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Optimization and modelling of the preparation of activated carbons from neem (*Azadirachta Indica* A. Juss) seed hulls based on Response Surface Methodology (RSM)

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Abstract

The activated carbons have been elaborated from neem seed hulls by chemical process using H_3PO_4 as the activating agent. The effects of impregnation ratio, temperature and pyrolysis time on yield, methylene blue and iodine values were studied. The Response Surface Methodology (RSM) was used for process optimization and modelling. The influence of the parameters was studied by analysis of variance (ANOVA) method to determine significant (items) factors. The common optimum conditions to produce an activated carbons determined using the desirability function of the design Expert 11 software, correspond to an impregnation ratio of 3, at a pyrolysis temperature of 527.81°C for 1h. The optimal conditions resulted in 63.13% yield of activated carbon with methylene blue and iodine values of 39.20mg.g^{-1}and 788.24 mg.g^{-1} respectively. The ANOVA showed that temperature was the most effluent factor on pyrolysis yield while the impregnation ratio was the most influential factor on methylene blue and iodine adsorption capacity.

Keywords: Neem seed hulls, activated carbon, Box-Behnken design, optimization, methylene blue number, iodine number.

Introduction

Increasingly, industrial and urban wastewaters are contributing to significant parts of environmental pollution. Most of these wastewaters contain various contaminants (heavy metals, dyes, organic matter, etc.) which can bring about serious environmental problems and threats to human health when directly discharged into the environment, because the greatest part are dangerous and can cause cancer to human beings even at low concentrations[1]. The treatments of wastewaters containing recalcitrant molecules before discharge into the receiving environment are therefore more than necessary.

To minimize the impacts of these discharges on ecosystems, several technical treatments can be used, such as flocculation, settling[2-3], precipitation-filtration[4-5], reverse osmosis[6], advanced oxidation[7], photocatalytic degradation[8], ion exchange[9] etc. Adsorption is the most widely used technique to remove of recalcitrant molecules due to its efficiency compared to other processes[10]. Among the advantages of adsorption are its implementation simplicity, its cheapness and its possibility of regeneration of the adsorbent[11]. Several adsorbents can be used to treat wastewaters: activated carbon, zeolite, silica gel, etc. Activated carbons are the mostly used as adsorbent. A lot of works has been done on activated carbon production from industrial waste and lignocellulosic materials such as coconut[12], rice husk[13], sugarcane bagasse[14], peanut hulls[15], tamarind seed[16], lignin[17], jatropha hulls[18], desert date palm hulls[19], baobab hulls[20], mango hulls[21] etc.

The performances of activated carbon are strongly influenced by the elaboration process. However, several parameters are likely to have an influence on this process, of which, the most important are the impregnation ratio, the pyrolysis conditions (temperature and time)[22-23]. Therefore, the optimization of these parameters is necessary to produce quality activated carbon. For this purpose, several methods can be used. The response surface methodology (RSM) is one of the most effective methods[21, 24]. This methodology is a statistical approach that allows the maximum amount of information to be extracted with a minimum of experimental tests[22]. It makes it possible to model, to optimize and to analyse problems that the main reactions are impacted by numerous factors. The response surface methodology has several types of plans, including the central composite plane, the Box-Behnken plane, optimal planes, etc. The optimization of elaboration process of activated carbons from neem seed hulls using RSM is not well known yet.

The aim of this work is, in one point, to determine the optimal conditions to elaborate activated carbons, on the other hand (on another point) S to model the operating parameters of the synthesis of activated carbon based on neem hulls, a lignocellulosic waste widely available in Senegal[25-26], by chemical activation. The surface response methodology was used based on the Box-Behnken plane to reach the effects of impregnation ratio, pyrolysis conditions (temperature and time) on pyrolysis yield, methylene blue and iodine numbers.

Materials and methods

Raw material pretreatment: The raw material used was pulped neem seeds collected in Babol, a village located in the Kaolack region (Senegal). After collection, the seeds are sorted and dried. Manual shelling is carried out to separate the hull from the kernel. The resulting hulls are washed thoroughly with distilled water. The material is then dried in an oven at 105°C for 24 hours and then ground using an electric knife mill (Saachi NB-0002) and sieved to obtain particles with a diameter less than 800 µm.

Production activated carbon process: The process called wet process was used to prepare activated carbons. For this, neem hulls powders with less than 800µm of diameter are brought into contact with the activating agent (H_3PO_4) in a well-defined impregnation ratio. The mixture is stirred for 1h in a room temperature (25°C) to ensure good diffusion of the activation agent within the material. The mixture is then placed at 120°C for 6h in an oven. After drying, the material is carbonized in an oven at a temperature between 400 and 600°C for a defined period of time. The charcoals thus obtained are washed with distilled water and then dried under study at 105°C for 24h.

We use the following formula to calculate the impregnation ratio (1):

$$X = \frac{M_A}{M_P} \quad (1)$$

Where: X is the impregnation ratio, M_A is the weight of the acid solution (g) and Mp is the weight of the precursor (g).

Determination of some monitored responses: The performances of the activated carbons have been measured by determining three parameters, namely activated carbon yield, methylene blue and iodine values.

Determination of the pyrolysis yield: The pyrolysis yield, determined by calculation, results in the biomass loss of weight during its pyrolysis. It is calculated due to the following relationship (2):

$$R = \frac{Mf}{Mi} * 100 \quad (2)$$

Where: R is the pyrolysis yield (%); Mf the mass after pyrolysis (g); Mi the mass before pyrolysis (g).

Determination of the iodine number: The iodine molecule was chosen as the reference molecule to evaluate the micro-porosity of activated carbons[22]. The iodine number is determined according the AWWA B 600-78 method. A known mass of carbon previously dried at 105°C for 24h is brought into contact with a known volume of iodine solution of a known concentration. The mixture is stirred for 30 minutes (and then separated) before being separated. The filtrate is assayed with a solution of sodium thiosulphate using starch as a colour indicator. The amount of iodine adsorbed is then determined.

Determination of the methylene blue value: Methylene blue has been chosen as reference molecule to evaluate macro-porosity of activated carbons[22]. In other words, the methylene blue index is considered as a basis to measure the adsorption capacity of large and medium sized molecules. A mass of approximately 1g of previously dried charcoal is brought into contact with 50mL of a methylene blue solution with concentration 200mg.L^{-1} for 30 min under continuous stirring. After adsorption, the residual methylene blue concentration is measured using a UV spectrophotometer (Agilent Technologies Cary 60UV-Vis) at a wavelength (λ= 654 nm). The methylene blue value is calculated according to the following formula (3):

$$I_{MB} = \frac{(c_i - c_f)V}{W_{CA}} \quad (3)$$

Where I_{MB} represents the methylene blue value (mg.g^{-1}); C_i is the initial mass concentration of methylene blue (mg.L^{-1}); C_f is the final mass concentration of methylene blue (mg.L^{-1}); V is the volume of the solution adsorbed methylene blue (L); W_{AC}: Mass of the adsorbent (g).

Design of a plan experiments: Box-Behnken plane: The Box-Behnken plans used in this study are response surface designs developed by George BOX and Donald BEHNKEN[27]. This methodology is a statistical approach which makes it possible to obtain a maximum of information on the variation of a parameter with a minimum of experiments[22]. The number of runs, N, to be carried out is given by the following relationship (4):

$$N = 2k(k-1) + r \quad (4)$$

Where k stands for the number of factors and r represents the number of replicates in the centre trials.

The combination of the different factors is given by the Box-Behnken matrix with 3 factors at three levels comprising 17 experiments including 5 centre trials (Table-3). The center trials were used to assess the experimental error and reproducibility of the experiments. The responses followed for this experimental design are pyrolysis yield, methylene blue and iodine values. The mathematical equations to calculate the responses as a function of the factors are written in the following form:

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

Where Y represents the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i, x_j are the coded values of the operating parameters.

Choice of experimental area: The operating parameters (factors) studied during the elaboration of activated carbons are: impregnation ratio (X_1), pyrolysis temperature (X_2) and pyrolysis time (X_3). The choice of the areas of variation of these parameters was guided by the works of Anuwar and Khamaruddin[28], Lia et al.[29] and Ahmad et al.[30]. The experimental range is presented in Table-1.

Table-1: Experimental domain of activated carbons process,

Factors	Units	Coded factors	Levels	
			Low	High
Impregnation ratio	-	X_1	1	3
Pyrolysis temperature	°C	X_2	400	600
Pyrolysis time	min	X_3	60	180

The design expert software, version 11.1.2.0 (Stat-Ease Inc) was used to establish the 3-factor Box-Behnken plane with 12 trials and 5 trials in the centre for the exploitation of the experimental results and for the statistical analysis of the studied models.

Results and discussion

Experimental results: The responses obtained (Table-2), (156.14% to 74.35% from pyrolysis yield, 672.52 to 830.40 $mg.g^{-1}$ from iodine value and 1,00 to 39.20$mg.g^{-1}$ from methylene blue value), vary in a relatively dispersed way that indicate the relevance of the experimental area chosen for the different factors. These results also show that the factors studied influence strongly the different responses monitored (pyrolysis yield, methylene blue and iodine numbers). Similar ranges of pyrolysis yield (55.12% to 77.7%)[32], (16.10% to 80.06%)[33] are reported in the literature. Similarly, similar iodine values (611.00 $mg.g^{-1}$ to 1024.00 $mg.g^{-1}$) are reported by Duan et al., who worked on the optimization of activated carbon preparation from jatropha hulls[22]. The values of methylene blue index (1.00 to 39.20 $mg.g^{-1}$) obtained are comparable with those of activated carbon based on sugar dregs (2.73 $mg.g^{-1}$ to 23.69 $mg.g^{-1}$)[10]. The results also show that the optimum operating conditions (Table-3) are not the same for the three responses. The best pyrolysis yields are obtained at an impregnation ratio of 2 and at the lowest temperatures and pyrolysis times. The best methylene blue and iodine values are obtained at an impregnation ratio of 3 and at the highest pyrolysis temperatures of 600°C and 500°C respectively for the methylene blue and iodine values. This shows that the factors studied do not have the same effects on pyrolysis yield, methylene blue and iodine values.

Table-2: Box-Behnken matrix of experimental conditions and experimental results.

Runs	Factors			Responses		
	X_1 (w/w)	X_2 (°C)	X_3 (min)	R (%)	I_{MB}($mg.g^{-1}$)	I_2 ($mg.g^{-1}$)
1	2	500	120	68.54	24.82	736.01
2	2	500	120	68.31	25.22	735.45
3	3	**600**	**120**	56.35	**39.20**	766.19
4	2	600	180	56.14	16.66	774.90
5	2	**400**	**60**	**74.35**	08.20	743,33
6	2	500	120	67.92	25.33	734.12
7	3	500	60	64.63	36.96	789.85
8	2	600	60	63.96	26.32	740.79
9	2	500	120	68.16	24.82	733.21
10	1	400	120	74.17	05.36	672.59
11	3	400	120	68.26	28.01	732.06
12	**3**	**500**	**180**	59.87	16.73	**830.40**
13	1	600	120	61.98	18.52	705.26
14	1	500	180	64.56	11.50	728.41
15	2	400	180	70.89	10.27	696.97
16	1	500	60	70.75	01.00	780.56
17	2	500	120	68.22	25.48	735.11

Development of regression model equations: The analysis of the different models studied (Linear model, 2FI model, Quadratic model, and Cubic model) reveals that the Quadratic model is the most adequate to predict the responses with coefficients of correlation higher than 98.50 % (99.37 for yield, 98.71 for methylene blue index and 99.65% for iodine index) (Table-4). For all tracked responses, the difference between R^2-fit and R^2-predicted is less than 0.20, which confirms the validity of the models chosen to explain the tracked responses[31,32]. The quadratic models linking the responses to the different study factors are illustrated by the following equations (6), (7) and (8):

Pyrolysis yield: Y_1 (%) = 68.23 – 2.79375X_1 – 6.155X_2 – 2.77875X_3 + 0,07 + 0.3575X_1X_2 – 1.09 X_2X_3 – 2.21125X_1^2 – 0.82875X_2^2 - 1.06625X_3^2 (6)

Methylene blue value: Y_2 (mg.g^{-1}) = 25.134 + 10.565X_1 + 6.1075X_2 – 2.165X_3 – 0.4925X_1X_2 – 7.6825X_1X_3– 2.9325 X_2X_3–0.58825X_1^2–1.77325X_2^2–7.99825X_3^2 (7)

Iodine value: Y_3 (mg.g^{-1}) = 734.78 + 28.96X_1 + 17.7738X_2 – 2.98125X_3 + 0.365X_1X_2 + 23.175X_1X_3 + 20.1175X_2X_3 + 13.7762X_1^2 – 29.5313 X_2^2 + 33.7488X_3^2 (8)

The results coefficients with a positive sign have a synergistic effect on the response studied and the others have an antagonistic effect[33-35].

Table-3: Optimal experimental conditions for the activated carbon process.

Responses	Units	Exp values	X_1	X_2 (°C)	X_3 (min)
Y_1	%	74.35	2	60	400
Y_2	mg.g^{-1}	39.20	3	600	120
Y_3	mg.g^{-1}	830.40	3	500	180

Table-4: Sequential analysis of proposed models for yield.

Source	Dev. std	R²	R²-ajusté	R²-prédit	Press	Comment
Activated carbon yield (%)						
Lineair	1.68	92.13	90.31	87.44	58.25	
2FI	1.77	93.26	89.22	81.71	84.84	
Quadratic	0.2447	99.91	99.79	99.19	3.76	Suggested
Cubic	0.2256	99.96	99.82		*	Aliased
Methylene blue value (mg.g^{-1})						
Lineair	06.61	68.39	61.09	40.22	1074.16	
2FI	05.45	83.49	73.59	41.79	1046.08	
Quadratic	0.4646	99.92	99.81	98.95	18.94	Suggested
Cubic	0.3011	99.98	99.92		*	Aliased
Iodine value (mg.g^{-1})						
Lineair	6.61	68.39	61.09	40.22	1074.16	
2FI	5.45	83.49	73.59	41.79	1046.08	
Quadratic	0.446	99.92	99.81	98.95	18.94	Suggested
Cubic	0.3011	99.98	99.92		*	Aliased

The very high coefficients of determination R^2 are confirmed by a low dispersion of the prediction plans obtained (Figure-1, 2 and 3).

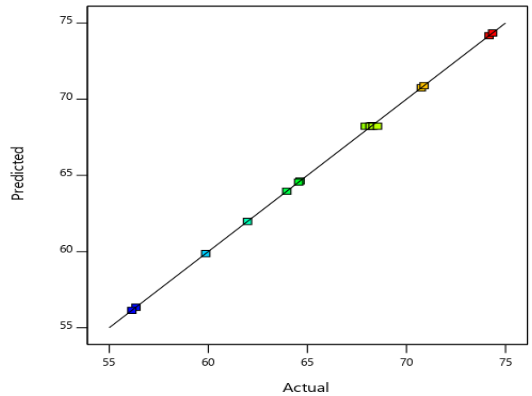


Figure-1: Predict versus experimental pyrolysis yield (%).

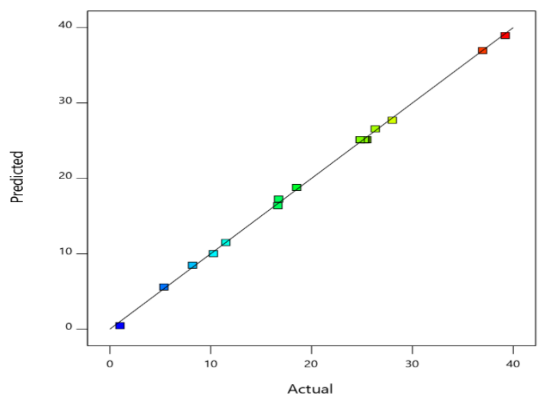


Figure-2: Predict versus experimental methylene blue value (mg.g^{-1}).

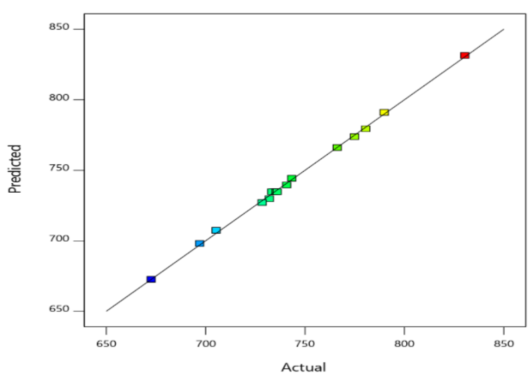


Figure-3: Predict versus experimental iodine value (mg.g^{-1}).

Statistical analysis of the models: The ANOVA was used to assess the adequacy and relevance of the selected quadratic models. The ANOVA results from different models are shown in Table-5, 6 and 7. The results show that the models chosen for the different responses have p-values less than 0.05, which shows that the models are significant[31]. The lack of fit measures the difference between the residual error and the pure error. A non-significant lack of fit is desirable and the results show that the lack of fit of all models is not significant. The results show that temperature is the most significant parameter on the yield (Table-5) while the impregnation ratio is the most influential factor on the methylene blue index and iodine index (Table-6 and 7) although the other terms are significant except for the X_1X_2 interactions.

Table-5: ANOVA analysis for activated carbons yield.

Source	F-value	p-value
Model	860.12	< 0.0001
X_1-Imprégnation ratio	1043.09	< 0.0001
X_2-Pyrolysis temperature	5062.96	< 0.0001
X_3-Pyrolysis time	1031.92	< 0.0001
X_1X_2	00.33	0.5851
X_1X_3	08.54	0.0223
X_2X_3	79.39	< 0.0001
X_1^2	343.93	< 0.0001
X_2^2	48.31	0.0002
X_3^2	79.97	< 0.0001
Lack of Fit	01.41	0.3627

Table-6: ANOVA analysis for methylene value.

Source	F-value	p-value
Model	924.29	< 0.0001
X_1-Impregnation ratio	4137.27	< 0.0001
X_2-Pyrolysis temperature	1382.62	< 0.0001
X_3-Pyrolysis time	173.74	< 0.0001
X_1X_2	04.50	0.0717
X_1X_2	1093.83	< 0.0001
X_2X_3	159.38	< 0.0001
X_1^2	06.75	0.0355
X_2^2	61.34	0.0001
X_3^2	1247.99	< 0.0001
Lack of Fit	04.22	0.0990

Table-7: ANOVA analysis for iodine value.

Source	F-value	p-value

Model	692.91	< 0.0001
X_1-Impregnation ratio	1905.76	<0.0001
X_2-Pyrolysis temperature	717.84	<0.0001
X_3-Pyrolysis time	20.20	0.0028
X_1X_2	00.15	0.7088
X_1X_3	610.21	< 0.0001
X_2X_3	459.82	< 0.0001
X_1^2	226.98	< 0.0001
X_2^2	1042.99	< 0.0001
X_3^2	1362.17	< 0.0001
Lack of Fit	05.28	0.0710

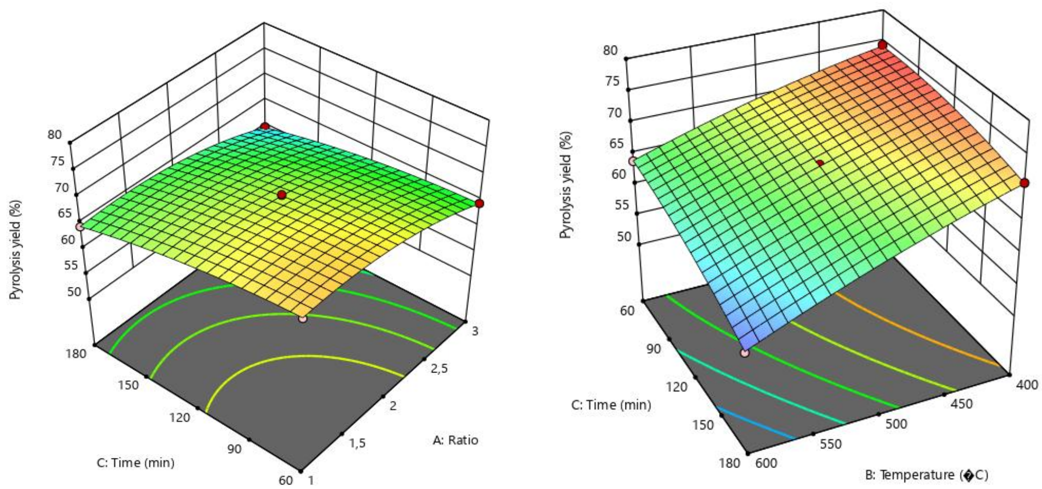
Analysis of the responses: Pyrolysis yield: The results (Figure-4(a)) show the combined effects of impregnation ratio and pyrolysis time on the yield. When the pyrolysis temperature is set at 500°C, the pyrolysis yield decreases with increasing impregnation ratio and activation time. When the pyrolysis time and the impregnation ratio are increased, it favors dehydration and degradation reactions, which are accompanied by volatile matter losses[36-38]. This result complies with the literature[37,39]. Similarly, the increase in temperature and the increase in contact time when the impregnation ratio is fixed at 2, leads to a decreasing yield (Figure-4(b)). Indeed, increasing the temperature at longer pyrolysis times also favours mass losses of the precursor material. The results reveal that the pyrolysis yield decreases with impregnation ratio, temperature and pyrolysis time. The best yields are observed when the impregnation ratio, temperature and contact time are in their minimum levels.

Methylene blue and iodine values: Figure-5(a) shows that the methylene blue index increases with the impregnation ratio and the pyrolysis time. The ratio and the activation time have a synergistic effect on the adsorption capacity of the carbon. This increases in adsorption capacity can be explained by the fact that the extension pyrolysis time favours the action of phosphoric acid on the precursor material. Indeed, phosphoric acid promotes the dehydration and retention of carbon and leads to the redistribution of the bio-polymers which constitute the material. The increase of temperature and ratio facilitates the conversion of these bio-polymers into an aromatic ring which leads to the increase of the porosity of the activated carbon by the creation of macropores and mesopores responsible for the adsorption of big molecules such as the methylene blue[37], and micropores. These letters are responsible for the adsorption of small molecules such as the iodine molecule[40-42]. The best elimination areas for methylene blue and iodine correspond to those with high impregnation ratios and long activation times. Similar results have been obtained by other researchers[42-43]. Figure-5(b) shows the effect of temperature and time on the methylene blue index when the impregnation ratio is set at 2. The results show that the methylene blue index initially increases with temperature and time and then gradually decreases. Indeed, the methylene blue index increases with the rise in temperature between 400 and 527.81°C. Between 527.81 and 550°C, the methylene blue index is almost stable. When the temperature exceeds 550°C, the texture of the activated carbon can be destroyed. This destruction can be accompanied by a reduction in porosity leading to a decrease in methylene blue adsorption capacity[44]. Figure-6(a) shows the effect of the interactions of the operating parameters of pyrolysis (temperature and time) on the iodine value when the impregnation ratio is fixed 2. Figure-6(b) shows an increase in the iodine value with increasing temperature and pyrolysis time. This increase may be due to the prolongation of pyrolysis, which promotes elimination reactions that lead to the development of microporosity through the development of existing pores and the appearance of new pores. This situation increases the number of adsorption sites and the iodine index[45-47]. When the temperature is increase, it accelerates the reaction and facilitates the removal of volatiles and tars, while increasing the pyrolysis time extends the activation, resulting in the generation of new pores and the expansion of existing ones. Iodine adsorption is optimal when the ratio, temperature and pyrolysis time are in their maximum levels.

Optimisation of the activated carbons process: When the pyrolysis yield increases, the methylene blue and iodine values decrease and vice versa. Thus, in order to find a compromise between these three responses, the desirability function approach was applied. For this, the input variables (factors) as well as the yield are kept within their ranges while for the output variables, maximum values of methylene blue and iodine values are sought. In so doing, the maximum value obtained for desirability corresponds to the common optimal conditions of the three responses.

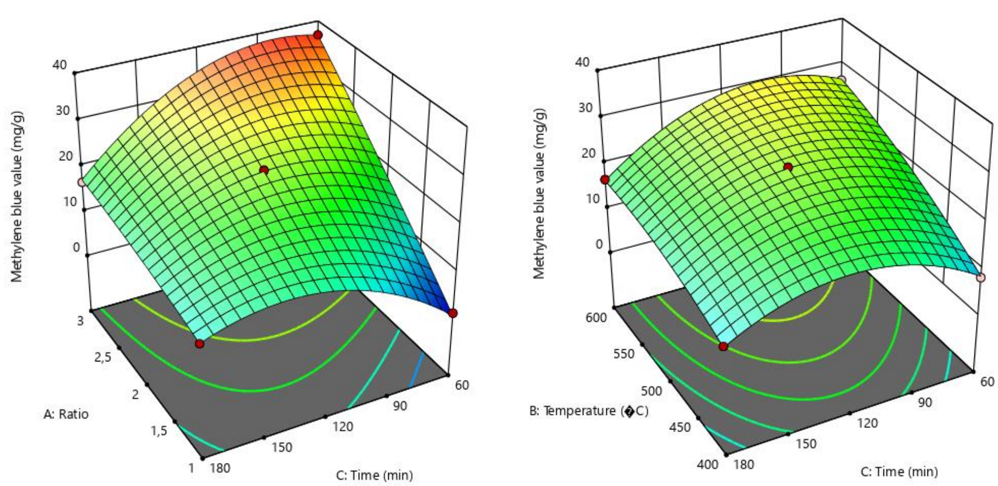
The results obtained (Figure-7) show that the optimum operating conditions for the activated carbon process from neem seed hulls correspond to an impregnation ratio of 3, a pyrolysis temperature of 527.81°C and a pyrolysis time of 60 min, and make it possible to obtain a pyrolysis yield of 63.13%, and methylene blue and iodine indices of 39.20 $mg.g^{-1}$ and 788.24 $mg.g^{-1}$, respectively. Similar optimal operating conditions are reported by Maguan et al., who worked on the optimization of activated carbon preparation based on barbary seed cake[23]. The optimal temperature (527.81°C) obtained is in agreement with the literature, which report that the optimal activation temperature with H_3PO_4 is close to 500°C[46-49]. The methylene blue index (39.20 $mg.g^{-1}$) obtained shows that the developed activated carbon is more efficient for the adsorption of methylene blue than the commercial activated carbon produced by Kureha Chemical Industry (Tokyo, Japan)[50]. The iodine value (788.24 mg.g^{-1}) obtained is higher than those of activated carbon based on corn cobs[51] and activated carbon based on coconut shells[52]. The high values of the methylene blue and iodine indices show that the developed activated carbon can be used for wastewaters treatment.

Model Validation for preparation of the activated carbons: To assess the validity of the model, an activated carbon has been elaborated under the previously determined common optimal conditions. The experimental and predicted results by the models are shown in Table-8. The results reveal that the predicted values are very close to the experimental ones. The percentage errors are 0.19, 0.87 and 0.02% respectively for the yield, methylene blue index and iodine index respectively. This validates the developed models. The small differences between the values predicted by the models and those obtained experimentally confirm the adequate accuracy of the models and the reproducibility of the experiments. This confirms the validity of the models developed. The models thus developed can therefore be used to predict responses within the experimental range.



(a) (b)

Figure 4: Interaction effects between impregnation ratio and pyrolysis time (a), pyrolysis time and pyrolysis temperature (b) on pyrolysis yield.



(a) (b)

Figure-5: Interaction effects between impregnation ratio and pyrolysis time (a), pyrolysis time and pyrolysis temperature (b) on methylene blue value.

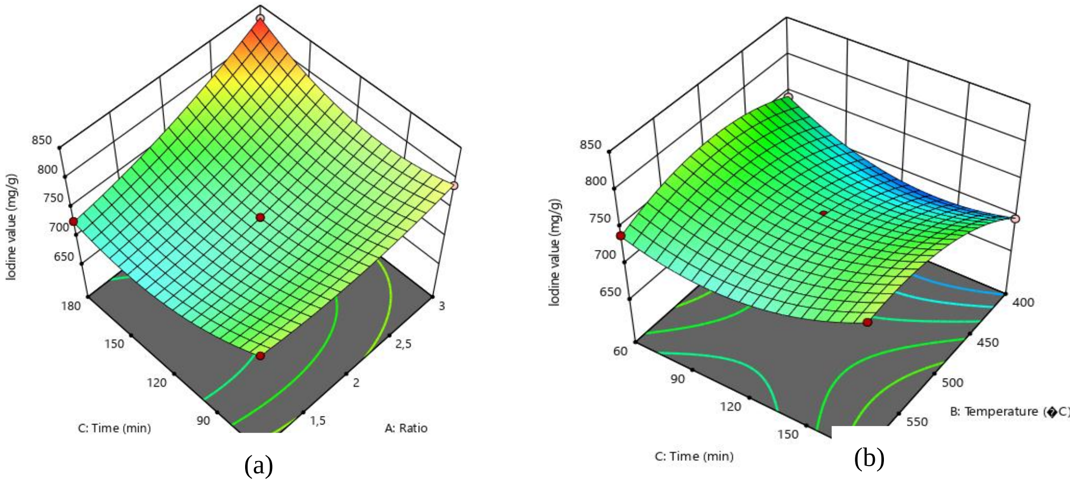


Figure-6: Interaction effects between ımpregnation ratio and pyrolysis time (a), pyrolysis time and pyrolysis temperature (b) on iodine value.

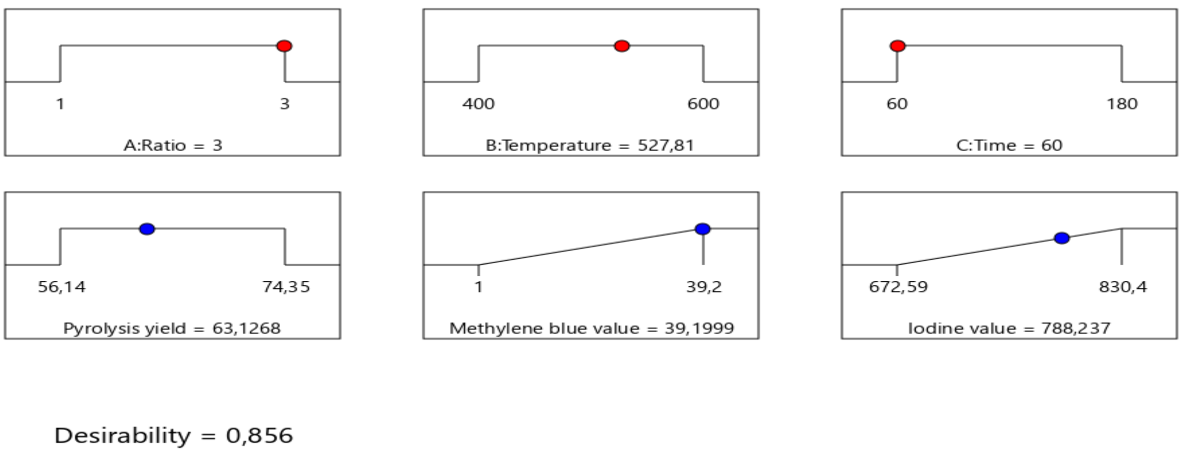


Figure-7: Optimal conditions for the activated carbon process using desirability function.

Table-8: Models validation for preparation of activated carbons from neem hulls.

Factors			Responses					
Temperature	Time	Ratio	Y_1 (%)		Y_2 ($mg.g^{-1}$)		Y_3 ($mg.g^{-1}$)	
°C	min	-	Exp	Pred	Exp	Pred	Exp	Pred
527,81	60	3	63.01	63.13	38.87	39.21	788.07	788.24

Conclusion

The treatment of wastewaters loaded with heavy metals and dyes is very difficult to achieve by conventional wastewater treatment methods. Elimination of these molecules on activated carbon is one of the most effective methods. The adsorbents used for this purpose are usually developed from agro-resources, such as oilseed hulls. In this work, the optimal conditions for the elaboration of activated carbons from neem seed hulls were carried out using the Response Surface Methodology. The optimal conditions common to the yield and the methylene blue and iodine indexes chosen as indicators of the productivity and efficiency of the activated carbons correspond to an impregnation ratio equal to 3, a pyrolysis temperature of 527.81°C and a residence time of 60 min and allow a yield of 63.13%, a methylene blue value of 39.21mg.$g^{-1}$and an iodine value of 788.24 mg.g^{-1}. A statistical analysis has showed that temperature was the most influential factor on the yield while the impregnation had the most significant effect on the adsorption capacity of methylene blue and iodine. The study has also determined the optimum conditions for the elaboration of neem seed hulls activated carbons and has developed models to predict the responses to the factors.

References

1. Al Subhi, H., Adeeb, M. S., Pandey, M., Al Sadeq, H., Kumar, D. & Shukla, S. K. (2020). Effect of different activation agents on the pollution removal efficiency of date seed activated carbon: process optimization using response surface methodology. *Applied water science*, 10(7), 1-9.

2. Dao, M. U., Le, H. S., Hoang, H. Y., Tran, V. A., Doan, V. D., Le, T. T. N. & Sirotkin, A. (2021). Natural core-shell structure activated carbon beads derived from Litsea glutinosa seeds for removal of methylene blue: Facile preparation, characterization, and adsorption properties. *Environmental Research*, 198, 110481.

3. Piaskowski, K., Świderska-Dąbrowska, R. & Zarzycki, P. K. (2018). Dye removal from water and wastewater using various physical, chemical, and biological processes. *Journal of AOAC International*, 101(5), 1371-1384.

4. Mozumder, M. S. I. & Islam, M. A. (2010). Development of treatment technology for dye containing industrial wastewater. *Journal of Scientific Research*, 2(3), 567-567.

5. Maiti, S., Prasad, B. & Minocha, A. K. (2020). Optimization of copper removal from wastewater by fly ash using central composite design of Response surface methodology. *SN Applied Sciences*, 2, 1-14.

6. Atheba, P., Drogui, P. & Trokourey, A. (2018). Adsorption kinetics and thermodynamics study of butylparaben on activated carbon coconut based. *Journal of Encapsulation and Adsorption Sciences*, 8(2), 39.

7. Xiao, W.; Jiang, X.; Liu, X.; Zhou, W.; Garba, Z. N.; Lawan, I.; Wang, L. and Yuan, Z. (2021). Adsorption of organic dyes from wastewater by metal-doped porous carbon materials. *Journal of Cleaner Production***,** 284, 124773.

8. Laskar, N. & Kumar, U. (2018). Adsorption of Safranin (Cationic) dye from water by Bambusa tulda: Characterization and ANN modeling. *Environmental Engineering Science*, 35(12), 1361-1375.

9. Wu, J., Wang, T., Wang, J., Zhang, Y. & Pan, W. P. (2021). A novel modified method for the efficient removal of Pb and Cd from wastewater by biochar: Enhanced the ion exchange and precipitation capacity. *Science of the Total Environment*, 754, 142150.

10. Elhadiri, N., Bouchdoug, M., Benchanaa, M. & Boussetta, A. (2018). Optimization of preparation conditions of novel adsorbent from sugar scum using response surface methodology for removal of methylene blue. *Journal of Chemistry*, 2018.

11. Paksamut, J. & Boonsong, P. (2018). Removal of Copper (II) Ions in Aqueous Solutions Using Tannin-Rich Plants as Natural Bio-Adsorbents. In IOP Conference Series: Materials Science and Engineering, Vol. 317, No. 1, p. 012058. IOP Publishing.

12. Shah, K. & Palmer, A. (2018). Physico-chemical characteristics of Activated Carbon prepared from coconut shell. *Int. J. Latest Eng. Res. Appl*, 3(1), 27-31.

13. Rahman, M. A., Amin, S. R. & Alam, A. S. (2012). Removal of methylene blue from waste water using activated carbon prepared from rice husk. *Dhaka University Journal of Science*, 60(2), 185-189.

14. El Naga, A. O. A., El Saied, M., Shaban, S. A. & El Kady, F. Y. (2019). Fast removal of diclofenac sodium from aqueous solution using sugar cane bagasse-derived activated carbon. *Journal of Molecular Liquids*, 285, 9-19.

15. Liu, J., Liu, Y., Peng, J., Liu, Z., Jiang, Y., Meng, M., ... & Ni, L. (2018). Preparation of high surface area oxidized activated carbon from peanut shell and application for the removal of organic pollutants and heavy metal ions. *Water, air & soil pollution*, 229, 1-17.

16. Andas, J. & Satar, N. A. A. (2018). Synthesis and characterization of tamarind seed activated carbon using different types of activating agents: a comparison study. *Materials Today: Proceedings*, 5(9), 17611-17617.

17. Fu, K., Yue, Q., Gao, B., Sun, Y. & Zhu, L. (2013). Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation. *Chemical Engineering Journal*, 228, 1074-1082.

18. Okeola, O. F., Odebunmi, E. O. & Ameen, O. M. (2012). Comparison of sorption capacity and surface area of activated carbon prepared from Jatropha curcas fruit pericarp and seed coat. *Bulletin of the Chemical Society of Ethiopia*, 26(2).

19. Yunusa, U., Usman, B. & Ibrahim, M. (2020). Modeling and Regeneration Studies for the Removal of Crystal Violet Using Balanites aegyptiaca Seed Shell Activated Carbon. *Journal of the Turkish Chemical Society Section A: Chemistry*, 8(1), 195-208.

20. Vunain, E. & Biswick, T. (2019). Adsorptive removal of methylene blue from aqueous solution on activated carbon prepared from Malawian baobab fruit shell wastes: Equilibrium, kinetics and thermodynamic studies. *Separation Science and Technology*, 54(1), 27-41.

21. Kwaghger, A. & Ibrahim, J. S. (2013). Optimization of conditions for the preparation of activated carbon from mango nuts using HCl. *American Journal of Engineering Research*, 2(7), 74-85.

22. Kouotou, D., Manga, H. N., Baçaoui, A., Yaacoubi, A. & Mbadcam, J. K. (2013). Optimization of activated carbons prepared by and steam activation of oil palm shells. *Journal of Chemistry*, 2013.

23. El Maguana, Y., Elhadiri, N., Bouchdoug, M., Benchanaa, M. & Jaouad, A. (2019). Activated carbon from prickly pear seed cake: optimization of preparation conditions using experimental design and its application in dye removal. *International Journal of Chemical Engineering*.

24. Mhemed, H. A., Gallego, M. M., Largeau, J. F., Kordoghli, S., Zagrouba, F. & Tazerout, M. (2020). Gas adsorptive desulfurization of thiophene by spent coffee grounds-derived carbon optimized by response surface methodology: Isotherms and kinetics evaluation. *Journal of Environmental Chemical Engineering*, 8(5), 104036.

25. Faye, M. (2010). Nouveau procédé de fractionnement de la graine de Neem (Azadirachta Indica A. Jussi) sénégalais: production d'un bio-pesticide d'huile et de tourteau (Doctoral dissertation).

26. Djibril, D., Mamadou, F., Gérard, V., Geuye, M. D. C., Oumar, S. & Luc, R. (2015). Physical characteristics, chemical composition and distribution of constituents of the neem seeds (Azadirachta indica A. Juss) collected in Senegal. *Research Journal of Chemical Sciences*, 3(2), 606-612.

27. Burak, D. A. M. (2021). Artifical neural network based wing optimization. M. Sc. Thesis, Department of Mechanical Engineering, Gazi University Institute of Sciences

28. Anuwar, N. A. & Khamaruddin, P. F. M. (2020). Optimization of Chemical Activation Conditions for Activated Carbon From Coconut Shell Using Response Surface Methodology (RSM) and Its Ability to Adsorb CO_2. In Third International Conference on Separation Technology 2020 (ICoST 2020) (pp. 234-248). Atlantis Press.

29. Lia, G., Fangb, X., Lib, J., Wub, N., Wangb, H. & Wanga, X. (2018). Preparation of super activated carbon of vetiver root: optimization by response surface method and study of adsorption behavior on bisphenol A in solution. In Presented at the 11th International Conference on Challenges in Environmental Science & Engineering (CESE-2018), Vol. 4, p. 8.

30. Ahmad, M. A., Afandi, N. S. & Bello, O. S. (2017). Optimization of process variables by response surface methodology for malachite green dye removal using lime peel activated carbon. *Applied Water Science*, 7, 717-727.

31. Mohammad, Y. S., Shaibu-Imodagbe, E. M., Igboro, S. B., Giwa, A. & Okuofu, C. A. (2014). Modeling and optimization for production of rice husk activated carbon and adsorption of phenol. *Journal of Engineering*.

32. Singh, R. & Bhateria, R. (2020). Optimization and experimental design of the Pb^{2+} adsorption process on a nano-Fe_3O_4-based adsorbent using the response surface methodology. *ACS Omega*, 5(43), 28305-28318.

33. Brahmi, L., Kaouah, F., Boumaza, S. & Trari, M. (2019). Response surface methodology for the optimization of acid dye adsorption onto activated carbon prepared from wild date stones. *Applied Water Science*, 9, 1-13.

34. Bouazizi, S., Jamoussi, B. & Bousta, D. (2016). Application of response surface methodology for optimization of heavy metals biosorption on natural gum of acacia nilotica. *International Journal of Engineering Research*, 5(05).

35. Ab Ghani, Z., Yusoff, M. S., Zaman, N. Q., Zamri, M. F. M. A. & Andas, J. (2017). Optimization of preparation conditions for activated carbon from banana pseudo-stem using response surface methodology on removal of color and COD from landfill leachate. *Waste management*, 62, 177-187.

36. Tchakala, I., Bawa, L. M., Djaneye-Boundjou, G., Doni, K. S. & Nambo, P. (2012). Optimisation du procédé de préparation des Charbons Actifs par voie chimique (H3PO4) à partir des tourteaux de Karité et des tourteaux de Coton. *International Journal of Biological and Chemical Sciences*, 6(1), 461-478.

37. Fregue, T. T. R., Ionel, I., Gabche, A. S. & Mihaiuti, A. C. (2019). Optimization of the activated carbon preparation from avocado seeds, using the response surface methodology. *Revista de Chimie*, 70(2), 410-416.

38. Sureshkumar, A. & Susmita, M. (2018). Optimization of preparation conditions for activated carbons from polyethylene terephthalate using response surface methodology. *Brazilian Journal of Chemical Engineering*, 35, 1105-1116.

39. Tan, I. A. W., Ahmad, A. L. & Hameed, D. B. (2008). Preparation of activated carbon from coconut husk: optimization study on removal of 2, 4, 6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials*, 153(1-2), 709-717.

40. Balamourougane, J. S. (2021). Production and Characterization of Activated Carbon from Dashen Brewery Gondar Spent Label as Precursor. *Turkish Journal of Computer and Mathematics Education*, 12(10), 628-635.

41. Villota, S. M.; Lei, H.; Villota, E.; Qian, M.; Lavarias, J.; Taylan, V.; Agulto, I.; Mateo, W.; Valentin, M. and Denson, M. (2019). Microwave-assisted activation of waste cocoa pod husk by H_3PO_4 and KOH—comparative insight into textural properties and pore development. *ACS Omega*, 4(4), 7088-7095.

42. Md-Desa, N. S., Ab Ghani, Z., Abdul-Talib, S. & Tay, C. C. (2016). Optimization of activated carbon preparation from spent mushroom farming waste (SMFW) via Box–

Behnken design of response surface methodology. *Malaysian Journal of Analytical Sciences*, 20(3), 461-468.

43. Salman, J. M. (2014). Optimization of preparation conditions for activated carbon from palm oil fronds using response surface methodology on removal of pesticides from aqueous solution. *Arabian Journal of Chemistry*, 7(1), 101-108.

44. Ateş, F. & Özcan, Ö. (2018). Preparation and characterization of activated carbon from poplar sawdust by chemical activation: comparison of different activating agents and carbonization temperature. *European Journal of Engineering and Technology Research*, 3(11), 6-11.

45. Almahbashi, N. M. Y., Kutty, S. R. M., Ayoub, M., Noor, A., Salihi, I. U., Al-Nini, A., ... & Ghaleb, A. A. S. (2021). Optimization of preparation conditions of sewage sludge based activated carbon. *Ain Shams Engineering Journal*, 12(2), 1175-1182.

46. Louarrat, M., Enaime, G., Baçaoui, A., Yaacoubi, A., Blin, J. & Martin, L. (2019). Optimization of conditions for the preparation of activated carbon from olive stones for application in gold recovery. *Journal of the Southern African Institute of Mining and Metallurgy*, 119(3), 297-306.

47. Balogoun, C. K., Bawa, M. L., Osseni, S. & Aina, M. (2015). Préparation des charbons actifs par voie chimique à l'acide phosphorique à base de coque de noix de coco. *International Journal of Biological and Chemical Sciences*, 9(1), 563-580.

48. Alau, K. K., Gimba, C. E., Kagbu, J. A. & Nale, B. Y. (2010). Preparation of activated carbon from neem (Azadirachta indica) husk by chemical activation with H_3PO_4, KOH and ZnC_{l2}. *Arch Appl Sci Res*, 2(5), 451-5.

49. Yenisoy-Karakaş, S., Aygün, A., Güneş, M. & Tahtasakal, E. (2004). Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics. *Carbon*, 42(3), 477-484.

50. Armand, A. E., Augustin, Y. Y., Urbain, K. Y. & Albert, T. (2020). Optimisation de la préparation de charbons activés à base d'épis de maïs et caractérisation physico-chimique. *International Journal of Innovation and Applied Studies*, 29(4), 1161-1171.

51. Liang, Q., Liu, Y., Chen, M., Ma, L., Yang, B., Li, L. & Liu, Q. (2020). Optimized preparation of activated carbon from coconut shell and municipal sludge. *Materials Chemistry and Physics*, 241, 122327.