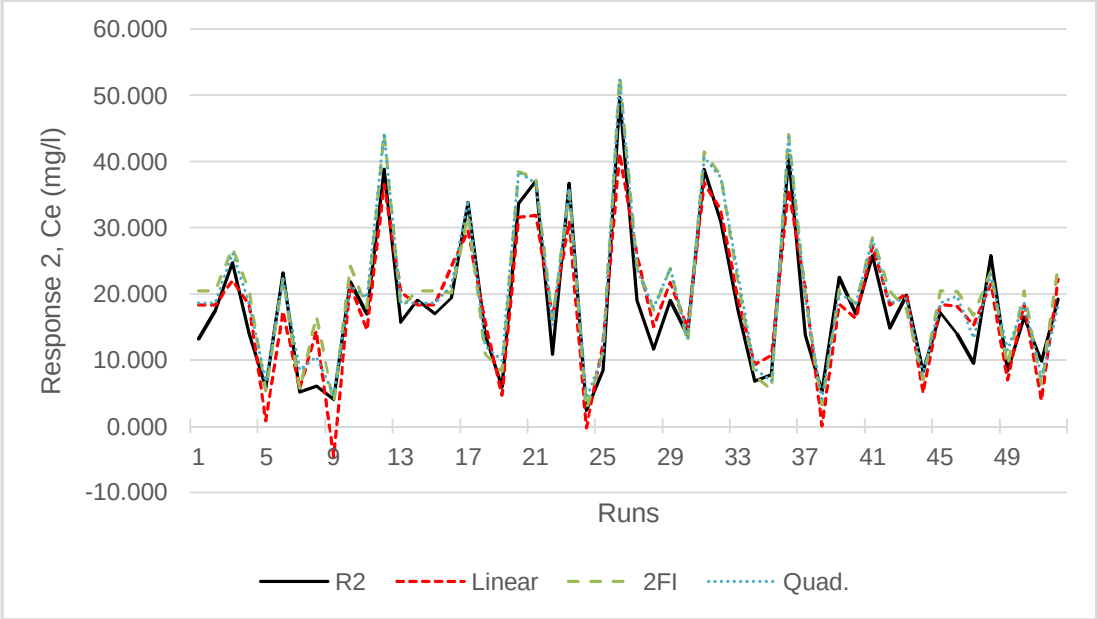
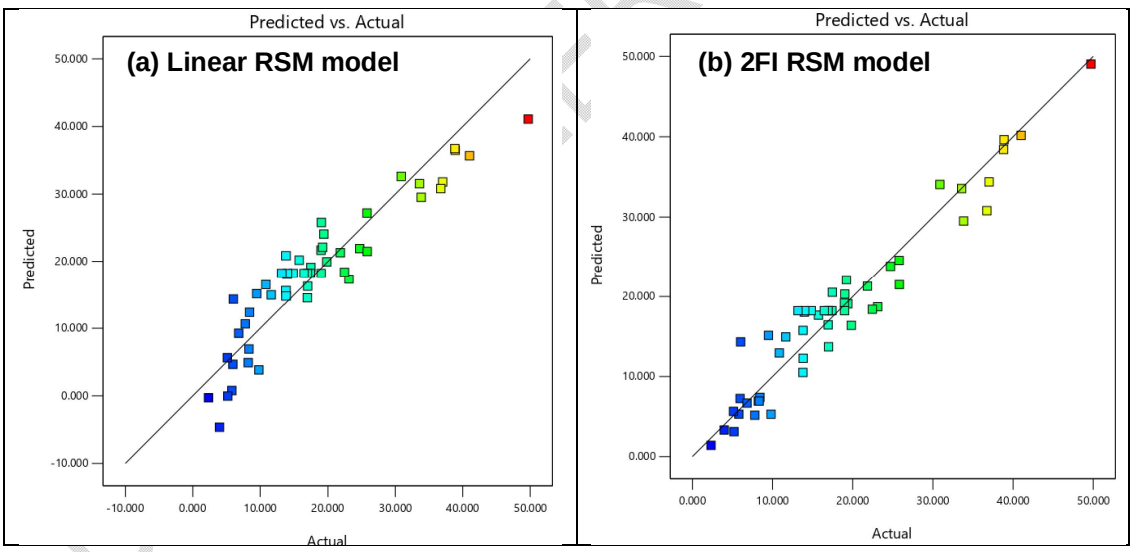


Fig. 4: Comparative plot of predicted R2 of all 3 RSM models studied and actual R2

Figure 5shows the Design Expert software plot of actual values versus predicted values for R2.



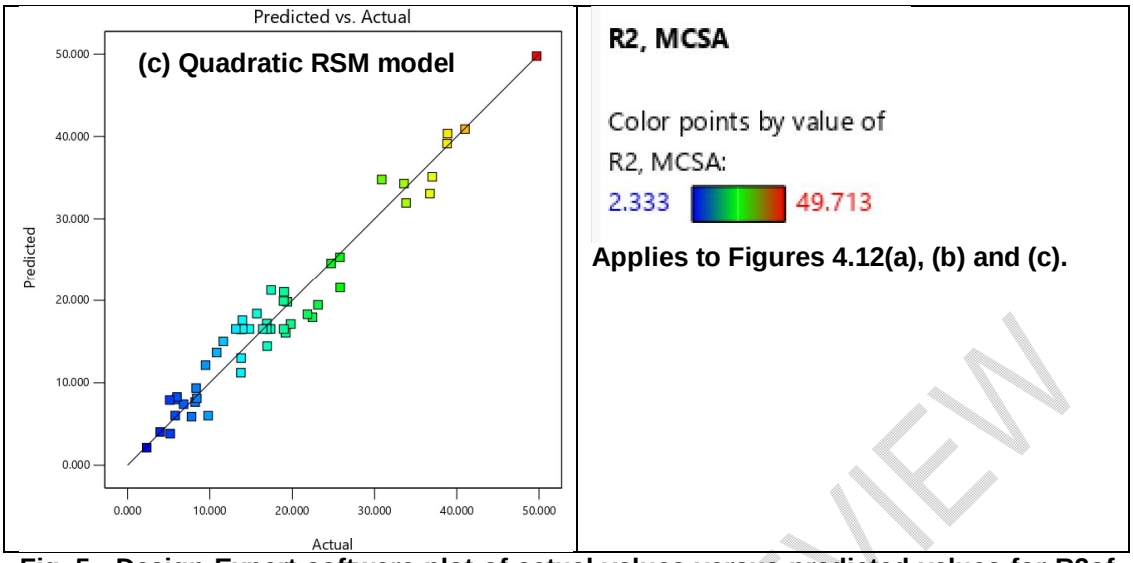


Fig. 5: Design Expert software plot of actual values versus predicted values for R2of all three RSM models studied

The summary of all three RSM models studied for R2 is shown in Table 6.

Table 6: Model summary statistics for R2

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	
Linear	4.43	0.8550	0.8357	0.7991	
2FI	3.78	0.9298	0.8807	0.7588	
Quadratic	**3.38**	**0.9550**	**0.9044**	**0.7317**	**Suggested**

Table 7 shows the generated equations for all three RSM models studied for R2.

Table 7: Generated RSM model equations for R2

Model	RSM Model equation	
Linear	R2 = 43.908 - 1.881A - 0.218B - 1.297C + 0.601D - 0.206E + 0.210F	
2FI	R2 = -11.7537 - 3.371A + 0.192B + 3.760C + 42.984D - 0.031E + 0.513F + 0.025AB - 0.030AC - 0.603AD + 0.039AE - 0.016AF - 0.012BC - 0.427BD - 0.004BE - 0.001BF - 1.467CD - 0.034CE - 0.015CF + 0.041DE + 0.053DF - 0.000638EF	
Quadratic	**R2 = 60.493 - 5.203A - 1.223B + 7.624C + 23.607D + 0.375E + 0.293F + 0.025AB - 0.030AC - 0.603AD + 0.039AE - 0.016AF - 0.012BC - 0.427BD - 0.004BE - 0.001BF - 1.467CD - 0.034CE - 0.015CF + 0.041DE + 0.053DF - 0.000638EF + 0.115A^2 + 0.008B^2 - 0.483C^2 + 13.841D^2 - 0.006E^2 + 0.001F^2**	**Suggested**

From Figures 2 and 4, Figures 3(a), (b) and (c) and 5(a), (b) and (c) and Tables 4 and 7, the quadratic model with the best tracking of both R1 and R2, none of its prediction response value falling on the negative region, closest nearness of the data points to the linear line emanating from point 0,0 and highest R^2 values signifies a better fit of the predicted response to the actual experimental response, hence it had the best prediction accuracy and was used for the optimization process of both R1 and R2.

Table 8 shows the summary of ANOVA table for both response 1 and response 2.

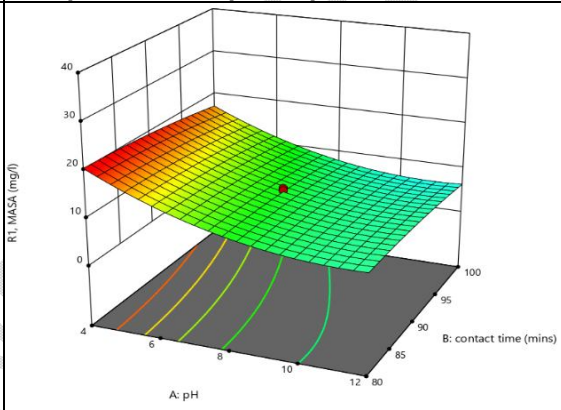
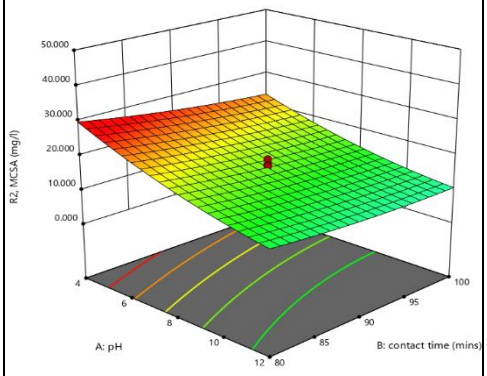
Table 8: ANOVA table summary for quadratic model of R1 and R2

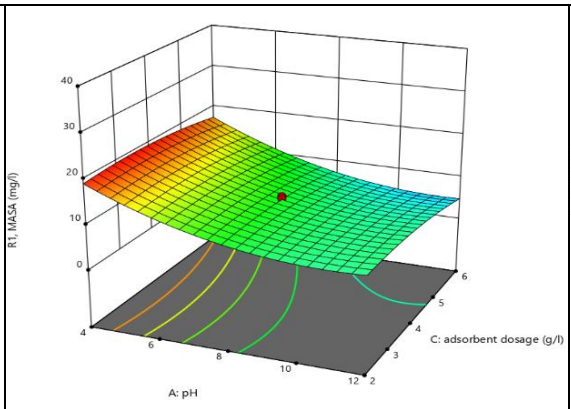
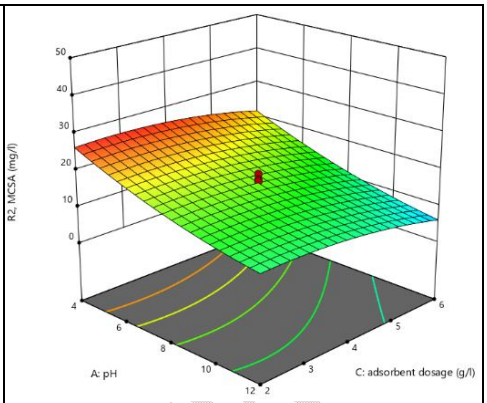
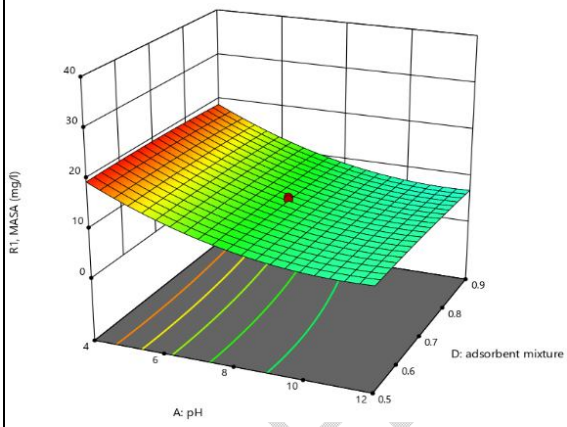
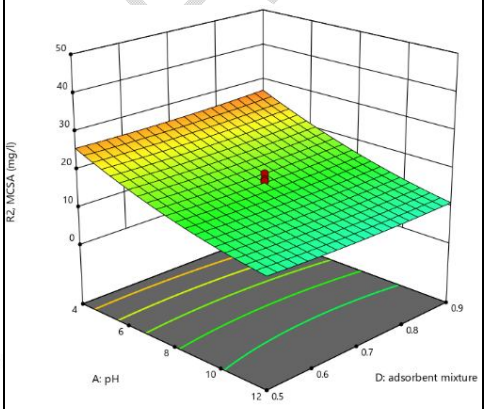
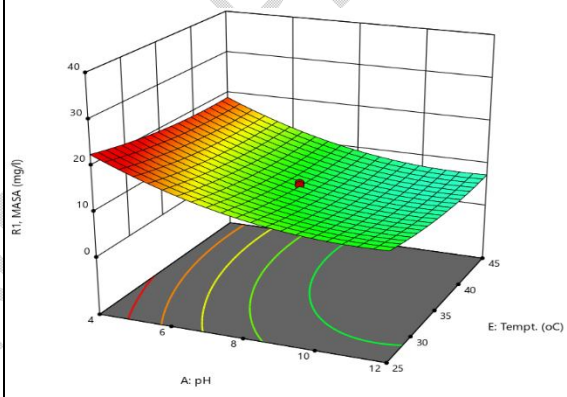
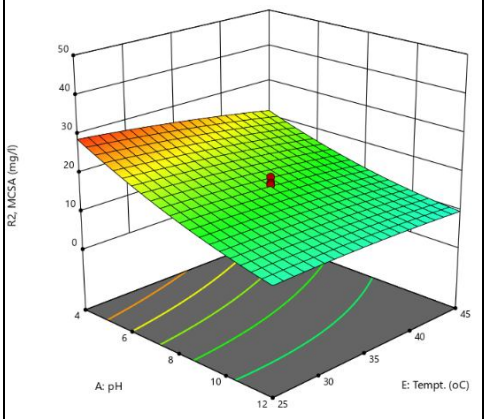
	RESPONSE 1, MASA			RESPONSE 2, MCSA		
Source	**Sum of Squares**	**F-value**	**p-value**	**Sum of Squares**	**F-value**	**p-value**
Model	106.56	26.74	< 0.0001	5817.86	18.86	< 0.0001
pH	1260.98	316.46	< 0.0001	2066.87	180.95	< 0.0001
Contact time (min)	62.67	15.73	0.0006	173.74	15.21	0.0007
Adsorbent dosage (g)	68.84	17.28	0.0004	245.50	21.49	0.0001
Adsorbent mixture	7.86	1.97	0.1731	0.5275	0.0462	0.8317
Temperature (^{o}C)	118.74	29.80	< 0.0001	154.40	13.52	0.0012
Initial C-N conc. (mg/l)	931.75	233.83	< 0.0001	2567.78	224.80	< 0.0001

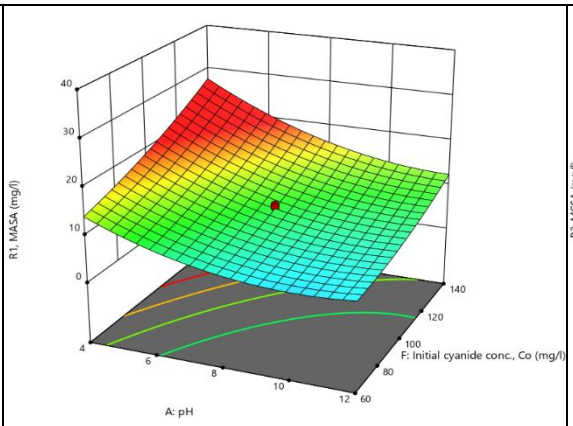
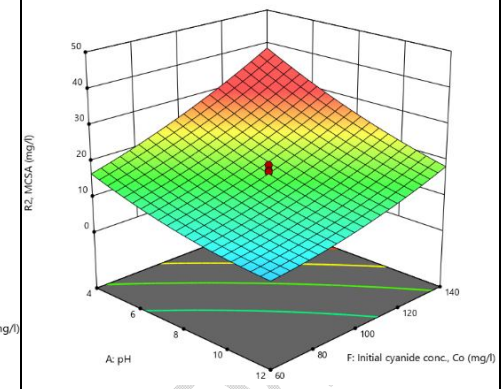
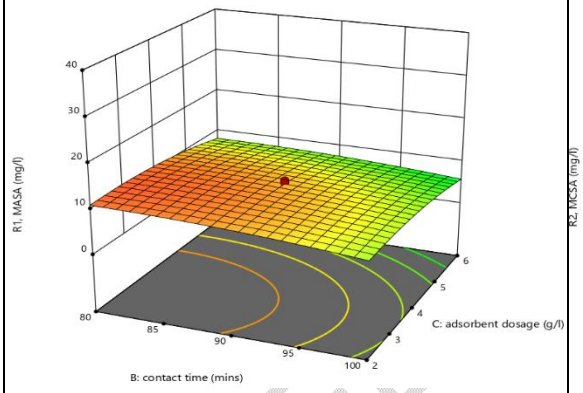
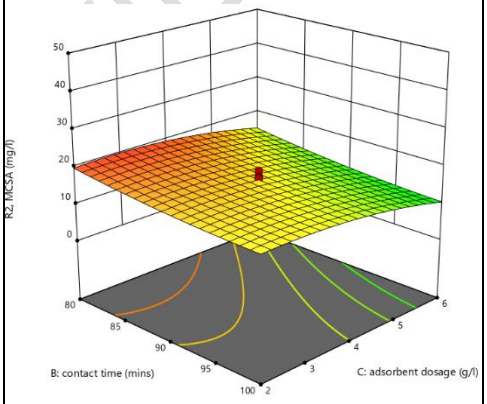
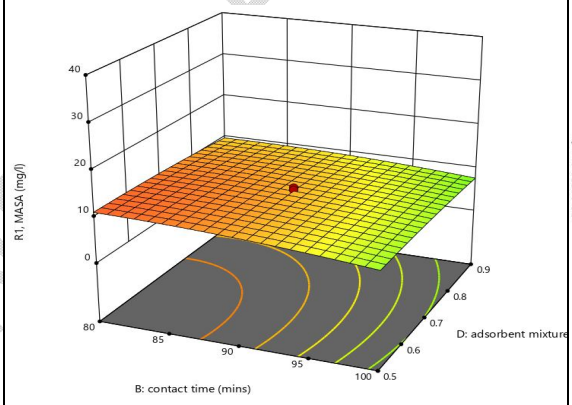
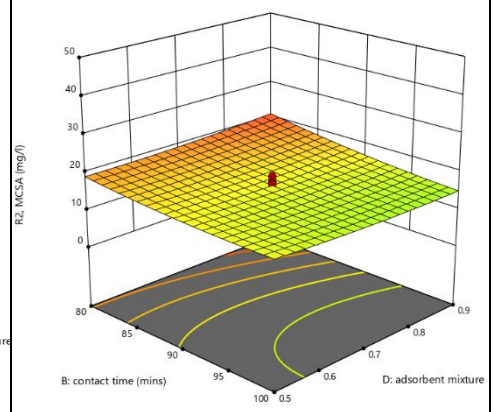
The sum of square values of the quadratic RSM model in the ANOVA shown in Table 8 indicate that pH with highest value of 1260.8 was the most determining parameter of the adsorption response for MASA followed by initial concentration with a value of 931.75. Whereas, for MCSA, initial concentration having the highest sum of square value of 2567.78 was the most determining parameter followed by pH with value of 2066.87.

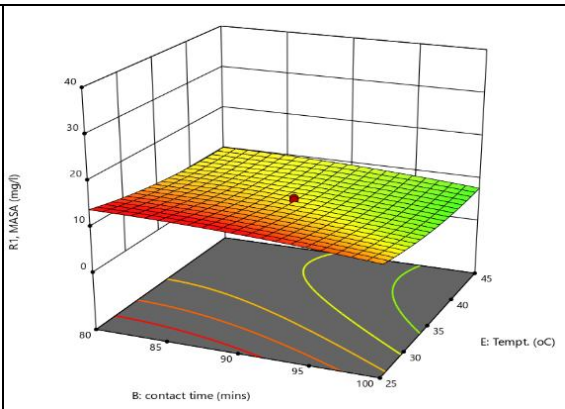
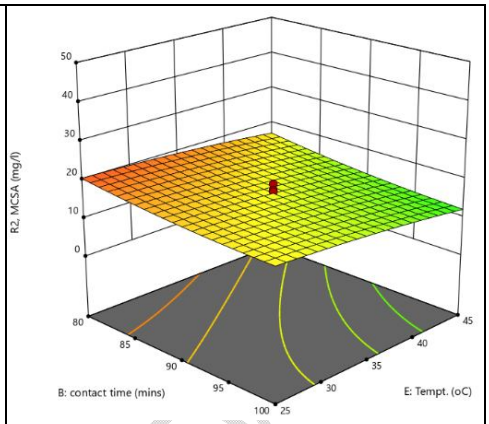
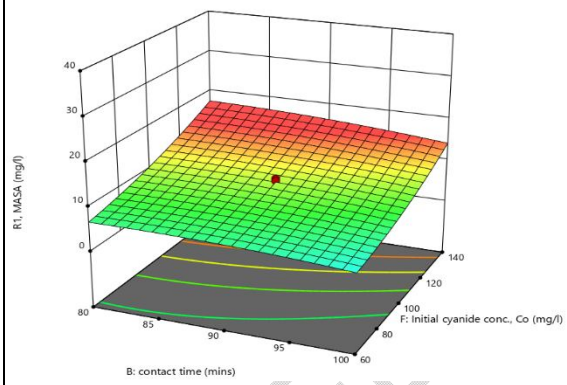
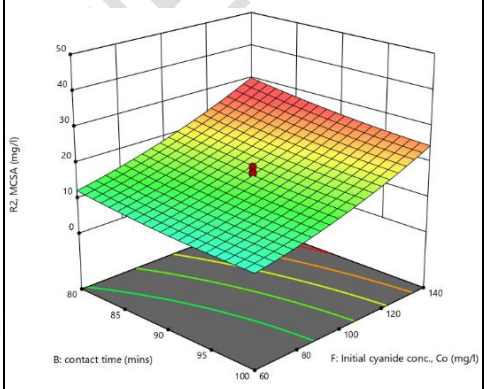
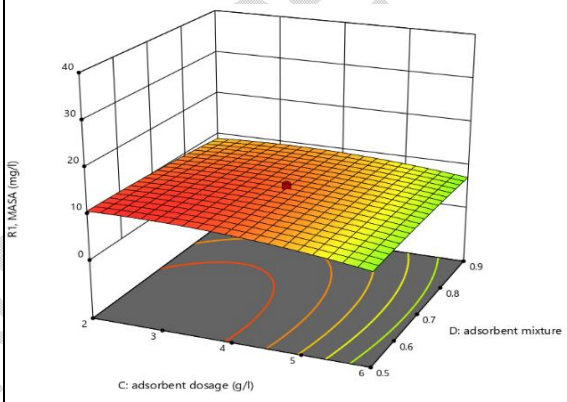
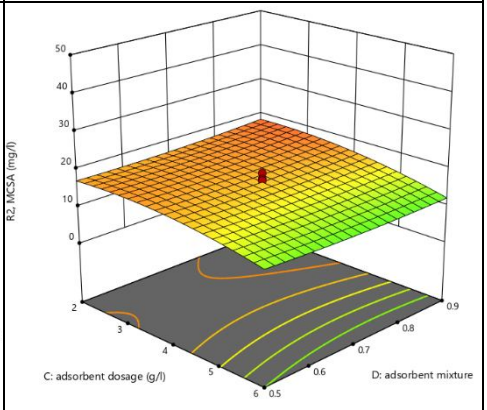
3.5 Three-Dimensional (3D) plots showing interaction between the adsorption process parameters on R1 and R2

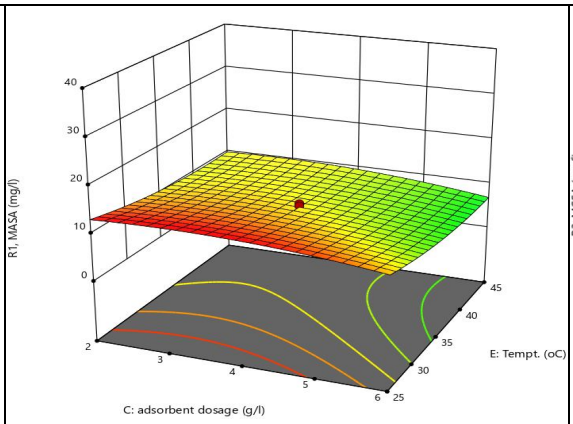
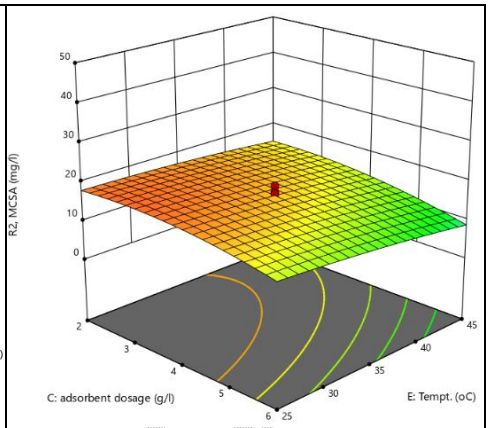
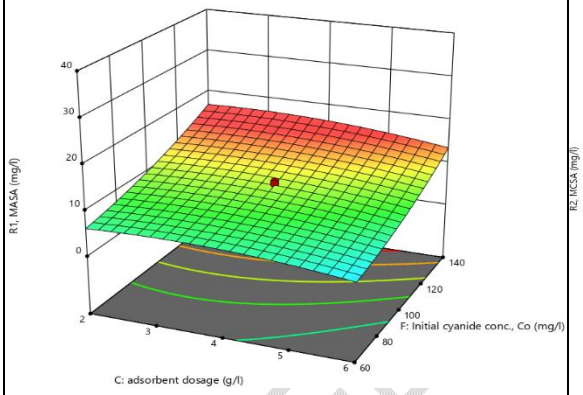
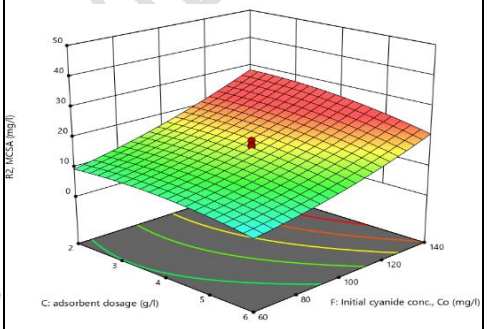
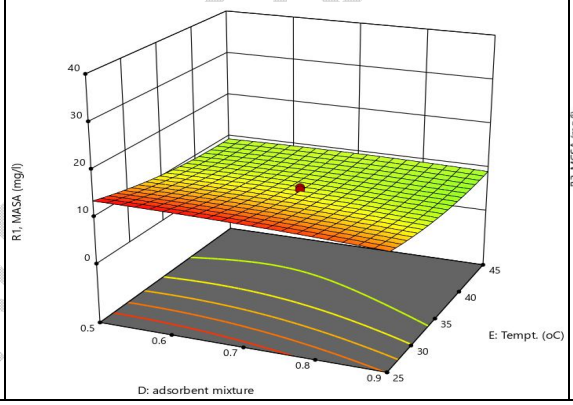
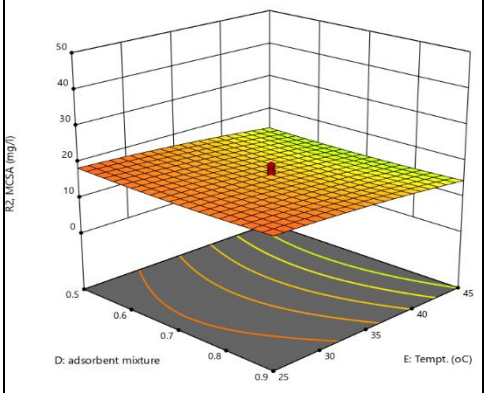
Figures 6 (A) to (O) shows the interaction between the adsorption parameters on R1 and the corresponding R2.

Interaction	Response 1, R1 (MASA)	Response 2, R2 (MCSA)
(A). pH and contact time on response **C = 4 g** **D = 0.7** **E = 35^{o}C** **F = 100mg/l**		

(B). pH and adsorbent dosage on response **B = 90min** **D = 0.7** **E = 35°C** **F = 100mg/l**		
(C). pH and adsorbent mixture ratio on response **B = 90min** **C = 4g** **E = 35°C** **F = 100mg/l**		
(D). pH and temperature (tempt.) on response **B = 90min** **C = 4g** **D = 0.7** **F = 100mg/l**		

(E). pH and initial cyanideconc entration (conc.)on response **B = 90min** **C = 4g** **D = 0.7** **E = 35°C**		
(F). Contact time and adsorbent dosage on response **A = 8** **D = 0.7** **E = 35°C** **F = 100mg/l**		
(G). Adsorbent mixture ratio and contact time on response **A = 8** **C = 4g** **E = 35°C** **F = 100mg/l**		

(H). Tempt. and contact time on response **A = 8** **C = 4g** **D = 0.7** **F = 100mg/l**		
(I). Initial cyanide conc. and contact time on response **A = 8** **C = 4g** **D = 0.7** **E = 35°C**		
(J). Adsorbent dosage and adsorbent mixture on response **A = 8** **B = 90min** **E = 35°C** **F = 100mg/l**		

(K). Tempt. and adsorbent dosage on response **A = 8** **B = 90min** **D = 0.7** **F = 100mg/l**		
(L). Initial cyanide conc. and adsorbent dosage on response **A = 8** **B = 90min** **D = 0.7** **E = 35°C**		
(M). Tempt. and adsorbent mixture ratio on response **A = 8** **B = 90min** **C = 4g** **F = 100mg/l**		

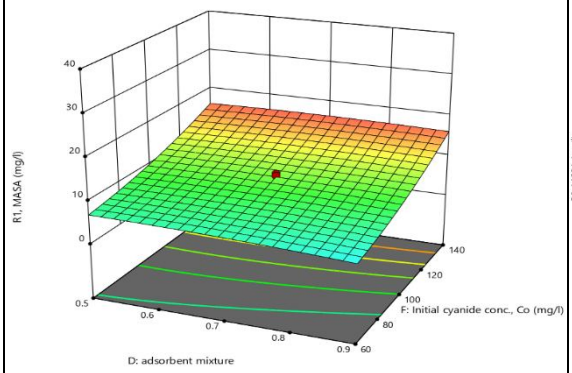
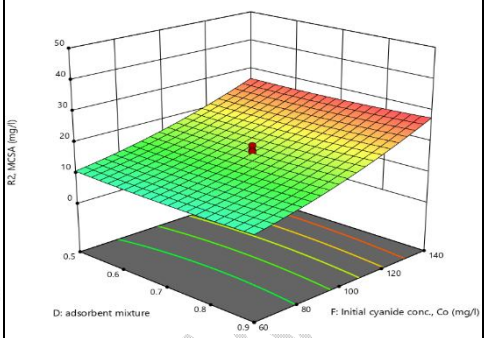
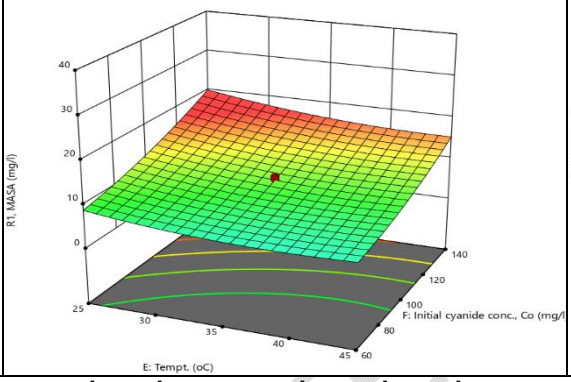
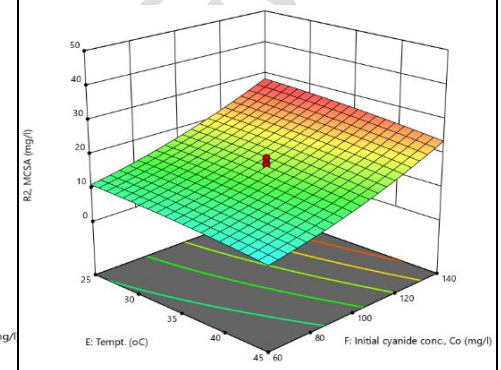
(N). Adsorbent mixture ratio and interaction of initial cyanide conc. on response **A = 8** **B = 90min** **C = 4g** **E = 35°C**		
(O). Tempt. and initial cyanide conc. on response **A = 8** **B = 90min** **C = 4g** **D = 0.7**		

Fig. 6: 3D interaction between the adsorption parameters on R1 and the corresponding R2.

3.6 Optimization and confirmation test

From the numerical optimization of R1 and R2 done using the Design Expert 11, the factor values and optimal response of cyanide adsorption (minimization of final cyanide concentration at equilibrium, Ce for R1 and R2) is shown in Table 9, where:

CT = Contact time (min), AD = Adsorbent dosage (g), AM = Adsorbent mixture ratio, D = Desirability

Table9: Optimal adsorption parameter values for R1 and R2

No.	pH	CT	AD	AM	Tempt. (°C)	Initial C-N conc. (mg/l)	R1, MASA (mg/l)	R2, MCSA (mg/l)	D
1	**11.134**	**96.656**	**5.957**	**0.758**	**40.550**	**61.034**	**1.734**	**1.984**	**1.000**
2	11.262	96.117	5.882	0.899	36.017	61.997	1.591	2.307	1.000
3	11.897	99.504	5.918	0.815	43.997	72.880	2.004	1.178	1.000
4	11.344	97.886	5.957	0.681	44.129	63.917	1.917	1.834	1.000
5	9.774	94.572	5.739	0.900	42.643	60.007	2.004	2.290	1.000
6	10.561	96.593	6.000	0.883	36.175	60.002	1.233	2.218	1.000
7	10.888	98.863	5.996	0.676	44.963	79.125	1.883	2.312	1.000
8	11.919	99.739	5.665	0.900	37.446	60.231	1.727	2.250	1.000

9	11.734	99.744	5.994	0.896	31.286	61.746	1.781	2.088	1.000
10	10.811	97.866	5.774	0.878	42.959	61.231	1.656	1.340	1.000

In this study, more adsorbent dosage (between 5.665g to 6.0g) yielded the optimal cyanide adsorption as shown in the optimization results of Table 9. The reason for this is that the more the inoculation of adsorbent mass, the more the available active sites for adsorption to take place [34]. However, at some point, the percentage cyanide removal was expected to either remain constant or minimally decrease as there would have existed overlap of active sites on the MASA and MCSA at higher adsorbent masses resulting in a decrease in the effective surface area for adsorption [35]. But this scenario did not occur in the study probably because the range of adsorbent dosage utilized did not accommodate this phenomenon.

The initial cyanide concentration between the ranges of 61.034mg/l to 79.125mg/l shown in Table 9 yielded the optimal cyanide adsorption. At higher initial cyanide concentrations, the percentage cyanide removal decreased and this may be due to the surface saturation of both adsorbents (MASA and MCSA) by the adsorbate (cyanide) leading to reduced number of available active sites on both adsorbents for adsorption to take place. This trend is in agreement with other similar findings ([3], [14], [24],[36]).

Temperature also played a vital role in the adsorption process as temperature between the ranges of 36.01^{o}C to 44.96^{o}C yielded the optimal cyanide adsorption. The percentage cyanide adsorbed increased with increase in temperature and this could be as a result of decreasing solution viscosity and increasing molecular motion of the adsorbate (cyanide) as temperature increased allowing the uptake of molecules into the pores of the adsorbents (MASA and MCSA) more easily [34].

This study also showed that contact time between the ranges of 94 minutes to 99.7 minutes yielded the optimal cyanide adsorption. More contact time favoured higher percentage cyanide adsorption and this could be as a result of the cyanide molecules having more time to travel through the solution and cling to the pores of the adsorbents (MASA and MCSA) thereby increasing adsorption capacity [34] and also from the optimization results shown in Table 9, the ranges of 0.758 to 0.9 for adsorbent mixture ratio yielded the optimum cyanide adsorption. This implies that more of the periwinkle shell in the adsorbent mixtures at any given adsorbent dosage favoured the adsorption process.

The confirmation test was done in quadrupleat a 95% confidence using pH of 8, contact time of 90min, adsorbent dosage of 4g, adsorbent mixture ratio of 0.7, temperature of 35^{o}C and initial cyanide concentration of 100mg/l and the results shown in Table 10, where:

PM = Predicted mean (final equilibrium cyanide concentration predicted by the Design Expert software, in mg/l); PE = Predicted efficiency (adsorption efficiency predicted by the Design Expert software, in %); AM = Actual mean (final equilibrium cyanide concentration observed during the laboratory experiment, in mg/l); AE = Actual efficiency (adsorption efficiency calculated using the actual mean, in %)

Table10:Confirmation test results of R1 and R2

R1, MASA				R2, MCSA			
PM	**PE**	**AM**	**AE**	**PM**	**PE**	**AM**	**AE**
10.17	89.83	9.826	90.174	16.525	83.475	17.726	82.274

4. CONCLUSION

Based on the results obtained from the study and the discussions made, it can be concluded that:

i. The untreated cassava wastewater properties shows that the concentration of the wastewater is above the permissible limit of 0.2 mg/l, hence the need for the wastewater to be treated before disposing it to the environment.
ii. The physico-chemical properties of the APSA, AOSA, CPSA and COSA show that they had the potentials to remove cyanide from cassava wastewater.Activated and calcined periwinkle-oyster shell composite mixture is effective adsorbent for cyanide adsorption from cassava wastewater.
iii. Temperature, pH, dosage, contact time, mixture ratio and initial concentration are determining factors affecting cyanideadsorption from cassava wastewater using MASA and MCSA as adsorbents with pH and initial cyanide concentration being the most determining factors of the adsorption process.
iv. MASA is more effective when compared to MCSA for the removal of the cyanide from the cassava wastewater but its corresponding MCSA also gives a close cyanide adsorption capacity, take for instance the adsorption capacity difference of 7.9% between the optimal response of MASA and MCSA shown in Table 10.
v. Quadratic model best predicts cyanide adsorption from cassava waste water using both MASA and MCSA.
vi. More of periwinkle shell in oyster-periwinkle adsorbent mix at any given adsorbent dosage favours cyanide adsorption from cassava wastewater, see Table 9.
vii. This research work is beneficial to especially the rural settlements/communities in Nigeria, Africa and the world at large (who may not be properly enlightened/equipped to go through the rigors of first incurring more costs purchasing the ortho-phosphoric acid, properly activating the composite adsorbent mixtures with it, properly handling and finally recovering the acid after the cyanide adsorption process) as it would help in curbing the menace of cyanide polluted water being discharged to the environment.

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