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OPTIMIZATION OF THE PROCESS VARIABLES USING RESPONSE SURFACE METHODS (RSM), FOR THE REMOVAL OF ULTRAMARINE RED FROM AQUEOUS SOLUTION BY MELON PEELS

A.K. Asiagwu

DEPARTMENT OF CHEMISTRY, DELTA STATE UNIVERSITY, ABRAKA, NIGERIA

Abstract

This study was conducted in order to optimize the process variables for the removal of ultramarine red dye from aqueous solution by melon peel. The potential application of melon peel biomass as a valuable adsorbent for the sorption of ultramarine red dye was examined by using the response surface methodology. In this study, a 5 factors 3 – levels Box – Behnken Design (BBD), option was used. The three levels (-1, 0, 1) of the surface factors were chosen from the optimum ranges of each variables. In the laboratory experiment for the surface variables coded as Time X1, Dye X2, pH X3, Melon Peel X4, Temperature X5 and % Dye Removal as Y. the variables were further used to generate experimental matrix by MINITAB Statistical Software (Version 16). A quadratic polynomial model was suggested. The model was statistically tested by ANOVA, Fischer test at 95% degree of significance and $P \leq 0.05$ confidence level. The design option contained a total of 32 runs and the response values (% dye removed) reveal a second order polynomial as a suitable model for the adsorption process. The model further generated optimized variables for the process as Time 80mins, Dye concentration 4.30 mg/L, pH 12, Dose 4.90 g and temperature 64.30 ^{O}C. The maximum dye removal was 98.60% at the optimized conditions for the sorption process.

***Keywords*:** Ultramarine red adsorption by melon peels.

INTRODUCTION

Pollution arising from the poor management of industrial effluents has become an issue of major concern in our society today [1]. The presence of coloured substances in industrial effluents is a major threat to aesthetics of our surface water, humans, animal's life and environment at large [2]. Consequently the residual and unseen coloured materials are discharged into the ecosystem and especially the aquatic environment. Colour appears to be one of the clearest indicator of water pollution [3]. Coloured substance are generally harmful to humans and thus removal from wastewaters is of growing importance [4].

Several technologies are available for the sorption of colour from wastewaters. These techniques include; oxidation, osmosis, coagulation adsorption. Despite of all these, adsorptions appears to be the most attractive options for the removal colourant in industrial wastewaters [5]. Studies on the application of bio – materials for the removal of colours has been of promising exercise [6,7]. Available research adopted the one factor at a time experiment. This involves the variation of one adsorption factor with respect to adsorption. There are little or no literature available to examine the cumulative effect of all adsorption variables with effect to adsorption.

This current work thereby adopted the examination of the collective effect of all adsorption variables with respect to colour removal by using the response surfaces methodology. Process optimization is one of the most critical categories in the development of efficient and economic bioprocess. The objective of this study was to therefore optimize the adsorption conditions so as to determine the optimal variables that will give the maximum colour (ultramarine red) removal by melon peel adsorbent.

Materials and Methods

Preparation of ultramarine red dye solution

The ultramarine red purchased used in this work was from a commercial market without any further purification. The ultramarine red stock solution was prepared by dissolving accurately weighed dye in deionised and made water to the required concentration for each of the experimental factors been investigated.

Equipment/Apparatus

The equipment/apparatus employed in this study include thermostatic bath, spectrometer, measuring cylinder, spatula, volumetric flask, whatman No. 45 filter paper, test tubes, digital balance, conical flask and pH meter.

Corresponding Author**:** Asiagwu A.K., Email: drasiagwu@yahoo.com, Tel: +2348035089967

Sample Collection and Preparation of Adsorption

The adsorption (melon peels) of about 3.5g was obtained from a commercial market at Koko in Warri North Local Government Area of Delta State, and was sun dried for several days. Then the dried melon peels was ground and sieved using 300μm sieve. The sieved adsorption (melon peels) obtained was preserved in a container for further use in this study.

Experimental Analysis

Effect of Contact Time on Adsorption

The modified melon peels 2g was weighed into five separate conical flasks. The concentration of 10mg/l of the ultramarine red solution was prepared with distilled water. The 50ml of the ultramarine solution was measured into the five flasks. The conical flasks were further labeled for the time intervals of 100, 80, 60, 40, 20 minutes. These flasks were then tightly covered and further at their respective time intervals. The suspensions were then filtered using whatman No. 45 filter paper before it was centrifuged. The dye ion concentration was estimated DR 2010 Spectrophotometer [8].

Determination of the effect of adsorbent dosage on adsorption of ultramarine red solution

2,3,4, 5 and the melon peels modified adsorbent were weighed into the five different flasks. 50ml of the ultramarine red solution were then measured into the five distinct flasks. The conical flasks were further labeled for of 2,3,4,5 and 6g differences in dosage. The conical flasks were tightly covered and then agitated for 20 minutes before the suspensions were filtered with whatman No. 45 filter paper and centrifuged. The ultramarine red ion concentration was estimated using DR 2010 spectrophotometer[8].

Determination of the effect of dye ion concentration on the adsorption of ultramarine red

This work was carried out in time on the effect of dye ion concentration on adsorption with the previous works of [8]. Different standard dye solution of 50, 40, 30, 20 & 10 mg/g were prepared. Only 50ml of each of the dye solution was added to weighed 2 $\pm$ 0.01g melon peels modified adsorbent in five separate flasks and then agitated for 20 minutes. Towards the end of the time, the suspensions were filtered with Whatman No. 45 filter paper and centrifuged. The dye ion concentrations were obtained using DR 2010 spectrophotometer.

Determination of the effect of temperature on the adsorption of ultramarine red in solution

This parameter was investigated the effect of temperature on adsorption was following the procedure as recommended by [9]. 2g of melon peels (the adsorbent) was weighed into five several conical flasks and the 50ml of the ultramarine red dye solution (10mg/g) was measured into the five different flasks. The flasks were further labeled for temperature readings of 30, 40, 50, 60 and 70^{O}C. The conical flasks were then tightly covered and heated at their respective temperatures with thermostatic bath, at 20 minutes for each. Towards the end of the time, each of the flasks were brought out and agitated for another 5 minutes. The suspensions were then filtered via whatman No. 45 filter paper before it was centrifuged. The dye ion concentrations were obtained using DR 2010 spectrophotometer.

Determination of the pH adsorption of ultramarine red in solution

Modified melon peels adsorbent (2$\pm$0.01g) was weighed into (5) five different flasks, 50ml of the ultramarine red dye solution (10mg/l) was measured and poured into the different five flasks. The solutions were then, adjusted to pH 2.0, 4.0. 6.0, 8.0 and 10.0 by the addition of a solution of HCl (0.1m) or NaOH (0.1m) and the pH values were determined by the use of pH meter. Thereafter the flasks were then covered and agitated for 20 minutes. Towards the end, the suspensions were filtered with the aid of whatman No. 45 filter paper and then centrifuged. The dye concentrations were determined with DR 2010 spectrophotometer [8].

Data Calculation

Evaluate of the degree of removal of ultramarine red

The quantity ultramarine red removed by the melon peels during the series of the batch determinations were estimated using a mass balance equation as expressed below:

$$qe = (Co - Ce)\frac{V}{M} \quad (1)$$

Where

qe = dye concentration on the biomass (mgg^{-1}) at equilibrium.

Ce = dye concentration in solution (mgL^{-1}) at equilibrium.

Co = Initial dye concentration in solution (mg/l)

V = Volume of dye solution used (ml)

M = mass of adsorbent used (g)

DESIGN OF EXPERIMENT (DOE)

The response surface methodology was adopted in the DOE for optimization, and X1(time mins), X2 (initial dye concentration mg/L), X3 (pH), X4 (melon peel dose g) and X5 (temperature ^{O}C) were taken as the independent variable also called the surface, while % dye removed as the response or the dependent variable (%Y). in the design, a 5 factors, 3-levels Box Behnken design (BBD) option was use , the 3-levels (-1, 0, 1) of the surface factors were selected from the optimum range of each variable in the OFAT experiment as shown in table 1.

Table 1. Surface variables and their coded value for dye removal from aqueous solution

Surface variables	Designations	Levels		
		-1	0	1
Time(mins)	X_1	80	100	120
Dye conc (mg/L)	X_2	40	50	60
pH	X_3	8	10	12
Melon peel dose (g)	X_4	4	5	6
Temperature (°C)	X_5	50	60	70
% Dye removed	Y			

The parameters values in table 1 were used to generate an experimental matrix via MINITAB statistical software (version 16) as presented in table 2. This matrix made a possible interactions of all the variables in the 32 runs, also the experiment was conducted under randomized order so as to minimized biasness and unwanted variability response [10].

Table 2. Experimental matrix for dye removal by melon peels

StdOrders	RunOrder	PtType	Block	X1)	X2	X3	X4	X5	% Y
7	1	1	1	80	60	12	4	70	78.0
9	2	1	1	80	40	8	6	50	65.0
22	3	-1	1	100	50	12	5	60	90.0
17	4	-1	1	80	50	10	5	60	94.0
18	5	-1	1	120	50	10	5	60	90.0
1	6	1	1	80	40	8	4	70	77.0
5	7	1	1	80	40	12	4	50	80.0
16	8	1	1	120	60	12	6	70	64.5
21	9	-1	1	100	50	8	5	60	84.9
6	10	1	1	120	40	12	4	70	70.0
10	11	1	1	120	40	8	6	70	60.0
8	12	1	1	120	60	12	4	50	65.0
23	13	-1	1	100	50	10	4	60	83.0
4	14	1	1	120	60	8	4	70	60.0
11	15	1	1	80	60	8	6	70	75.3
27	16	0	1	100	50	10	5	60	88.0
2	17	1	1	120	40	8	4	50	85.0
28	18	0	1	100	50	10	5	60	89.0
32	19	0	1	100	50	10	5	60	88.0
15	20	1	1	80	60	12	6	50	76.0
12	21	1	1	120	60	8	6	50	80.0
13	22	1	1	80	40	12	6	70	77.0
29	23	0	1	100	50	10	5	60	87.9
30	24	0	1	100	50	10	5	60	88.1
3	25	1	1	80	60	8	4	50	66.0
26	26	-1	1	100	50	10	5	70	81.3
19	27	-1	1	100	40	10	5	60	80.0
24	28	-1	1	100	50	10	6	60	79.7
20	29	-1	1	100	60	10	5	60	77.0
14	30	1	1	120	40	12	6	50	67.0
25	31	-1	1	100	50	10	5	50	84.8
31	32	0	1	100	50	10	5	60	88.4

The DOE result was evoked to developed a quadratic polynomial as indicated below,

$$Y_{\%dyeremoved} = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_{ii} + \sum_{i<j}^{n} \beta_{ij} X_i X_j \ldots \ldots \ldots . + \in \quad (2)$$

Where β_0 is equation constant, $\beta_{ii} and \beta_i$ are quadratic and linear coefficients respectively and $X_i X_j$ are the surfaces levels [10, 11].

The statistical examination of the model was done through ANOVA with Fischer test of significance at 95% confident level ($p \leq 0.05$), this was to ascertain the level of variable influence as well as their crossing effects on the response, similarly, the fitness and efficiency of the model was tested using R2, adjusted R2 and Lack of fit [12].

Results and Discussion

Models derivation

The response values (%dye removed) for the 32 runs were displayed in table 2, a second order polynomial equation was derived from the result with the aid of minitab software and the coefficients for the model items are presented in table 3 along with R^2 and adjusted R^2. Consequently, the actual model is presented below,

Table 3. Estimated Regression Coefficients for % DYE REMOVED using data in uncoded values

Term	Coef
Constant	-395.133
TIME (MINS)	-0.208912
DYE CONC(mg/L)	7.23801
pH	5.23310
DOSE(g)	41.6134
TEMPERATURE	6.55183
TIME (MINS)*TIME (MINS)	0.0106414
DYE CONC(mg/L)*DYE CONC(mg/L)	-0.0924343
pH*pH	-0.0733566
DOSE(g)*DOSE(g)	-6.39343
TEMPERATURE*TEMPERATURE	-0.0469343
TIME (MINS)*DYE CONC(mg/L)	-0.00275000
TIME (MINS)*pH	-0.0721875
TIME (MINS)*DOSE(g)	-0.00250000
TIME (MINS)*TEMPERATURE	-0.0196250
DYE CONC(mg/L)*pH	-0.0150000
DYE CONC(mg/L)*DOSE(g)	0.436250
DYE CONC(mg/L)*TEMPERATURE	0.00237500
pH*DOSE(g)	-0.0250000
pH*TEMPERATURE	0.0787500
DOSE(g)*TEMPERATURE	-0.00125000

$Y_{\%dyeremoved} =$ -395.133 - 0.208912TIME + 7.23801DYE CONC +5.23310pH +41.6134DOSE +6.55183TEMPERATURE +0.0106414(TIME)^2 - 0.0924343(DYE CONC)^2 - 0.0733566(pH)^2 -6.39343(DOSE)^2 - 0.0469343(TEMPERATURE)^2 - 0.00275TIME*DYE CONC - 0.0721875TIME*pH -0.0025TIME*DOSE - 0.0196250 TIME*TEMPERATURE - 0.015DYE CONC*pH + 0.43625DYE CONC*DOSE + 0.002375DYE CONC*TEMPERATURE - 0.025pH*DOSE + 0.07875pH*TEMPERATURE - 0.00125DOSE*TEMPERATURE (3)

The model above described the experimental process for dye removal. The plus sign connotes cooperative interaction effect of the independent variables while the minus stands for unfavourable interaction effects.
The fitness of the model was tested using four in one residual plots as reflected in figure 1

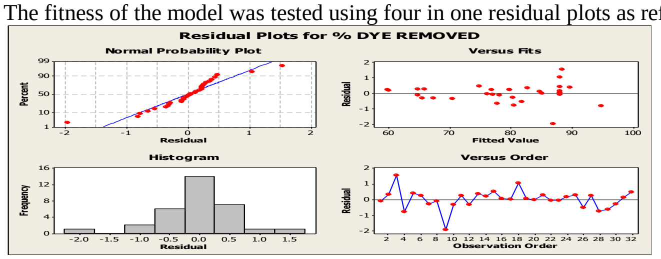

Fig. 1. Residual plots for % dye removed using melon peels

Analysis of variance

The significance test of the model terms was done with ANOVA and the result is presented in table 4.

Table 4. Analysis of Variance for % DYE REMOVED

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	20	2849.60	2849.60	142.480	143.81	0.000
Linear	5	211.34	211.34	42.268	42.66	0.000
TIME (MINS)	1	121.68	121.68	121.680	122.81	0.000
DYE CONC(mg/L)	1	20.48	20.48	20.480	20.67	0.001
pH	1	11.36	11.36	11.361	11.47	0.006
DOSE(g)	1	21.13	21.13	21.125	21.32	0.001
TEMPERATURE	1	36.69	36.69	36.694	37.04	0.000
Square	5	1906.91	1906.91	381.382	384.94	0.000
TIME (MINS)*TIME (MINS)	1	975.42	44.59	44.586	45.00	0.000
DYE CONC(mg/L)*DYE CONC(mg/L)	1	694.84	210.25	210.252	212.21	0.000
pH*pH	1	37.25	0.21	0.212	0.21	0.653
DOSE(g)*DOSE(g)	1	145.20	100.59	100.587	101.52	0.000
TEMPERATURE*TEMPERATURE	1	54.21	54.21	54.207	54.71	0.000
Interaction	10	731.35	731.35	73.135	73.82	0.000
TIME (MINS)*DYE CONC(mg/L)	1	4.84	4.84	4.840	4.89	0.049
TIME (MINS)*pH	1	133.40	133.40	133.403	134.65	0.000
TIME (MINS)*DOSE(g)	1	0.04	0.04	0.040	0.04	0.844
TIME (MINS)*TEMPERATURE	1	246.49	246.49	246.490	248.79	0.000
DYE CONC(mg/L)*pH	1	1.44	1.44	1.440	1.45	0.253
DYE CONC(mg/L)*DOSE(g)	1	304.50	304.50	304.503	307.34	0.000
DYE CONC(mg/L)*TEMPERATURE	1	0.90	0.90	0.903	0.91	0.360
pH*DOSE(g)	1	0.04	0.04	0.040	0.04	0.844
pH*TEMPERATURE	1	39.69	39.69	39.690	40.06	0.000
DOSE(g)*TEMPERATURE	1	0.00	0.00	0.003	0.00	0.961
Residual Error	11	10.90	10.90	0.991		
Lack-of-Fit	6	10.05	10.05	1.674	9.81	0.012
Pure Error	5	0.85	0.85	0.171		
Total	31	2860.50				

From table 4, the regression model was found significant with p = 0.000 ($p<0.05$) and high F- value of 143.81, therefore the derived model is appropriate for the description of the dye adsorption process, also the process parameters (time, initial dye dose, pH, melon peels dose and temperature) with p-values of 0.000, 0.000, 0.001, 0.006, and 0.000 respectively were all significant, this means they all have great influence on the % ultramarine dye removed, furthermore, the magnitude of effects of the surface factors on the response are shown in table 3, by implication, melon peels dose has the highest effect followed by initial dye concentration, similar observation has been made by [10]. It was also observed that, the interaction and quadratic terms were significant, this indicated that the interaction of the parameters have effects on % dye removed. However, quadratic term pH^2 was not significant as well as DOSE*TEMPERATURE, pH*DOSE, DYE CONC*TEMPERATURE, DYE CONC*pH interaction terms were not significant, this evident in their respective low F-value and high p-Values.

Interaction Effects analysis.

In order to visualize the effects of the independent variables on % dye removed (dependent variable), 3-D and contour plots were made as presented below, were two factors are investigated against dye removed, holding the rest variables constant at middle values.

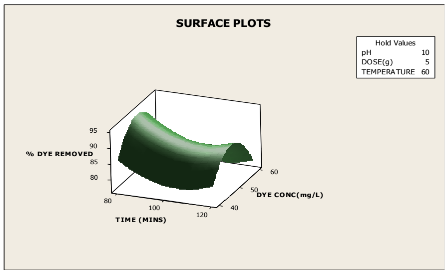

Fig. 1. 3-D plot for Time and Initial Dye Conc Vs % dye removed at constant middle values for pH, Dose and temperature.

The interaction effect of time and initial dye concentration on % dye removal using melon peels is shown in Fig. 1. rapid increase in % dye removal was observed as the initial dye concentration increases from 40 to 53 mg/L compared to increase in time, this showed antagonistic interaction effect on dye removal. This could be due to the fact that as time prolong with increase in dye ion in the solution, the active sites of the melon peels were outnumbered by the excess dye ion present.

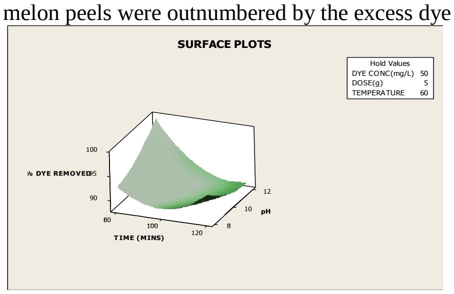

Fig. 2.surface plot Time and pH interactive effect on % dye removed.

From the plot, the effect is also unfavorable as similar to that of Fig 1, this could be as a result of excess OH^- groups present in the solution as the pH increases to more basic medium.
Fig 3 also showed related trend as % dye removed decreases with increase in time while increased with increase in dose up to optimum point as shown.

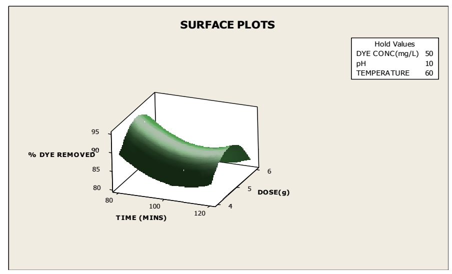

Fig. 3. Surface plot for Time and melon peels Dose effect on dye removal.

It was also observed that increase in time with temperature did not favour % dye removed as presented in Fig. 4, this could be that, the bio material (melon peels) were destroyed at high temperature.

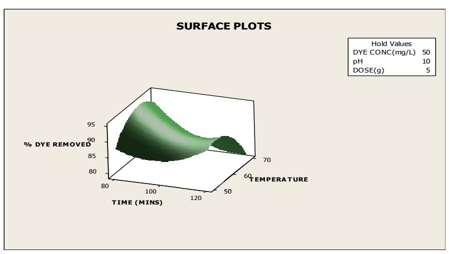

Fig.4. 3-D Plot for Time and Temperature Effects on Dye Removal.

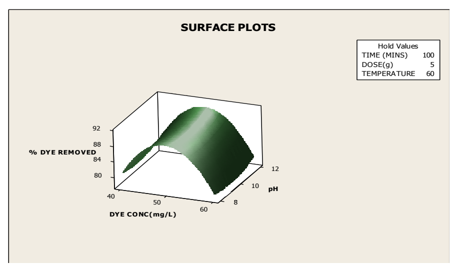

Fig.5. Initial Dye Conc. and pH Interactive Effects Plot

Similar observation was also noticed in Fig 5 below for initial dye conc. and pH.

A positive synergetic effect was observed on the interaction of dye initial concentration and melon peels dose, as the dose increases with increase in dye initial concentration, % dye removed was favoured as reflected in Fig 6, this could be related to the fact that as the dye ion increases, more of it were removed with more active site of the melon peels presents. Similar trend was observed in Fig 7 were % dye removed was increased with increase in dye initial concentration and temperature. This maybe as a result of high number of dye ions were released due to increase in kinetic energy gained from increased temperature.

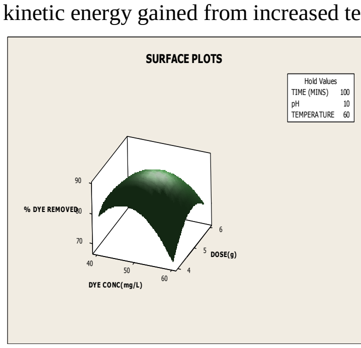

Fig. 6. Effect of Dye Conc and Dose

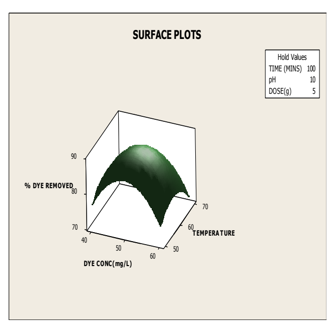

Fig.7. Effect of Dye Conc and Temperature

These plots were also represented in contours as shown below.

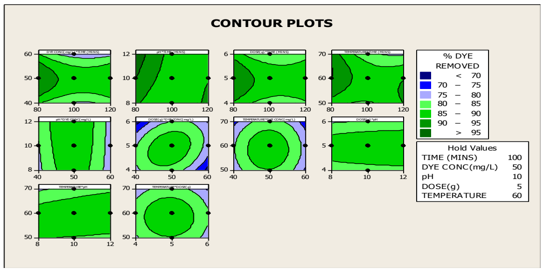

Fig.8. Contour plot for all interaction effects

Optimization of response.

The optimization was done using the Minitab (version 16) response optimizer with the starting points of (Dye Conc= 50mg/L, time= 80mins, pH= 10, melon peels Dose = 5g and Temperature 60ºC) with the chosen option of maximization response goal. The result is shown in Fig 9.

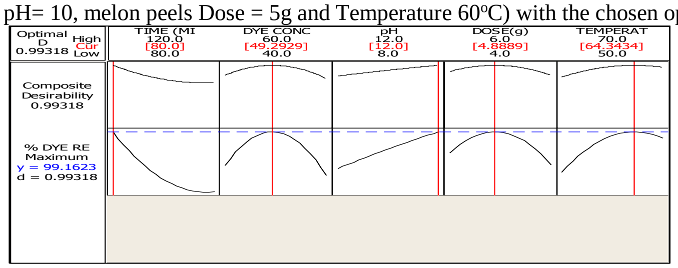

Fig.9. optimization plots for dye removal using melon peels.

The results in Fig 9 showed maximum response (y) of 99.1623% dye removal with optimized parameters of Time = 80minites, Dye conc = 49.2929mg/L, pH = 12, dose = 4.889 and temperature = 64.3434 respectively

However, these value are referred to as global solution for optimum % dye removal using melon peels.

Verification of predicted parameters.

The predicted global solution was verified by running the experiment with three replicate, and the result in table 5 shows a closed value for the average % dye removed.

Table 5 experimental runs using the optimized values.

Time (mins)	Dye conc (mg/L)	pH	Dose (g)	Temp. oC	%Y1	%Y2	%Y3	%Y_{avr}
80	4.3	12	4.9	64.3	98.4	98.1	98.6	98.37

CONCLUSION

The removal of ultramarine red from aqueous solution using melon peels was very successful. Optimization of the process variables enabled optimal conditions for the sorption process to be developed. This will assist in the adoption and utilization of the process. Over 98% colour removal was achieved, which makes the process efficient and attractable.

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