Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **13(1),** 35-45, February **(2023)** *Res. J. Chem. Sci.*

Modeling and optimization of methyl violet 2B removal on activated carbon based neem hulls using Response Surface Methodology (RSM)

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Available online at: www.isca.in, www.isca.me
Received 7th December 2022, revised 8th January 2023, accepted 14th February 2023

Abstract

The direct discharge of industrial effluents loaded with dyes into nature constitutes a major environmental pollution problem. Thus, the treatment of these wastewaters is now a necessity to protect of people and the environment. The aim of this study was to determine the optimal operating conditions of the adsorption removal of Methyl Violet (MV) in aqueous solution. The activated carbon adsorbent that used in this study is chemically prepared from neem seed hulls. The Surface Response Methodology (SRM), was used for the optimisation and modelling of the adsorption fixation process of MV on the prepared activated carbon elaborated adsorbent. The effects of the operating parameters such as the initial concentration of MV in the solution (40 - 80mg.L^{-1}), the amount of activated carbon adsorbent (1-2g.L^{-1}), the contact time (50-100 min) and the initial pH of the solution (4 - 8) have been studied. The results for ANOVA analysis has showed that the quadratic model is the best fitting model to describe the fixation of MV on the activated carbon the studied adsorbent. The results has also showed that the adsorption of MV on activated carbon the elaborated adsorbent is strongly influenced by the studied parameters. Indeed, the dose of an activated carbon gets the most significant effect on dye removal. The optimal conditions of MV adsorption correspond to an initial MV concentration of 40.75mg.g^{-1}, an activated carbon dose of 1.78g.L^{-1}, a pH of 4.06 and a adsorption time of 99.40 min and allow a MV removal yield of 99.53 %. Therefore, the MSR can be used to model the removal of MV as a function of the parameters studied and to determine the optimal operating conditions for MV fixation on neem seed shell activated carbon. This study has showed that an activated carbon based on neem hulls is a credible option for the treatment of industrial effluents loaded with dyes.

Keywords: Adsorption, activated carbon, neem hulls, Methyl Violet, Response Surface Methodology.

Introduction

Textile industries, tanneries and paper mills are among the largest sources of organic pollution in the word[1-2]. They generate large quantities of wastewaters loaded with various types of dyes. Indeed, the worldwide production of dyes is estimated between700,000 and 1 million tonnes[3]. Every year, around 10-15% of the used dyes, are directly discharged into the environment without being priorly treated[4].

The direct discharge of these wastewaters can cause various environmental problems. Indeed, some dyes are harmful to humans because of their mutagenic and carcinogenic properties[5]. They can cause allergies and skin irritations[4]. They can also interfere with the good functioning of the central nervous system, in the human reproduction system, and in the kidney and liver functions[6]. In addition, dye-laden effluents have a negative ecological impact on the life of aquatic species when discharged directly into receiving environments, as they can affect water quality[7] and also decrease the scattering of sunlight in water[8]. As dyes absorb and reflect sunlight, this reduces photosynthesis and therefore impairs the growth of aquatic species[8].

In order to protect human-being sand to preserve the environment, several techniques are used to treat dye-laden wastewaters. Among these, we have flocculation, decantation[9,10], precipitation-filtration[11-12], reverse osmosis[13], advanced oxidation[14], photo catalytic degradation[15], ion exchange[16], etc. These conventional water treatment methods are very inefficient for the complete removal of many dyes due to their high water solubility and non-biodegradability[17].

Adsorption on activated carbon is the most widely used techniques due to its effective and simple implementation. Numerous studies have shown the effectiveness of activated carbons based on lignocellulosic materials such as coconuts[18], apricot nuts[19], date pits, rice husks[20], sugarcane bagasse[21], sorghum pods[22], tamarind seeds[23], etc., for the elimination of dyes in aqueous solution.

In Senegal, the number of neem plants (Azadirachta Indica A. Juss) is estimated between 18 and 30 millions[24]. The annul production capacity of a neem plant can reach 50 kg at maturity, i.e. 30kg of seeds including 15kg of hulls. The neem seed processing industry would therefore generate a large quantity of hulls in the form of solid waste, the recovery of which would contribute to the economy of the sector. These hulls could constitute a precursor material for the production of activated carbon elaboration of adsorbent, in the image of the work carried out on the hulls of jatropha[25], balanite[26], groundnut[27], baobab[28], mango[29], etc. The use of elaborated adsorbent based on neem seed hulls for the treatment of wastewater laden with colouring agents is not known yet.

The efficiency of the adsorption process depends on the one hand on the nature of the adsorbent used and on the other hand on the operating parameters of the adsorption[30-32]. In order have a good removal of dyes from wastewaters; the optimization of the adsorption process is necessary. Conventional modeling methods can only determine the individual effect of the parameters on the responses. The combined effects of the different factors cannot be determined. In addition, they are more time-consuming and require a significant number of experiments, and are therefore more expensive. This is in contrast to the Response Surface Methodology (RSM), which allows the maximum amount of information to be drawn from a minimum of experimental runs[33].

The aim of this study is firstly, to optimize the operating parameters of the adsorption of MV in aqueous solution by adsorption on activated carbon from neem hulls, a by-product of neem seed processing, considered as a waste product and secondly, to model the operating parameters of the adsorption process using the MSR. The influence of parameters such as initial methyl violet concentration, activated carbon dose, pH of the initial solution and contact time and their interactions were studied using the Composite Centered Design (CCD), a very efficient method suitable to optimizea study of independent process parameters.

Material and methods

Preparation of adsorbat: In this study, Methyl Violet (MV), hexamethylpararosaniline chloride, (Figure-1) has been used to prepare the synthetic dye wastewaters. The stock dye solution has been prepared by dissolving 1000mg of dye in 1 000mL of distilled water and the diluted solutions have been obtained by diluting the stock solution. Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of the solutions.

Pre-treatment of the raw material: The raw material used in this study is neem seeds collected in Babol, a village located in the Kaolack region (Senegal). After collection, the seeds are dried and sorted. Manual hulling is carried out to separate the hull from the kernel. The resulting hulls are washed thoroughly with distilled water to remove dust and other water-soluble compounds. After washing, the material is oven dried at 105°C for 24 hours and then ground using an electric knife mill (Saachi NB-0002) and sieved to obtain a powder size of less than 0.800 nm. The neem hulls powder thus obtained is used for the preparation of activated carbon.

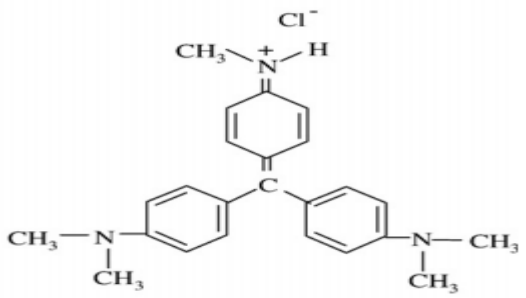

Figure-1: Structure of methyl violet.

Preparation of the adsorbent: Activated carbon is chemically prepared using phosphoric acid (H_3PO_4, 85%) as the activating agent. The precursor material is mixed with the acid solution at an impregnation ratio (precursor weight/activating agent weight) of 1/3. The mixture obtained is stirred for 1 hour at room temperature (about 25°C) to make sure of a good diffusion of the activating agent within the material. After impregnation, the material is then placed in an oven at a temperature of 120°C for 6 h. The impregnated particles are then carbonised directly in the oven at a temperature of 528°C for 1 hour. The resulting carbons are washed with distilled water to remove traces of the activating agent and other impurities until a wash water of neutral pH is obtained. Finally, the charcoals were dried in an oven at 105°C for 24 h and then stored in plastic jars.

Determination of the physico-chemical parameters of elaborated adsorbent: Determination of the humidity: The moisture content is determined according to the standard (NF V 03-603) by the loss of weight of a sample of approximately 1 g which has been dried in an oven at 105°C until a constant weight is obtained.

Determination of mineral content: The mineral content or ash is determined by loss of weight from the dry matter by incinerating it in an electrically heated muffle furnace at approximately 550°C for 3 hours (NF V 03-922). The calcined sample is then cooled to laboratory temperature in a desiccator and weighed.

Determination of the bulk density: For the determination of the bulk density, a 50mL flask is filled up to the mark with one mass of activated carbon. The density is calculated from the weight of the sample and the bulk volume of the sample.

Determination of the iodine value: The iodine molecule was chosen as a reference molecule to evaluate the adsorption capacity of solutes of small molecular size <10 Å [33]. The iodine

value is defined as the amount, in milligrams of iodine, adsorbed by 1g of adsorbent. The iodine value is determined according to the AWWA B 600 - 78 method[27]. A known weight of charcoal previously dried at 105°C for 24 hours is just together with a known volume of iodine solution of known concentration. The mixture is stirred for 30min before being filtered. The filtrate is assayed with a sodium thiosulphate solution using starch as a colour indicator. The amount of iodine adsorbed is then determined.

Determination of the methylene blue value: Methylene blue has been considered as a reference molecule to evaluate the adsorption capacity of solutes >15 Å in size[33]. Methylene blue value represents the quantity, in milligrams of methylene blue, fixed by 1g of adsorbent. A weight of previously dried charcoal is brought into forth 0.050mL of a methylene blue solution with a concentration of 200ppm for 30min under continuous stirring. After adsorption, the residual methylene blue concentration is measured using a UV spectrophotometer (Agilent Technologies Cary 60 UV-Vis) at a wavelength (λ= 654nm). The methylene blue index is calculated using the following formula (1):

$$I_{BM} = \frac{(c_i - c_f)V}{m_{CA}} * 100 \quad (1)$$

I_{BM} is the methylene blue index in mg.g-1, C_i the initial concentration of methylene blue in mg.L-1, C_f the final concentration of methylene blue in mg.L-1, V the volume of the adsorbed methylene blue solution in L, mCA the weight of adsorbent in g.

Adsorption of MV on elaborated adsorbent from neem hulls: The adsorption tests have been carried out in a stirred batch reactor in 250mL Erlenmeyer flasks, at 25°C and at a stirring speed of 400rpm. After each adsorption test, the suspension has been filtered and the filtrate was analysed using a spectrophotometer (UV-Vis Cary 60 Agilent Technologies) at a wavelength (λ=550nm) to determine the residual methyl violet concentration. The MV removal rate is calculated using the following equation (2):

$$T = \frac{(c_i - c_f)}{c_i} * 100 \quad (2)$$

T represents the MV removal in %, C_i, the initial concentration of MV in $mg.L^{-1}$, C_f the final concentration of MV in the solution after adsorption in $mg.L^{-1}$.

Choice of the experimental area: To optimize the operating parameters for the removal of methyl violet, the response surface methodology has been used. This is a statistical approach that allows a maximum information to be drawn with a minimum of experimental trials [33]. The factors investigated in this study were the initial concentration of methyl violet solution (X_1) (40-80 $mg.L^{-1}$), the dose of adsorbent (X_2) (1.00-2.00$g.L^{-1}$), the initial pH of the solution (4-8) (X_3) and the contact time (X_4) (50-100 min). The choice of these parameters and their range is based on the work of Yasin et al.[34-35] of Gebresemati et al.[36] and those of Singh and Bhateria[37].

Design of the experiment: Centred composite design: To investigate the influence of initial methyl violet concentration (X_1), adsorbent dose (X_2), initial solution pH (X_3) and contact time (X_4) and their interactions on methyl violet removal performance, the Composite Centred Design (CCD) has been chosen. The CCD has the highest efficiency for modelling and optimising a four-factor study. The number of experiments (N) to be performed and the distance (α) between an axial point and the centre point are given by the following relations (3) and (4) respectively.

$$N = 2^k + 2k + C \quad (3)$$

$$\pm \alpha = (2^k)^{1/4} \quad (4)$$

N, k and C represent the number of experiments to be performed, the number of independent factors, and the number of repetitions of the tests at the centre and α is the distance between the axial point and the centre point. Thus, the combination of the different factors is given by a matrix of 30 experiments among which we have 16 factorial, 8 axial and 6 central. The experimental domain is reported in Table-1.

Table-1: Experimental range of the factors for MV elimination.

Factors	Symbols	Levels			
		-α	Min	Max	+α
Initial concentration ($mg.L^{-1}$)	X_1	20	40	80	20
Adsorbent dose ($g.L^{-1}$)	X_2	0.50	1.00	2.00	0.50
pH	X_3	2	4	8	2
Contact time (min)	X_4	25	50	100	25

Determination of the monitored response: The response monitored is the methyl violet removal efficiency. The quadratic equation to calculate the predicted response from the factors studied is given as:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + (\sum_{i=1}^{n} b_{ii} X_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (5)$$

Where Y is the predicted response, b_0 the constant coefficient, bi the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients X_i and X_j are the coded values of the facteurs of the adsorption operating conditions.

The regression model of the experimental data has been presented, the statistical significance of the model and the regression terms have been evaluated by the analysis of variance

using the Design Expert software, version 11.1.2.0 (Stat-Ease Inc).

Results and discussion

Physico-chemical characterization of activated carbon: The characteristic physico-chemical parameters of the activated carbon produced are presented in Table-2.

Table-2: Physicochemical properties of activated carbon.

Parameters	Units	Values
Humidity	%	2.21
Ash content	%	1.13
Bulk density	$g.cm^{-3}$	0.45
Methylene value	$mg.g^{-1}$	39.21
Iodine value	$mg.g^{-1}$	788.20

The prepared activated carbon is characterised by a low moisture (2.21%) and ash (1.13%). This makes it an excellent adsorbent. The low bulk density ($0.45 g.cm^{-3}$) of activated carbon could be an advantage for its industrial use as a filter bed. The values obtained for the methylene blue value (39.21 $mg.g^{-1}$) and iodine value ($788.20 mg.g^{-1}$), which respectively indicate the capacity of the carbon to adsorb large molecules such as organic molecules and small molecules such as heavy metals, highlight the heterogeneity of the carbon's porosity.

In sum, these results show that carbon can be used to treat wastewaters containing pollutants of different nature.

Experimental results of the experimental matrix: Table-3 shows the operating conditions of 30 experiments carried out and the experimental results obtained.

The responses obtained show a pyrolysis yield that varies between 90.64 and 99.43 % in a relatively dispersed manner, indicating the relevance of the experimental area chosen. This variation also indicates that the factors studied have a strong influence on the adsorption of methyl violet.

Regression model: The choice of a model is generally based on a low standard deviation, a correlation coefficient close to unity, and the model should not be aliased[38]. Analysis of the different models studied (Linear model, 2FI model, Quadratic model, and Cubic model) shows that the Quadratic model is the most adequate to predict the removal rate of methyl violet with a correlation coefficient (R^2) equal to 99.56%. The difference between the predicted R^2 (97.71%) and the adjusted R^2 (99.14%) is less than 0.2% (Table-4). This shows that the quadratic model describe well the studied phenomenon[38].

The adequate accuracy (69.07) greater than 4 indicates a good predictive ability of the chosen model[38]. The standard derivation coefficient (0.47%), associated with the model, is very low. The low Coefficient of Variation (CV=0.19) shows the reliability of the results (reproducibility of the experiments)[39]. Thus, the quadratic mathematical equation to calculate the predicted elimination rate from the different factors studied is illustrated by the following equation (6):

Table-3: Matrix of experiments and experimental results.

Runs	Factors				Response
	X_1 ($mg.L^{-1}$)	X_2 ($g.L^{-1}$)	X_3 (-)	X_4 (min)	Y (%)
1	80	2.00	4	50	98.05
2	60	1.50	6	125	98.17
3	40	1.00	8	100	96.80
4	60	1.50	6	75	96.68
5	60	1.50	6	75	96.64
6	40	1.00	4	100	97.75
7	80	1.00	8	50	95.01
8	60	1.50	6	75	96.65
9	40	2.00	8	100	98.24
10	20	1.50	6	75	99.08
11	40	2.00	4	50	98.34
12	80	1.00	4	50	92.71
13	40	2.00	4	100	99.43
14	80	2.00	8	50	98.88
15	60	1.50	2	75	97.53
16	40	2.00	8	50	96.57
17	80	1.00	8	100	96.02
18	60	0.15	6	75	96.78
19	80	2.00	4	100	97.35
20	60	1.50	10	75	98.28
21	60	0.5	6	75	90.64
22	80	2.00	8	100	98.82
23	40	1.00	4	50	95.67
24	80	1.00	4	100	93.41
25	40	1.00	8	50	94.00
26	60	1.50	6	25	95.69
27	60	1.50	6	75	96.82
28	60	2.50	6	75	96.71
29	60	1.50	6	75	96.94
30	100	1.50	6	75	97.51

$$Y\ (\%) = 96{,}7517 - 0{,}40375X_1 + 1{,}51875X_2 + 0{,}130417X_3 + 0{,}564583X_4 + 0{,}474375X_1X_2 + 0{,}799375X_1X_3 - 0{,}418125X_1X_4 - 0{,}184375X_2X_3 - 0{,}286875X_2X_4 + 0{,}140625X_3X_4 + 0{,}384063X_1^2 - 0{,}770938X_2^2 + 0{,}286563X_3^2 + 0{,}0428125X_4^2 \quad (6)$$

Coefficients with a positive sign have a synergistic effect on the response studied, whereas those with a negative sign have an antagonistic effect. Thus, we can see that the removal rate increases with the dose of activated carbon, the pH of the initial solution and the contact time and decreases with the initial concentration of MV.

The adequacy of the developed mathematical model can also be assessed based on diagnostic plots such as the percentage normal probability versus residuals plots (Figure-3) which show that the residuals are randomly dispersed without outliers around ± 3 and follow a straight line, which shows that the residuals are normally distributed. The experiments therefore come from a normally distributed population. This means that the normality test is therefore satisfied[40].

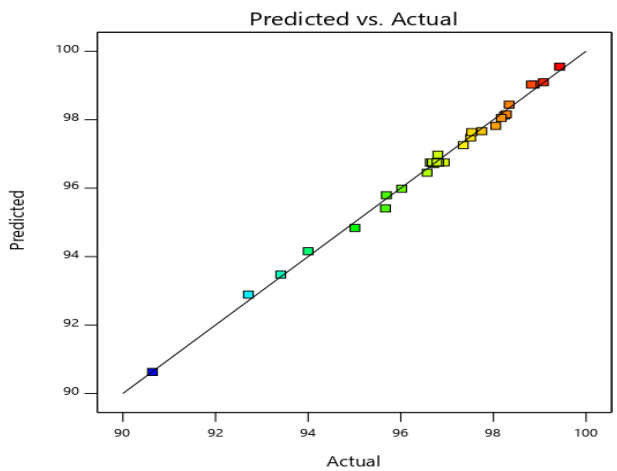

Figure-2: Predicted versus experimental for MV removal.

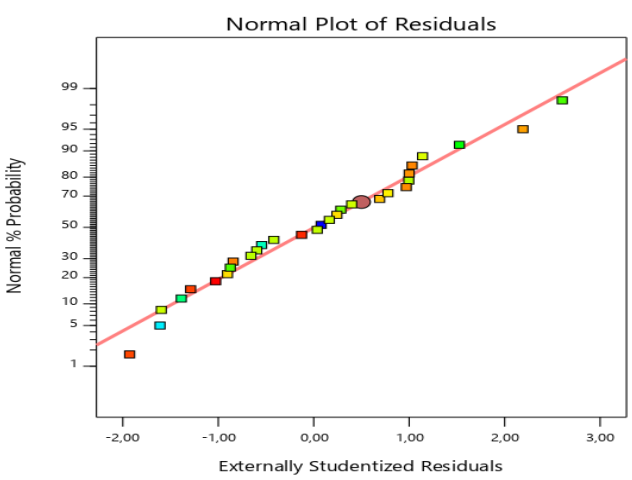

Figure-3: Normal probability plot.

Table-4: Statistical coefficients of quadratic model for MV removal.

Variables	Values
Standard derivation	0.1826
Mean	96.71
Coefficient of derivation (%)	0.1889
R^2	99.56
Adjusted R^2	99.14
Predicted R^2	97.71
Adequate precision	69.07

Statistical analysis of the model results: We have used ANOVA to evaluate the relevance and significance of the factors effects. The model ANOVA results (Table-5) shows that the p-value of the model is less than 0.05. This means that the chosen model is significant[39]. Furthermore, the results also show that all terms have significant effects except the X_1X_2 interaction. However, the dose of activated carbon (X_2) has the most significant effect on the elimination of methyl violet followed by the initial concentration of MV in the solution. The results also show a non-significant lack of fit of the chosen model. The lack of fit measures the difference between the residual error and the pure error. A non-significant lack of fit is desirable[41-42].

Effects of the factors studied on MV adsorption: Perturbation diagrams were used to study the effects of the factors and 3D response surface plots were used to study the effects of their interactions on MV removal.

Effect of the factors on the fixation of MV: The perturbation diagram for the adsorption of methyl violet on activated carbon is shown in Figure-4. The results obtained show that all the factors studied have an influence on the methyl violet removal rate. However, the removal rate is more sensitive to the variation of the adsorbent mass.

Effects of interactions on MV adsorption: Responses surface showing the interactions of the different parameters on MV removal are presented in 3D (Figure-5).

Figure-5(a) shows the effect of the interactions between the initial concentration and the amount of adsorbent on the removal of MV shows that the latter is the most influential factor on the removal of MV. This result is in agreement with the work of Nojavan and Gharbani, on the optimisation of the adsorption of blue reagent 21 on kaolin[43]. Indeed, the removal rate increases with the mass of activated carbon and the initial

concentration of MV. This evolution is linked to the increase in the overall exchange surface with the mass of activated carbon[44]. The decrease of the fixation rate with the initial concentration of the VM solution can be explained, on the one hand, by a saturation of the adsorption sites at high concentrations leading to increased electrostatic repulsions between the molecules on the surface of the activated carbon at high concentrations[45] and, on the other hand, to the availability of binding sites in relation to the amount of VM at low concentrations.

Table-5: ANOVA for methylene violet removal quadratic model.

Source	F-value	p-value	Comment
Model	240.97	< 0.0001	Significant
X_1-Initial concentration in VM	117.27	< 0.0001	
X_2-Adsorbent dose	1659.40	< 0.0001	
X_3-Initial pH of solution	12,24	0.0032	
X_4-Contact time	229,32	< 0.0001	
X_1X_2	107.93	< 0.0001	
X_1X_3	306.47	< 0.0001	
X_1X_4	83.85	< 0.0001	
X_2X_3	16.30	0,0011	
X_2X_4	39.47	< 0.0001	
X_3X_4	9.48	0,0076	
X_1^2	121.28	< 0.0001	
X_2^2	488.66	< 0.0001	
X_3^2	67.52	< 0.0001	
Lack of Fit	3.13	0.1097	Non significant

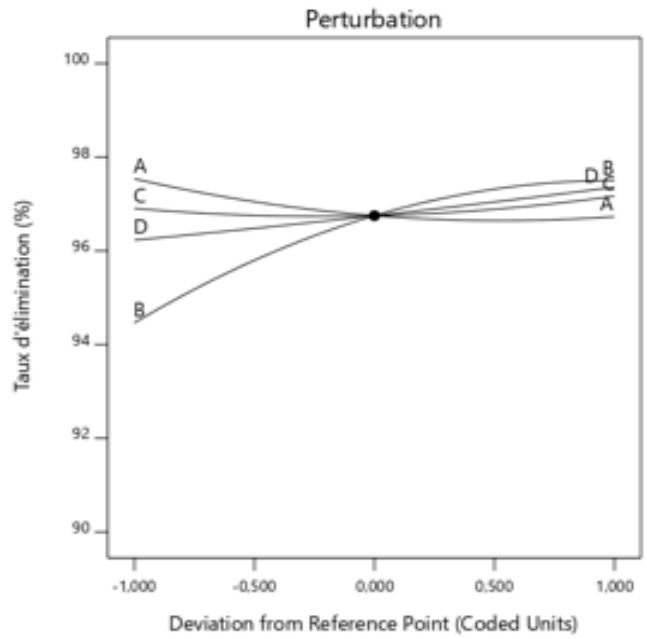

Figure-4: Influence of the factors studied on the removal of MV.

Figure-5(b) which shows the interactions between the initial concentration of MV and the initial pH of the solution shows that the removal rate is proportional to the pH and inversely proportional to the initial concentration of MV. Thus, at low pH, the positive charge of the solution (H+) is high. This can lead to a protonation on the surface of the adsorbent and thus create an electrostatic repulsion on the surface of the adsorbent and the positively charged MV dye molecule. On the other hand, as the pH of the initial solution increases, the negatively charged functional groups on the surface of the activated carbon increase, which promotes electrostatic attractions between the adsorbent and MV solution interface, resulting in an increase in the removal rate of MV[3,5].

Figure-5(c) shows the variation of the removal rate with initial concentration and contact time. Analysis of the results shows that the fixation rate naturally increases with the time and decreases with increasing initial concentration.

Figure-5(d) shows the effect of the interaction between the adsorbent dose and the initial pH of the solution. It shows that the fixation rate increases very significantly, as already indicated, with the amount of adsorbent, whereas the amount adsorbed increases only slightly with the initial pH of the solution.

Figure-5(e) shows the combined effect of adsorbent dose and contact time on the removal rate. The removal rate increases, as indicated, considerably with the mass of activated carbon but also with the contact time.

Figure-5(f) showing the effect of the interaction between time and initial pH of the solution indicates that these have no significant effect on the elimination of MV. The percentage fixation of MV increases slightly with increasing contact time. This can be explained by the fact that the adsorption of MV on activated carbon is a rapid process and the first phase of adsorption, where the removal rate increases significantly with contact time, seems to take place during the first minutes of the process due to the availability of a important adsorption sites on the surface of the activatedcarbon[46].

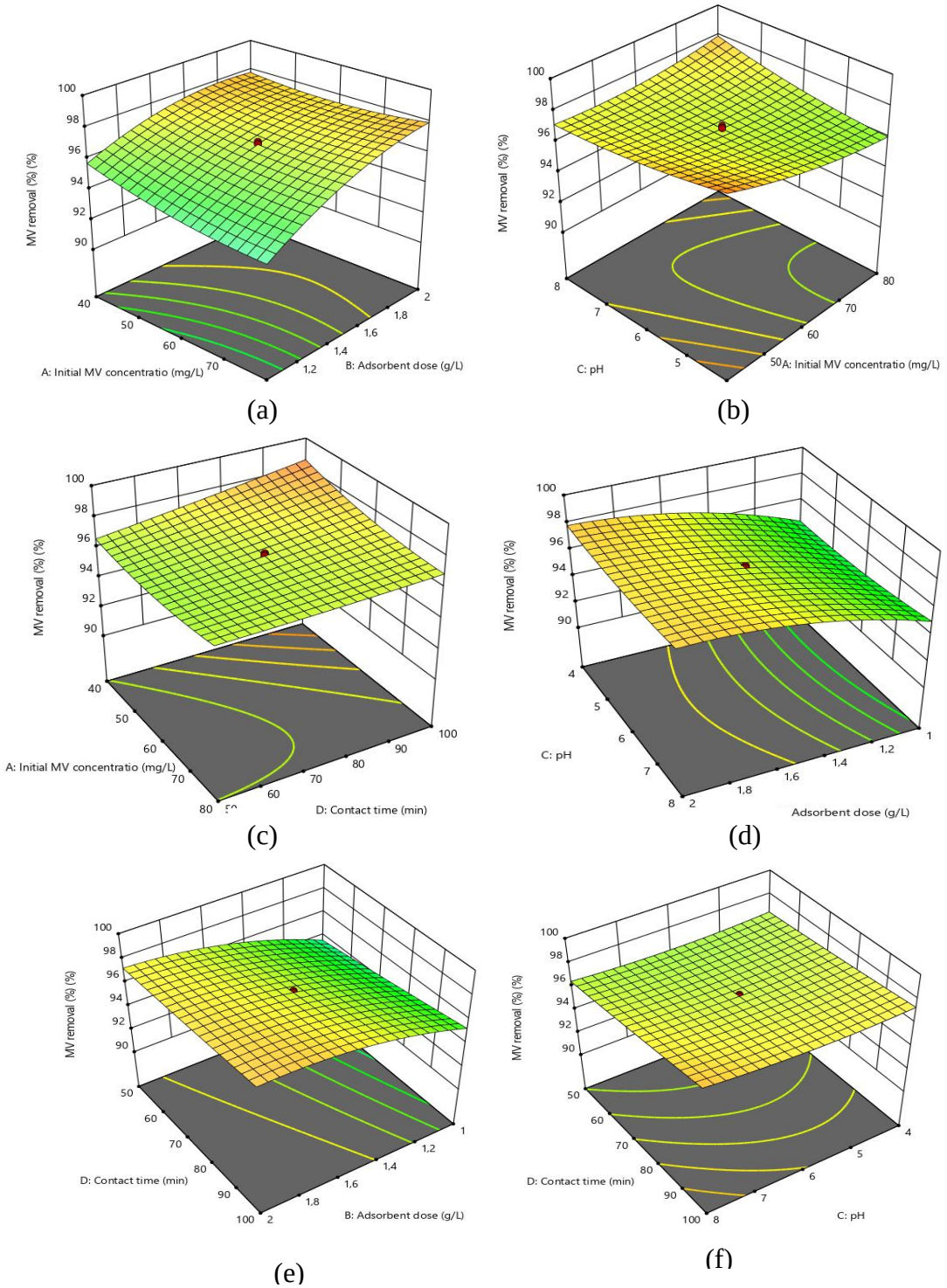

Figure-5: Surface plot of methyl violet removal efficiency on neem shell activated carbon.

Optimisation of the VM adsorption process on activated carbon: In order to optimize the operating parameters for the adsorption of MV in the studied experimental area, the Desirability Function Approach (DFA) was applied with the help of the Design Expert software version 13. Thus, the maximum value of desirability obtained corresponds to the optimal conditions of dye adsorption. The results obtained (Figure-6) show that the optimum operating conditions for the adsorption of MV on elabored adsorbent in the experimental field studied correspond to an initial concentration of MV of 40.75mg.L^{-1}, a dose of adsorbent of 1.78g.L^{-1}, a pH of the initial solution of 4.06 and a contact time of 99.40 min, and allow 99.53% of the dye to be removed.

Thus, in order to minimize the cost of the process for economic reasons, it is interesting to determine the optimal operating conditions for the adsorption of MV with a minimal dose of adsorbent in a short time for values of initial MV concentration and initial pH of the solution located in the studied experimental range.

The results (Figure-7) show that the optimal conditions for an industrial process correspond to an initial MV concentration of 40mg.L^{-1}, an amount of adsorbent of 1.08g.L^{-1}, an initial solution pH of 4.00 and a time of 50 min and allow 95.85% of the dye to be removed.

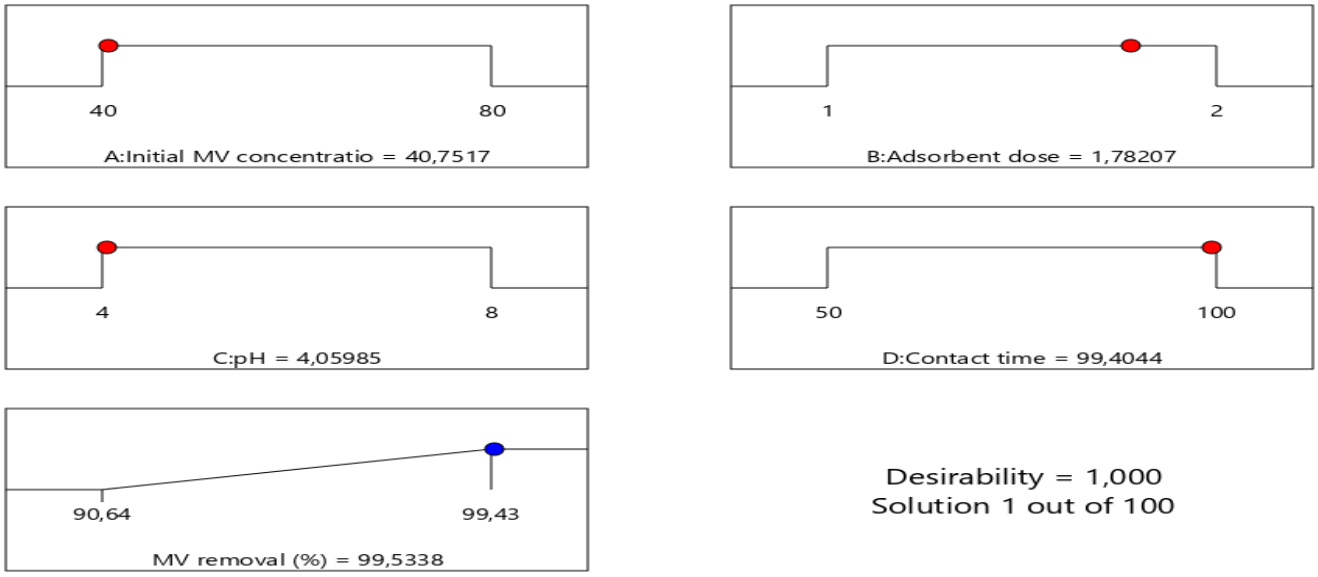

Figure-6: Optimal conditions for MV adsorption in the experimental area studied.

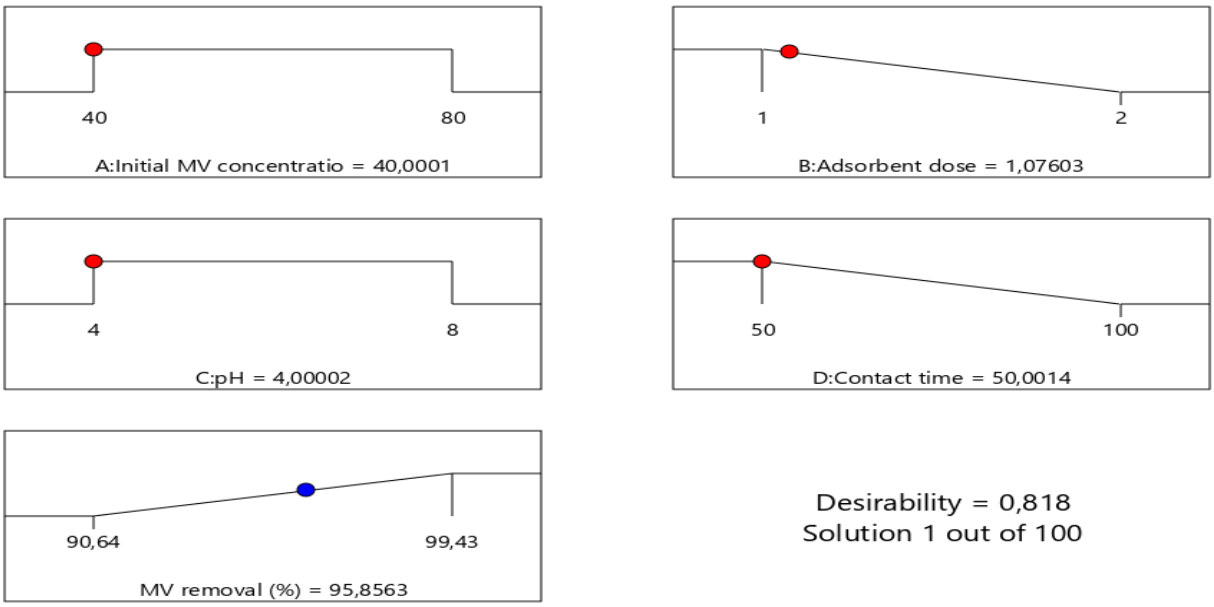

Figure-7: Optimal conditions of economic adsorption of MV.

Validation of the model: To access the validity of the model, we have carried out adsorption tests under the optimal operating conditions of the experimental field studied. The experimental results and the results predicted by the models are shown in Table-6. The results obtained show a small difference (0.05%) between the experimental value (99.48%) and the predicted value (99.53%). This shows that the models developed are valid and applicable to the predicting responses.

Table-6: Model validation.

Facteurs				Response	
X_1 ($mg.g^{-1}$)	X_2 ($g.L^{-1}$)	X_3 (-)	X_4 (min)	Y_{Exp} (%)	Y_{Pred} (%)
40.75	1.78	4.06	99.40	99,48	99,53

Conclusion

The results of the present study have shown that neem seed hulls activated carbon are effective in treating dye laden effluents like methyl violet. The optimum conditions for removal of this dye by adsorption on neem hulls labored adsorbent have been determined by the response surface methodology using the centered composite design. The results showed that the quadratic model was the best-fitting model to predict methyl violet removal as a function of the factors studied. The ANOVA has shown that the adsorbent dose was the most influential factor on methyl violet removal. The order of influence of the parameters is as follows: activated carbon dose > contact time > initial MV concentration > pH of the initial solution. The best removal rate (99.53 %) is obtained at a concentration of 40.75mg.L^{-1}, an activated carbon dose of 1.78 g.L^{-1}, a pH of 4.06 and a contact time of 99.40min. In sum, this study has shown the interest of using this type of adsorbent in the wastewater treatment loaded with recalcitrant contaminants such as dyes.

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