

Experimental Optimization of Naphthalene Bioadsorption from Aqueous Solution onto Water Melon Peels Using Response Surface Methodology

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Abstract: The objectives of this work were designed to study and optimize naphthalene bioadsorption from aqueous solution as well as to evaluate the effects of bioadsorption process variables such as initial naphthalene concentration, pH, temperature and contact time on the naphthalene bioadsorption potential of water melon. Response Surface Methodology (RSM) with a central composite face-centered design (CCFD) was used with three levels and four factors (initial naphthalene concentration, pH, temperature, contact time) as independent variables and percentage naphthalene removal as dependent variable (response). The naphthalene bioadsorption data was well fitted to a second-order quadratic polynomial regression model with a high coefficient of determination, $R^2 = 0.9997$ using Design-Expert Statistical program (v. 6.0.8). The quadratic regression model showed that the percentage naphthalene removal was significantly ($p < 0.05$) affected by the linear and interactive effects of initial naphthalene concentration, pH, temperature and contact time. Numerical optimization technique based on desirability function was carried out to optimize the bioadsorption process. The predicted optimum values for the four bioadsorption process variables to achieve a predicted maximum percentage naphthalene removal of 99.07 percent were found to be: Initial naphthalene concentration (270.20 mg/l), pH (5.85), temperature (47.45°C) and contact time (128.70 min). At these predicted optimum conditions, the experimentally observed percentage naphthalene removal was found to be 98.45 percent. The statistical analyses and the closeness of the experimental results and model predictions showed the reliability of the regression model. Thus, the results demonstrated the bioadsorption potential of water melon peels in the bioadsorption of organic pollutants from waste or contaminated waters.

Index Terms— Bioadsorption, Naphthalene, Optimization, Response surface, Water melon peels, Model, Regression

1 INTRODUCTION

Naphthalene is a hydrocarbon comprising two fused aromatic rings, with a melting point of 80.2°C and solubility in water at 25°C of 0.24mM [1, 2]. It is a raw chemical for a number of industrial syntheses, in particular the production of phthalic anhydride [3]. Naphthalene is a primary irritant and the US environmental protection agency (EPA) has classified it as a priority toxic pollutant [4]. Despite its low solubility in water it is frequently encountered in effluent in complex mixtures such as petroleum fractions, creosote or pharmaceutical waste [5]. In addition, naphthalene may originate from biological sources such as endophytic fungi [6,7], magnolia flowers [8], deer hair [9] and termite nests [10], or from plants and natural soil associated with termite nests [11]. Systematic exposure to naphthalene and its derivatives has been shown to give rise a variety of diseases and disturbances to the human metabolism [12, 13].

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of waste waters [14]. The removal of these kinds of pollutants from the environment cannot be accomplished by traditional methods [15]. It is now universally recognized that adsorption technology provides a feasible and effective method for the removal of pollutants from contaminated water resources and waste waters [16]. Activated carbons are the most commonly used adsorbent in the adsorption process due to their high adsorption capacity, high surface area and high degree of surface reactivity; however, regeneration is difficult and expensive [17]. In recent years, extensive research is now focused on new, efficient, low-cost and easily obtainable agricultural by-products such as orange peels, banana peels and banana stalks, plantain peels, spent tea

leaves, soya bean hull, grape fruit biomass [18, 19, 20, 21,22, 23,24] as adsorbents.

Bioadsorption capacity is highly influenced by some process conditions, such as temperature, pH solution, pollutant/contaminant concentration, stirring speed, contact time and particle size, among others. In addition, the physical-chemical properties of bioadsorbent and pollutants play significant role in bioadsorption processes. Several researchers have reported the individual effects of these process conditions. However, only a few researchers have reported the influence of the interactions between the process conditions using response surface methodology [25, 26, 27]. Response Surface Methodology (RSM) is a collection of mathematical and statistical approach for experimental design useful for analyzing and evaluating the effects of several independent variables and also interactive effects among the variables on the response. It also has an important application for searching optimum conditions of variable to predict targeted responses [28, 29]. Nevertheless, no study has been found in the literature for optimization of bioadsorption of organic pollutant/chemicals by agricultural solid waste neither modified nor unmodified. These interactions are required to generate a statistical model that represents adequately the response surfaces of bioadsorption processes.

Citrullus lanatus is a vine-like plant of Cucurbitaceae family. This flowering plant produces a special type of fruit known as water melon, a berry which has a thick rind (exocarp) and fleshy center (mesocarp and endocarp). The main purposes of this study are to investigate the potential of water melon peels as low-cost bioad-

sorbent in naphthalene removal from waste or contaminated water as well as to investigate the single and interactive effects of initial naphthalene concentration, pH, temperature and contact time on naphthalene bioadsorption using RSM. Empirical model correlating response to the four independent variables was then developed and optimization of process conditions for naphthalene bioadsorption was determined using central composite face-centered design (CCFD).

2.0 MATERIALS AND METHODS

2.1 Chemicals and stock solution

Naphthalene (99% pure, chemical grade) being products of Sigma-Aldrich, USA, was purchased from a chemical store, Lagos, Nigeria. Due to the low water solubility of naphthalene (polyaromatic hydrocarbons) the water– methanol solution was used as the aqueous solution. A stock solution was prepared by dissolving 1 g of naphthalene in de-ionized water-methanol solution. The water-methanol solution was composed of 50 ml of methanol and 950 ml of de-ionized water. From this original stock solution, test solutions with various concentrations (100, 200, 300 mg/l) were prepared with de-ionized water.

2.2 Adsorbent and preparation of adsorbent

Water Melon Peels (WMP), a waste product of water melon fruit pulp to be used as adsorbent were obtained from a local market in Ogbomoso, Nigeria. The water melon peels were washed with tap water, cut into small pieces and then sundried. The dried small-size WMP was washed repeatedly with hot water (70°C) to remove any soluble matter present and further oven-dried at 85°C for 48 h. The oven-dried small-size WMP was further reduced to small-sized particles by grinding using a serrated disk grinder. The powdered WMP particles were sieved using a 100-mesh sieve. The sieved WMP powdered particles were stored in an air-tight bottle prior to sorption experiment.

2.3 Batch adsorption studies

To optimize the range of batch adsorption experimentation for 2³ full-factorial Box-Behnken design, the bioadsorption tests were carried out in a glass-stoppered, Erlenmeyer flask with 100 ml of working volume and an initial concentration of 100 mg/l of naphthalene. A weighed amount (10 g) of bioadsorbent was added to the solution. The flasks were agitated for 180 min on a temperature-controlled water bath shaker at ambient temperature (25 ± 2°C). The influence of initial naphthalene concentration (100, 200, 300, 400, 500 mg/l), pH (5, 6, 7, 8, 9), temperature (30, 35, 40, 45, 50 °C) and contact time (30, 60, 90, 120, 150, 180 min) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual naphthalene concentration in the solution. Prior to analysis, samples were centrifuged to separate bioadsorbent from the sorbate and minimize interferences. At time t = 0 and equilibrium, the naphthalene concentrations were determined using UV-spectrophotometer at an absorbance wavelength of 275 nm. The percentage of naphthalene removal was calculated using Eq. (1) [30]:

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_o (mg/l) is the initial naphthalene concentration in waste water. C_t is the concentration of naphthalene in waste water at time, t .

2.4 Experimental design and data analysis

The Box-Behnken factorial experimental design employed

had four independent variables viz., initial naphthalene concentration, pH, temperature and contact time. Each of the independent variables was studied at three levels (1, 0, +1), with 30 experimental runs. The levels were selected based on above preliminary study results. The variables optimized were initial naphthalene concentration in the range of 100-300 mg/l, pH, 5 – 9, temperature, 30-50°C and time, 30-180 min, respectively. Change in naphthalene (i.e. percent naphthalene reduction) was considered as experimental response. Table 1 shows the coded and actual values of factors and levels used in the experimental design. The statistical software Design Expert6.0.8, (Stat-Ease Inc., Minneapolis, USA) was used to evaluate the analysis of variance ($P < 0.05$) to determine the significance of each term in the fitted equations and to estimate the goodness of fit in each case.

Table 1: Experimental range and levels of the variables

Dependent variable	- 1	0	+ 1
Initial Concentration (X ₁), mg/l	100	200	300
pH (X ₂)	5	7	9
Temperature (X ₃), °C	30	40	50
Contact time (X ₄) (min)	30	105	180

3.0 RESULTS AND DISCUSSION

3.1 Characterization of water melon peels

FT-IR spectrum of WMP were obtained in order to identify the functional groups like -OH, -CO, -CHO, N-H, - CONH, -C=C- and -COOH present in these peels that can be involved in bonding with 2,6-DCP during bioadsorption.. Table 3 shows the FT-IR spectrum elucidation of dried WMP structure.

Table 3: FT-IR spectrum elucidation of dried water melon peel structure

Wavelength Range (cm ⁻¹)	Absorption Peak Number (cm ⁻¹)	SuspectedFunctional Groups
3800-3600	3760	C-H (stretch), OH (stretch), OH (non-bonding), N-H (stretch)
3500-3300	3415	Bonded -OH group
3000-2800	2923.68	C-H stretching, CH ₂ and CH ₃ (alkane), COOH (carboxylic acid)
1650-1550	1615.55	C-H (alkane), C=C, C=O (stretch) Carbonyl groups
1450-1300	1409.23	C-O stretch C-H bend, C-O (alcohol), C-N, and OH (carboxylic acid)
1280-1240	1247.66	C-O (alcohol), C-H bend, SO ₃ ²⁻ stretching
1150-950	1034.33	C-O (alcohol), C-H, C=N bend (nitriles), PO ₄ ³⁻ stretching
650-480	540.31	N-containing bioligands, C-H bend, C=C (out of plane)

The absorption peaks (bands) at 3760 cm⁻¹ was assigned to OH stretch (alcohol and carboxylic acid), OH non-bonding, N-H stretch (amines) and C-H stretch (alkanes). The bands appearing at 3415 cm⁻¹ was assigned to bonded OH group, those at 2923.68 cm⁻¹ to C-H, CH₂, CH₃ (alkanes) and COOH (carboxylic acid) and the bands appearing at 1615.55 cm⁻¹ to C-H (alkane), C=C (aromatic) and C=O stretch. The absorption peaks (bands) at 1409.23 cm⁻¹ were attributed to C-H bend, C-O (alcohol), C-N, and OH (carboxylic acid) and that at 1247.66 cm⁻¹ to C-O (alcohol), SO₃²⁻ stretching, and C-H bend. The absorption peaks (bands) at 1034.33 cm⁻¹ were attributed to C-O (alcohol), C-H, C=N bend (nitriles), and PO₄³⁻ stretching while the

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Table 2: Experimental runs generated by Central Composite Rotable Design (CCRD).

Run	Concentration(mg/l)		pH		Temperature (°C)		Contact Time (min)	
	Actual	Coded	Actual	Coded	Actual	Coded	Actual	Coded
1	100	(-1)	5	(-1)	30	(-1)	30	(-1)
2	300	(+1)	5	(-1)	30	(-1)	30	(-1)
3	100	(-1)	9	(+1)	30	(-1)	30	(-1)
4	300	(+1)	9	(+1)	30	(-1)	30	(-1)
5	100	(-1)	5	(-1)	50	(+1)	30	(-1)
6	300	(+1)	5	(-1)	50	(+1)	30	(-1)
7	100	(-1)	9	(+1)	50	(+1)	30	(-1)
8	300	(+1)	9	(+1)	50	(+1)	30	(-1)
9	100	(-1)	5	(-1)	30	(-1)	180	(+1)
10	300	(+1)	5	(-1)	30	(-1)	180	(+1)
11	100	(-1)	9	(+1)	30	(-1)	180	(+1)
12	300	(+1)	9	(+1)	30	(-1)	180	(+1)
13	100	(-1)	5	(-1)	50	(+1)	180	(+1)
14	300	(+1)	5	(-1)	50	(+1)	180	(+1)
15	100	(-1)	9	(+1)	50	(+1)	180	(+1)
16	300	(+1)	9	(+1)	50	(+1)	180	(+1)
17	100	(-1)	7	(0)	40	(0)	105	(0)
18	300	(+1)	7	(0)	40	(0)	105	(0)
19	200	(0)	5	(-1)	40	(0)	105	(0)
20	200	(0)	9	(+1)	40	(0)	105	(0)
21	200	(0)	7	(0)	40	(0)	105	(0)
22	200	(0)	7	(0)	40	(0)	105	(0)
23	200	(0)	7	(0)	40	(0)	105	(0)
24	200	(0)	7	(0)	40	(0)	105	(0)
25	200	(0)	7	(0)	40	(0)	105	(0)
26	200	(0)	7	(0)	40	(0)	105	(0)
27	200	(0)	7	(0)	40	(0)	105	(0)
28	200	(0)	7	(0)	40	(0)	105	(0)
29	200	(0)	7	(0)	40	(0)	105	(0)
30	200	(0)	7	(0)	40	(0)	105	(0)

bioligands, C-H bend and C=C which are out of plane. The FT-IR spectra showed that carboxyl, carbonyl and hydroxyl groups were very prominent functional groups on the surface of the water melon peels which could play major role in naphthalene bioadsorption.

3.2 Naphthalene bioadsorption

Results of the naphthalene bioadsorption onto water melon with respect to percentage removal are presented in Table 4.

At each pair of experimental runs, run number 1 and 2; 3 and 4; 5 and 6; 7 and 8; 11 and 12; 13 and 14; 15 and 16; 17 and 18 had the same process conditions with different initial naphthalene concentration; results shows that percentage (%) naphthalene removal decreased with increased initial naphthalene concentration. This observation is due to the fact that all bioadsorbent have a limited number of active sites and at a certain concentration the active sites become saturated [31]. Effect of different solution pH were investigated at the same process condition of initial concentration, temperature and contact time for each pair of experimental runs (run numbers 1 and 3; 2 and 4; 5 and 7; 6 and 8; 13 and 15; 14 and 16; 19 and 25) and the findings demonstrated that increase in solution pH from 5 to 7 resulted in increased bioadsorption (i.e. percentage (%) naphthalene removal) and above the pH of 7, the naphthalene bioadsorption decreased. This observation is consistent with previous studies on the bioadsorption of naphthalene onto spent tea leaves [22], activated carbon derived from bean pods [15] and on chemically oxidized mesoporous carbon [32]. Solution pH affects the surface charge of the biosorbent and the metal speciation. Functional groups

of biosorbents can be protonated or deprotonated depending on their dissociation constant that is function of the solution pH. For example, carboxylic groups are ionized when solution pH is acidic [33, 34]. At this condition, positively charged pollutant/contaminant species can be adsorbed on negatively charged surface functional groups by means of electrostatic forces.

Relatively, run numbers 1 and 5; 2 and 6; 9 and 13; 10 and 14 had the same process operating condition with different temperature; finding shows that increase in temperature led to increased bioadsorption. This was mainly due to increased surface activity, suggesting that bioadsorption of naphthalene onto WMP was endothermic. A rise in temperature usually accelerates and increases mass transfer. Similar observations have been reported for the bioadsorption of naphthalene onto spent tea leaves [22] and organo-sepiolite [15].

Furthermore, runs number 1 and 9; 2 and 10; 3 and 11; 4 and 12; 5 and 13; 6 and 14; 7 and 15; 8 and 16 had the same process conditions for bioadsorption but carried out at different contact time; the results revealed that the amount of naphthalene removed from aqueous solution increased with increase in contact time.

Table 4: Experimental design and results for naphthalene bioadsorption onto water melon peels

Run	Percentage Naphthalene removal (%)	
	Observed Value	Predicted Value
1	51.00	51.13
2	47.00	47.40
3	45.00	44.88
4	42.00	41.52
5	51.50	51.52
6	49.00	48.42
7	46.50	46.89
8	44.00	44.16
9	90.00	90.02
10	89.00	88.41
11	86.00	86.38
12	85.00	85.15
13	91.50	91.78
14	90.50	90.80
15	90.00	89.77
16	89.50	89.17
17	97.00	96.14
18	93.00	93.97
19	95.00	95.02
20	91.00	91.08
21	92.70	92.80
22	95.00	95.00
23	51.00	51.08
24	93.00	93.02
25	96.00	95.36
26	95.50	95.36
27	95.00	95.36
28	95.50	95.36
29	95.00	95.36
30	95.50	95.36

3.3 Second order polynomial regression model and statistical analysis

The experimental data were fitted to a second order polynomial regression model (Eq. (2)) containing 4 linear, 4 quadratic and 5 interaction terms [35] using the same experimental design software to derive the equation for percentage (%) naphthalene removal.

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \beta_{12} AB + \beta_{13} AC + \beta_{14} AD + \beta_{23} BC + \beta_{24} BD + \beta_{34} CD \quad (2)$$

Where β_o is the value of the fixed response at the centre point of the design; $\beta_1, \beta_2, \beta_3, \beta_4$ are linear coefficients; $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are quadratic coefficients; $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are the interaction effect coefficients regression terms, respectively; A, B, C and D are the levels of independent bioadsorption process variables.

The significance of each coefficient in the equation was determined by Student t-test and P-values. F-test indicated that all the factors and interactions considered in the experimental design are statistically significant ($P < 0.05$) at the 95 per cent confidence level. The regression equation obtained after analysis of variance gives the

level of percentage (%) naphthalene removal (Eq. (3)) as a function of the different bioadsorption process variables: initial naphthalene concentration, pH, temperature and contact time. All terms regardless of their significance are included in the following equations:

$$Y_{\%N} = 95.36 - 1.08A - 1.97B + 1.10C + 20.97D - 0.31A^2 - 2.31B^2 - 1.46C^2 - 23.31D^2 + 0.094AB + 0.16AC + 0.53AD + 0.41BC + 0.66BD + 0.34CD \quad (3)$$

Where A is initial naphthalene concentration, B is pH; C is temperature and D is contact time.

To test the fit of the model, the regression equation and determination coefficient (R^2) were evaluated (Table 5). The model F-value of 3310.73 implies the model is significant for percentage (%) naphthalene removal. There is only a 0.01 per cent chance that a model F-value, this large could occur due to noise alone. The low probability value (< 0.0001) for naphthalene bioadsorption (i.e. % naphthalene removal) indicates that the model is significant. The value of the determination coefficient ($R^2 = 0.9997$) being a measure of goodness of fit to the model indicates a high degree of correlation between the observed value and predicted values. The determination coefficient ($R^2 = 0.9997$), suggests that more than 99.97 per cent of the variance is attributable to the variables and indicated a high significance of the model. Thus, 0.03 per cent of the total variance cannot be explained by the model. The fitted model is considered adequate if the F-test is significant ($P < 0.05$). The analysis of variances (ANOVA) quadratic regression model demonstrated that the model was highly significant as evident from the very low probability ($P < 0.0001$) of the F -test and insignificant result from the Lack of Fit model (Table 4). The Lack of Fit test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the factors. The Lack of Fit is designed to determine whether the selected model is adequate to describe the observed data, or whether a more complicated model should be used. The Predicted R-Squared value of 0.9983 is correspondently in reasonable agreement with the Adjusted R-Squared value of 0.9994. Adequate Precision measures the signal to noise ratio. A ratio > 4 is desirable. The ratio of 145.538 in this research indicates an adequate signal. This model can be used to navigate the design space. The coefficient of variation (CV) as the ratio of the standard error of estimate to the mean value of the observed response is a measure of reproducibility of the model, generally a model can be considered reasonably reproducible if its CV is not greater than 10 per cent. Hence, the low variation coefficient value (CV = 0.67 per cent) obtained indicates a high precision and reliability of the experiments.

Table 5: Analysis of variance (ANOVA) for the quadratic response surface model fitting to the bioadsorption of naphthalene onto water melon peels

Source	SS	DF	MS	F-value	Prob>F(P-value)
Model	13053.29	14	932.38	3310.73	<0.0001
Residual					
Lack of Fit	3.52	10	0.35	2.48	0.1638
Pure Error	0.71	5	0.14		
Correlation	13057.51	29			
Total					

$R^2 = 0.9997$; Adj $R^2 = 0.9994$; Predicted $R^2 = 0.9983$;

Adequate Precision = 145.538

SS = sum of square; DF = degree of freedom; MS = Mean square

The coefficient of the model (parameter estimation) and the corresponding P-values are presented in Table 6. The significance of regression coefficients was considered, ignoring those with an insignificant effect on the response at a significance level of 95 per cent.

The P-values of the regression coefficients suggest that among the independent test variables, linear, quadratic and interaction effects of solute concentration, temperature and process time are highly significant. The insignificant effects (factors and interactions) with P-values higher than 0.05 were ignored. In this study, A, B, C, D, B², C², D², AD, BC, BD and CD are significant model terms for naphthalene bioadsorption. Thus, statistical analysis of all the experimental data showed that initial concentration, pH, temperature and contact time had a significant effect on percentage (%) naphthalene removal in this study. Moreover, it is observed that contact time exerted more pronounced linear effect (higher positive coefficient value) on percentage (%) naphthalene removal and relatively followed by temperature. That is, percentage (%) naphthalene removal was mostly and positively influenced by contact time. The initial naphthalene concentration and pH negatively (due to negative coefficient value) influenced rate of naphthalene bioadsorption. The quadratic effect of the independent variables on the rate of naphthalene bioadsorption was negative.

Table 6: Coefficient of the model for naphthalene bioadsorption onto water melon peels

Factor	Coefficient Estimate	Standard Error	F-value	P-value
β_0	95.36	0.16	3310.73	0.0001*
β_1	-1.08	0.13	75.01	0.0001*
β_2	-1.97	0.13	248.61	0.0001*
β_3	1.10	0.13	77.34	0.0001*
β_4	20.97	0.13	28112.07	0.0001*
β_{11}	-0.31	0.33	0.90	0.3572
β_{22}	-2.31	0.33	49.23	0.0001*
β_{33}	-1.46	0.33	19.70	0.0005*
β_{44}	-23.31	0.33	5000.18	0.0001*
β_{12}	0.094	0.13	0.50	0.4906
β_{13}	0.16	0.13	1.39	0.2573
β_{14}	0.53	0.13	16.03	0.0011*
β_{23}	0.41	0.13	9.38	0.0079*
β_{24}	0.66	0.13	24.47	0.0002*
β_{34}	0.34	0.13	6.71	0.0205*

* Significant at $p < 0.05$

3.4 Influence of factors interaction on percentage naphthalene removal

Table 6 showed that percentage naphthalene removal was influenced positively by interaction of initial naphthalene concentration (A) and contact time (D), pH (B) and contact time (D), pH (B) and temperature (C); and, temperature (C) and contact time (D), respectively. However, there was no significant interaction between initial naphthalene concentration (A) and pH as well as between initial naphthalene concentration (A) and temperature (C). The linear effect of contact time and temperature exerted more pronounced positive influence (due to higher coefficient) on naphthalene bioadsorption than their interaction effects. The graphical representation of the response shown in Figs. 1 – 4 helped to visualize the effect of initial concentration (A), pH (B), temperature (C) and contact time (D) on percentage (%) naphthalene removal. The effect of interaction of initial concentration (A) and contact time (D) on percentage naphthalene removal is illustrated in Fig. 1. The plot shows that higher percentage naphthalene removal was attained with low initial naphthalene concentration as the contact time increased. When the bioadsorption was carried out at 40°C and pH 7, the highest percentage

naphthalene removal of 95.45 percent was obtained with 200 mg/l of initial naphthalene concentration and contact time of 105 min.

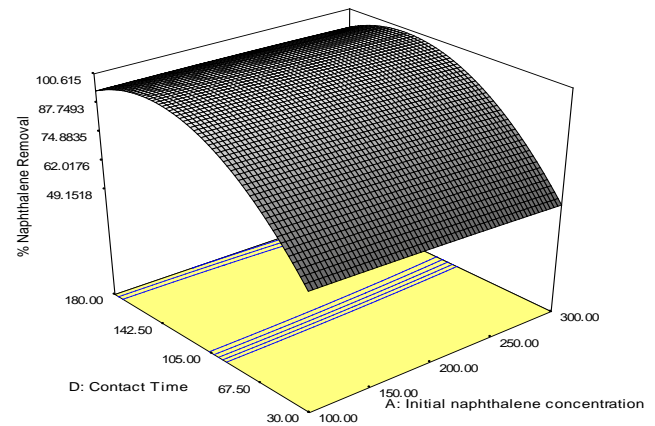


Fig. 1: Response surface plot for percentage naphthalene removal as a function of initial naphthalene concentration and contact time at 40°C temperature and pH 7

Fig. 2 shows the 3D response surface plot of the interaction effect between pH and temperature. This three dimensional plot explains that both pH and temperature has significant individual impact on percentage naphthalene removal as the individual coefficient of pH is negative and that of temperature is positive while their interaction effect is positive. However, the impact of temperature is more than that of pH as the individual coefficient value is higher for temperature (1.17). The percentage naphthalene removal increased with increase in temperature as pH increased from 5 to 7. Maximum percentage naphthalene removal of 95.45 percent was obtained at 40°C and a neutral pH of 7 when bioadsorption process was carried out at a contact time of 105 min using an initial naphthalene concentration of 200 mg/l. Further increase in both the pH (> 7)) and temperature (> 40°C) results in a significant decrease in percentage naphthalene removal.

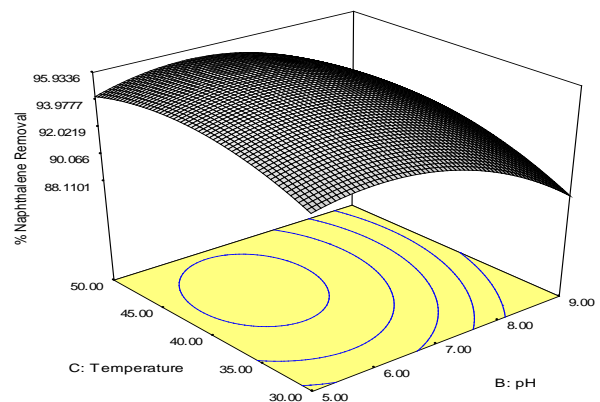


Fig. 2: Response surface plot for percentage naphthalene removal as a function of pH and temperature at 200 mg/l initial naphthalene concentration and 105 min contact time

The interaction effect of changing pH and contact time on percentage naphthalene removal is shown in Fig. 3. This plot demonstrates that both pH and contact time have positive mutual impact on percentage naphthalene removal during the bioadsorption process. At

a fixed initial naphthalene concentration and temperature, it is observed that percentage naphthalene removal increased with increase in pH from 5 to 7 and thereafter decreased as pH increased from 7 to 9. Maximum percentage naphthalene removal of 95.46 percent was obtained at a pH of 7 and contact time of 105 min when bioadsorption process was carried out at a temperature of 40°C using 200 mg/l initial naphthalene concentration.

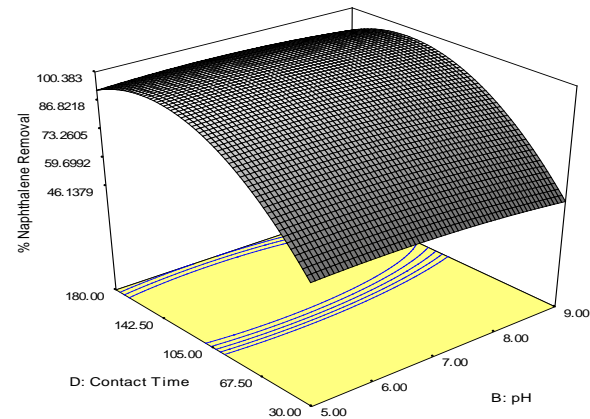


Fig. 3: Response surface plot for percentage naphthalene removal as a function of pH and contact time at 200 mg/l initial naphthalene concentration and temperature of 40°C

Fig. 4 shows the 3D response surface plot of the effect of interaction between temperature and contact time. This plot demonstrates that both temperature and contact time has significant individual impact on percentage naphthalene removal as the individual coefficient of temperature and contact time is positive and their interaction effect is positive. The percentage naphthalene removal increased with contact time as temperature also increased. At a fixed initial naphthalene concentration (200 mg/l) and pH 7, it is observed that maximum percentage naphthalene removal (95.46 percent) was attained at a temperature of 40°C and higher contact time of 105 min.

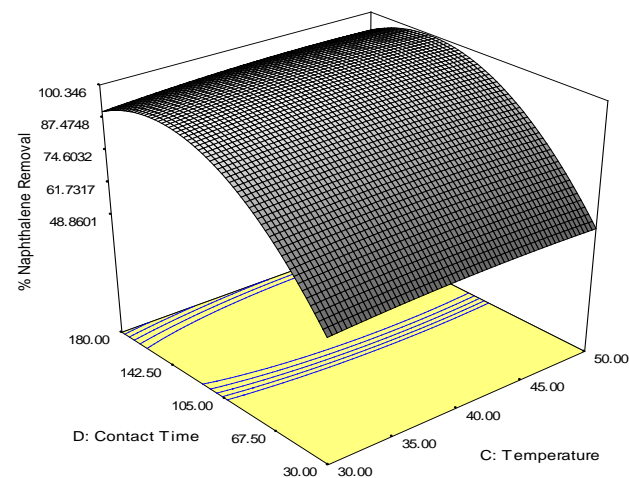


Fig. 4: Response surface plot for percentage naphthalene removal as a function of temperature and contact time at 200 mg/l

initial naphthalene concentrations and pH 7

3.5 Factor plot

The factor effect function plot (Fig 5) was used to assess the effect of each factor graphically. From the trace plot as shown in Fig 5, it can be seen that each of the four variables used in the present study has its individual effect on percentage naphthalene removal in the bioadsorption of naphthalene onto WMP. Gradual increase in contact time from low level (coded value -1) to a higher level (coded value +1) resulted in higher percentage naphthalene removal. Also, gradual increase in initial concentration, pH and temperature from low level (coded value -1) to a medium level (coded value 0) elicited marginal increase in percentage naphthalene removal and above the medium level, the percentage naphthalene removal decreased. Moreover, it is also to be noted from Fig 5 that over the range of 30 to 180 min of contact time, percentage naphthalene removal changed in a wide range. However, this was not the case for initial concentration, pH and temperature, respectively. This clearly indicates that keeping initial concentration, pH and temperature at the optimum level, a change in contact time will affect the percentage naphthalene removal process more severely than done otherwise.

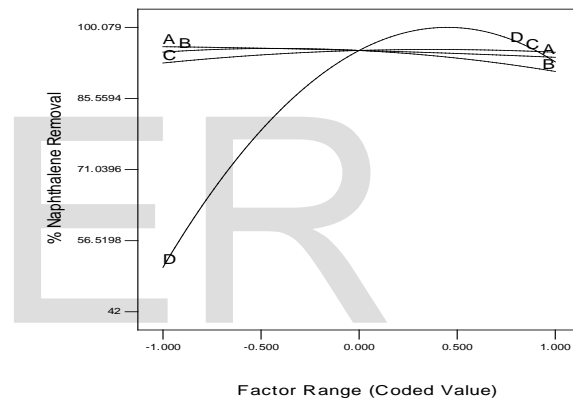


Fig. 5: Factor plot representing individual process variable effect on percentage naphthalene removal

3.6 Optimized condition for bioadsorption of naphthalene onto water melon peels

The optimum coded and uncoded value was obtained by solving equation 3 using numerical method. Numerical optimization based on desirability function was carried out. In order to provide an ideal case for naphthalene bioadsorption, the goal for initial concentration, pH, temperature and contact time was set in range based upon the requirements of the naphthalene bioadsorption and percentage naphthalene removal was set on maximize. The optimum coded and uncoded values of initial naphthalene concentration, pH, temperature and contact time were found to be 270.20 mg/l, 5.85, 47.45°C and 128.70 min, respectively, to attain a maximum percentage naphthalene removal of 99.07%. Desirability was 1.000 for the experiment (Fig. 6). Nevertheless, series of validation experiments were conducted to determine the optimum percentage naphthalene removal when the bioadsorption process variables were set at the favourable predicted optimum levels established above, through CCRD and RSM. At these optimum conditions, the percentage naphthalene removal was observed to be 98.45%. The results clearly indicated that no significant difference was observed.

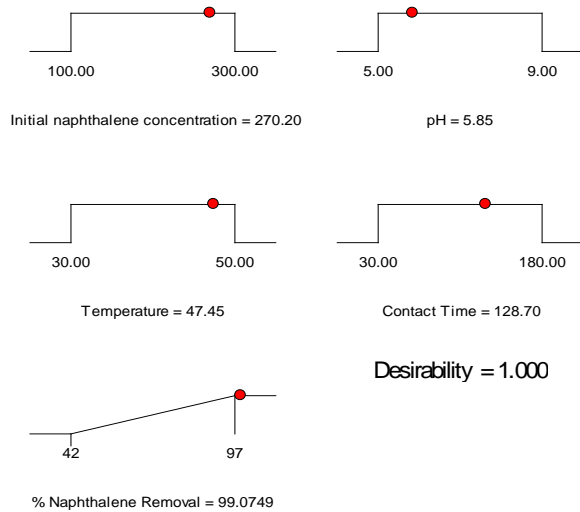


Fig. 6: Desirability plot to optimize bioadsorption experiment

4.0 CONCLUSIONS

This study demonstrated that the variables of initial naphthalene concentration, pH, temperature and contact time had a strong influence on the naphthalene bioadsorption using water melon peels as bioadsorbent. The percentage naphthalene removal during adsorption treatment was influenced positively by contact time and temperature, and negatively by initial naphthalene concentration and pH. The percentage naphthalene removal was influenced positively by interaction of initial naphthalene concentration and contact time, interaction of pH and temperature, interaction of pH and contact time and interaction of temperature and contact time, respectively. The obtained second-order polynomial quadratic regression model for the responses of percentage naphthalene removal was significant. Finally, the mathematical model obtained can also be employed to establish better process conditions.

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