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PREPARATION OF ACTIVATED CARBONS WITH ENHANCED ADSORPTION OF CATIONIC AND ANIONIC DYES FROM CHINESE HICKORY HUSK USING THE TAGUCHI METHOD

Waste Chinese Hickory husk biomass was used as a precursor in the preparation of low-cost activated carbon by $ZnCl_2$ activation. The activated carbon was to be used for the removal of both cationic and anionic dyes – methylene blue (MB) and methyl orange (MO). The preparation parameters, including impregnation ratio (the mass ratio of $ZnCl_2$ to the precursor), the activation temperature, the activation time and the impregnation time, were evaluated. The Taguchi method, in combination with analysis of variance (ANOVA), was used to determine the effects of the preparation parameters on the dye adsorptive capacities of the activated carbon, and to optimize preparation conditions with the goal of maximizing its adsorptive capacities. The optimized conditions were an impregnation ratio of 2.0 g/g, an activation temperature of 550 ºC and an activation time of 60 min. In such an optimal combination of parameters, the adsorption of MB and MO was expected to reach approximately 400 mg/g and 900 mg/g, respectively. The activation temperature had the most significant effect on the carbon capacity to adsorb MB and MO. The impregnation ratio had a significant effect on the adsorption of both dyes with the trend towards higher adsorption at higher impregnation ratio, while the activation time and the impregnation time were found to be insignificant.

1. INTRODUCTION

Dye compounds are widely used in various industries such as textiles, dyeing, printing, and pulp and paper. At the same time, these industries also consume substantial volumes of water. Consequently, wastewaters containing dye compounds are dis-

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charged in significant amounts, with high concentrations of dissolved organic matter and colorants [1]. These wastewaters cannot be released into the receiving waters unless the pollutants are largely eliminated from the discharges and meet the minimun requirements of environmental regulations. However, the removal of these pollutants from the effluents is known to be very difficult as a result of the presence of dyes. Although many treatment technologies such as biodegradation [1], [2] and chemical or electrochemical oxidation [3], [4] have been developed during the past three decades, together with attempts to provide more options for treating such industrial effluents, yet, no single process has been proved satisfactory to-date. The problem is that the dyes presented in the effluents are recalcitrant molecules with complex and stubborn chemical structures, and therefore, are resistant to bio-degradation and chemical oxidation [5].

Adsorption by activated carbon has been regarded as a promising method for treating wastewaters containing dye pollutants, given its efficient and versatile performance in removing diverse dye compounds [6], [7]. However, commercial activated carbon is expensive, and thus its practical application to the decoloring of dyes is restricted. To a great extent, this is a consequence of the use of relatively costly or insufficient precursor materials (such as coal, coconut shell, and lignite) for producing activated carbon. Recently, research has focused on seeking widely available and low-cost alternative precursors. Among these, biomass wastes from agriculture or forestry have captured more attention because they are renewable, locally available, and, thus, low cost [8], [9]. Chinese Hickory (*Carya cathayensis* Sarg.) is an important economic forest crop of Southern China, with original distribution in Zhejiang and Anhui provinces [10]. In the last decade, the plantations of this crop have been largely expanded, thanks to a better understanding of agronomic technique and silvicultural management [11]. As a result, an increasing amount of husk residues is generated following the harvesting and processing of Chinese Hickory nuts. Hence, there is currently an urgent need to dispose of and reuse this agricultural waste. One alternative approach to recycling this biomass waste is to produce activated carbon. This approach has clear advantages related to its technical feasibility as well as its environmental and economical benefits.

Activated carbons can be produced by physical or chemical activation methods. Chemical activation is widely applied as it requires a lower activation temperature and has a higher product yield than physical activation. Among the most common activating agents is zinc chloride ($ZnCl_2$), the use of which has been intensely investigated in the production of activated carbons from various agricultural wastes, such as hazelnut shells, bagasse, and rice husks [12], [13]. It is believed that chemical activation using such an activating agent can improve the pore development in the carbon structure, in addition to the advantages associated with product yield and activation temperature [14].

It is well known that the processing conditions during activated carbon production, including impregnation ratio, activation temperature, and activation time, play vital roles

in determining its properties and performances, such as surface area, pore volume, and adsorptive capacities to various pollutants. One major concern is how to optimize these processing variables to enhance these characteristics. Suitable experimental design technique is recognized to be a very useful tool for this purpose. The Taguchi method is a set of methodologies by which the effects of several variables can be simultaneously determined, effectively. Additionally, the optimum processing conditions and the corresponding process characteristics can be obtained with a minimized sensitivity to noise (noise is a hard-to-control variable that affects performance). This method has been extensively applied in various manufacturing industries and experimental designs with great success for determining the optimum process conditions [15]–[17]. However, information is very limited on its application to preparation of activated carbon. In this study, we describe the application of this design method to optimize activated carbon preparation from the husks of Chinese Hickory, with emphasis on the performance of the activated carbon in dye adsorption. The amounts of methylene blue (MB) and methyl orange (MO) absorbed are used to characterize the dye adsorptive capacity – MB (a cationic dye) and MO (an anionic dye) are the model compounds of dye contaminants and can serve as indicators to evaluate the adsorptive capacity of activated carbon [18], [19].

The objectives of this work were, therefore, to:

(1) explore the use of the Chinese Hickory husks as a potential precursor for the production of activated carbon for the removal of dye pollutants,

(2) apply the Taguchi method to optimize the preparation conditions for activated carbon using $ZnCl_2$ activation from the standpoint of maximizing the adsorptive capacity to dye pollutants,

(3) investigate the effects of key process parameters on the qualitative and quantitative adsorption efficiency of the activated carbon for the dyes.

Since many of the relevant papers suggest that impregnation ratio, activation temperature, and activation time are the important preparation parameters influencing the characteristics of the activated carbon [14], [20], these parameters were selected in this study, along with the parameter of impregnation time.

2. MATERIALS AND METHODS

2.1. MATERIALS

Husks of *Carya cathayensis* (Chinese Hickory) were given by one hickory farmer in Lin'an city of Zhejiang Province. The husks were washed with deionized water to remove extraneous matter and impurities, and then dried in an oven (Type SRJX-4-13, Shanghaijinping, China) at 60 ºC to a constant weight. The dried material was ground

in a cutting mill, then sieved to size fraction of 0.83–1.70 mm, and stored in an air-tight glass container in preparation for the experiment.

Table 1

Chemical structure and property of MB and MO

	Molecular formula	Molecular weight	Molecular size (nm)	Property
MB	$C_{16}H_{18}N_3SCl{\cdot}3\ H_2O$	373.90	1.43 × 0.61 × 0.40	cationic
MO	$C_{14}H_{14}N_3O_3SNa$	327.33	1.54 × 0.48 × 0.28	anionic

Two dye compounds, methylene blue (MB), a cationic dye, and methyl orange (MO), an anionic one, were selected as model adsorbates to indicate the adsorption efficiency of the activated carbon produced. Their chemical structures and properties are presented in table 1. These dyes, purchased from Shanghai SSS Reagent Co., Ltd, China, were of analytical reagent grade. Deionized water only was used throughout all experiments.

2.2. IMPLEMENTATION OF EXPERIMENT BASED ON THE TAGUCHI METHOD

The Taguchi method was used to implement the experiment. The major steps associated with this method are to:

(1) select a proper orthogonal array (OA) according to the number of processing parameters and their levels;

(2) perform the experiment based on the OA selected and obtain the response data (the amounts of MB and MO adsorbed and S/N ratios for both MB and MO);

(3) analyze the data of S/N ratio and determine the optimum conditions for preparing the activated carbon;

(4) predict the adsorption efficiency under the optimum preparation conditions,

(5) run a confirmation experiment to verify the predicted results and the optimum conditions obtained.

2.2.1. DETERMINATION OF ORTHOGONAL ARRAY

The first step in the Taguchi method is to select a suitable orthogonal array, which depends on the number of parameters and their levels. In this research, four parameters were selected to investigate their effects on the adsorptive capacities of the activated carbon prepared and to determine an optimal combination of parameters. Each parameter consisted of three levels (table 2). Accordingly, a standardized L_9 (3^4) orthogonal array was selected based on the Taguchi design methodologies, as shown in table 3.

Table 2

Determination of factors and their levels

Parameter	Level 1	Level 2	Level 3
A: impregnation ratio (g/g)	1:1	1.5:1	2:1
B: activation temperature (ºC)	350	550	750
C: activation time (min)	30	45	60
D: impregnation time (h)	16	20	24

Table 3

MB and MO amounts adsorbed on activated carbon and corresponding S/N ratios

Run No.	Parameters				MB adsorptive capacity		MO adsorptive capacity	
	A	*B*	*C*	*D*	Raw value (mg/g)	S/N ratio (dB)	Raw value (mg/g)	S/N ratio (dB)
1	1	1	1	1	306.89	49.74	723.61	57.19
2	1	2	2	2	360.74	51.14	797.17	58.03
3	1	3	3	3	359.62	51.12	831.84	58.40
4	2	1	2	3	336.04	50.53	790.09	57.95
5	2	2	3	1	388.94	51.80	884.64	58.94
6	2	3	1	2	363.52	51.21	833.94	58.42
7	3	1	3	2	364.18	51.23	818.07	58.26
8	3	2	1	3	383.65	51.68	869.28	58.78
9	3	3	2	1	371.94	51.41	846.05	58.55

2.2.2. PREPARATION OF ACTIVATED CARBON

A series of samples of activated carbon were prepared in a random sequence, according to the orthogonal array determined. The preparation processes in this study were based on the descriptions given by AHMADPOUR and DO [21] who used KOH and $ZnCl_2$ activation for the preparation of activated carbon derived from *Macadamia* nut shell. The steps followed for each sample were as follows:

(1) Five grams of the raw material was soaked in 50 cm^3 of $ZnCl_2$ solution under continuous agitation (120 rpm) so that the reagent was fully adsorbed into the raw material. The relevant impregnation ratio and impregnation time are presented in table 2.

(2) The mixture was then transferred to a muffle furnace, heated to the selected activation temperature, and held at that temperature for the selected activation time. The activation temperatures and activation times for each sample are listed in tables 2 and 3.

(3) The pyrolyzed sample was washed sequentially with 0.1 M hydrochloric acid and deionized water to remove residual $ZnCl_2$ until the pH of filtrate was neutral. The activated carbon obtained was dried at 105±2 ºC to a constant weight, ground and sieved to obtain fractions with particle size of 0.25–0.38 mm, which were then used to carry out adsorption experiments.

2.2.3. MEASUREMENT OF ADSORPTIVE CAPACITY

An adsorption study was conducted to determine the adsorbed amounts of MB and MO, which were used to indicate the adsorptive capacity of the activated carbon. Samples containing 0.10 g of the activated carbon and 100 cm^3 of the adsorbate solutions (MB and MO, 1000 mg/dm^3) were used. The adsorption test was carried out on a mechanical shaker for 24 h at a temperature of 30 ºC and with an agitation speed of 120 rpm. Blank runs with the samples containing 100 cm^3 of adsorbate solutions (MB and MO) with no adsorbent were conducted simultaneously. These were used to offset the effect due to the adsorption or reaction of the conical flasks with the adsorbates. Each adsorption test was repeated three times to ensure reproducibility and the replications of all the results agreed within a ±5 % error limit. The concentrations of the dye solutions, before and after the adsorption reaction, were determined by measuring their absorbancies using UV-visible spectrophotometry (Type Sp-2112 UVPC, Shanghai spectrum, China) at wavelengths of 665 nm (MB) and 465 nm (MO), respectively. The amount (q_e) of the dye adsorbed by the activated carbon was then calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}, \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentration (mg/dm^3). V is the volume of the adsorbate solution (dm^3), and W is the weight of the activated carbon (g). The average amount of the dye adsorbed was calculated based on three replications for each sample and used for further analysis.

2.2.4. ANALYSIS OF S/N RATIO

The Taguchi method recommends the use of the loss function to measure the performance characteristics of a product. The value of the loss function is further transformed into a signal-to-noise (S/N) ratio, which not only can reflect the average performance values of the product, but it can reveal corresponding variations in values under one trial run. The change in the performance characteristics of a product under investigation in response to a parameter is termed *signal*. However, when an experiment is conducted, there are numerous external factors which are not designed for the experiment. These external factors may influence the outcome of the experiment and are called *the noise factors*. Accordingly, their effect on the outcome of the performance characteristics under test is termed *noise*. Typically, there are three options for S/N ratios. These are the larger-the-better, the smaller-the-better, and the nominal-the-better. Because this study sought to maximize the adsorptive ability of the activated carbon, the larger-the-better option was selected. In this case, the value of the S/N ratio can be calculated as follows [22]:

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum\frac{1}{y_i^2}\right), \tag{2}$$

where the negative sign is used to set signal-to-noise ratio of larger-the-better (a larger signal and a smaller noise) relative to the square deviation of the smaller-the-better; the constant 10 in the formula magnifies the S/N ratio for easier analysis; n is the number of replications for each experiment; y_i is the efficiency value of each experiment.

2.2.5. PERFORMANCE PREDICTION

Based on the result of the S/N ratio analysis, the optimum combination of parameters for activated carbon preparation is expected to be established. In order to predict the adsorptive capacities for the dyes in such an optimum combination, the following additive model was selected to calculate the theoretically optimal S/N ratio [23]:

$$\eta_{\text{opt}} = m_t + \sum_{i=1}^{q}(\eta_i - m_t), \tag{3}$$

where η_{opt} represents the predicted S/N ratio, m_t is the overall mean S/N ratio of all the efficiency values, η_i is the mean S/N ratio at the optimal level, and q is the number of the main parameters that affect the adsorption efficiency.

At the same time, the confidence interval (CI) for the predicted S/N ratio was calculated [24]:

$$CI = \pm\left(\frac{F_\alpha(1, f_e)V_e}{n_{\text{eff}}}\right)^{0.5}, \tag{4}$$

where $F_\alpha(1, f_e)$ is the F-ratio at a confidence level of $(1 - \alpha)$ against degree of freedom (DOF) 1 and the DOF of error term f_e. V_e is the error variance (from ANOVA), and n_{eff} is calculated by:

$$n_{\text{eff}} = \frac{N}{1 + DOF_{\text{opt}}}, \tag{5}$$

where N is the total number of results, DOF_{opt} is the total degrees of freedom that are associated with the items used to estimate the value of η_{opt}.

2.2.6. CONFIRMATION EXPERIMENT

The final step in the Taguchi method is confirmation experiment, which is strongly recommended to verify the experimental conclusions. Accordingly, a confirmation experiment for the preparation of activated carbon was performed in triplicate at the

optimal combination obtained. The preparation procedure for the activated carbon and the measurement of adsorptive capacity during the confirmation experiment were the same as those described in Sections 2.2.2 and 2.2.3. If the values from the confirmation experiment correspond to the theoretically predicted efficiency, it can be proposed that the optimum condition obtained is valid. If not, further investigation is needed.

2.3. ANALYSIS OF VARIANCE

In order to quantitatively assess the influence of each parameter and more systematically determine its relative importance, an analysis of variance (ANOVA) was applied simultaneously to the data of the S/N ratio. A series of statistical variables including the sum of the square (SS), the degree of freedom (DOF), the variance (V), the pure sum of squares (SS'), F ratio of the factor (F) and percentage contribution (P) were established. These variables are widely used in ANOVA, and the methods for their calculations can be found elsewhere (see, for example, [25]).

3. RESULTS AND DISCUSSION

3.1. DETERMINATION OF THE OPTIMAL PREPARATION CONDITIONS

The Taguchi experimental design offers the possibility of optimizing processing parameters of a product. In this research, optimization of the preparation of activated carbon derived from the husks of *Carya cathayensis* was carried out according to such a method. The amounts of both methylene blue (MB) and methyl orange (MO) adsorbed were calculated using equation (1) and their corresponding S/N ratios were determined using equation (2). The results are shown in table 3. Moreover, according to the Taguchi method, the mean S/N ratio for each parameter should be computed. This can be used to optimize the process and to evaluate the effect of each parameter. The mean S/N ratios related to both MB and MO adsorption for the four investigated parameters were calculated (tables 4 and 5). The calculation was made by averaging the S/N data at each level of each parameter. For example, the mean of S/N ratio for MB from parameter B at level 1, with the value of 50.50 (see table 4), is calculated by averaging the values of 49.74, 50.53 and 51.23 (see table 3). The other mean S/N ratios were calculated in the same way. In addition, the maximum mean S/N ratio from each parameter indicated the optimal level (see tables 4 and 5 entries marked with an asterisk). The difference between the maximum and the minimum values of the mean S/N ratio for each parameter, as well as its cor-

responding rank were also presented to identify a qualitatively relative importance among these processing parameters.

Table 4

S/N ratio response table for the amounts of MB adsorbed

Parameters	Mean S/N ratio (dB)				
	Level 1	Level 2	Level 3	Max-Min	Rank
Impregnation ratio (*A*)	50.67	51.18	51.44*	0.77	2
Activation temperature (*B*)	50.50	51.54*	51.25	1.04	1
Activation time (*C*)	50.88	51.03	51.38*	0.50	3
Impregnation time (*D*)	50.98	51.19*	51.11	0.21	4

* The maximum mean S/N ratio for levels of each parameter.

Table 5

S/N ratio response table for the amounts of MO adsorbed

Parameters	Mean S/N ratio (dB)				
	Level 1	Level 2	Level 3	Max-Min	Rank
Impregnation ratio (*A*)	57.87	58.44	58.53*	0.66	2
Activation temperature (*B*)	57.80	58.58*	58.46	0.78	1
Activation time (*C*)	58.13	58.18	58.53*	0.40	3
Impregnation time (*D*)	58.22	58.24	58.38*	0.15	4

* The maximum mean S/N ratio for levels of each parameter.

Table 6

Analysis of variance of the S/N ratios for MB and MO adsorption

Source	S/N data of MB adsorption						S/N data of MO adsorption					
	DOF	*SS*	*V*	*F*	*SS*′	*P* (%)	*DOF*	*SS*	*V*	*F*	*SS*′	*P* (%)
A	2	0.92	0.46		0.92	29.58	2	0.75	0.38		0.75	35.16
B	2	1.73	0.87		1.73	55.41	2	1.06	0.53		1.06	49.46
C	2	0.40	0.20		0.40	12.84	2	0.29	0.14		0.29	13.31
D	2	0.07	0.03		0.07	2.17	2	0.04	0.02		0.04	2.07
Error	0						0					
Total	8	3.13					8	2.15				

SS, sum of squares; *DOF*, degree of freedom; *V*, variance; *F*, *F* ratio of the factor; *SS*′, pure sum of squares; *P*(%), percentage of contribution.

As can be seen in table 4, the optimum combination of processing parameters for MB adsorption was *A*3-*B*2-*C*3-*D*2. The activation temperature (parameter *B*) appeared to be the most important, followed by the impregnation ratio (parameter *A*), the activation time (parameter *C*) and the impregnation time (parameter *D*). For the MO ad-

sorption (table 5), the order of importance of these parameters was also *B*-*A*-*C*-*D*. However, the optimum combination for MO adsorption was *A*3-*B*2-*C*3-*D*3, differing from that for MB adsorption on optimal level of parameter *D*.

Moreover, to distinguish whether these processing parameters are statistically and quantitatively significant or not, the data for the S/N ratio in table 3 were assessed using an analysis of variance (ANOVA). From the results of ANOVA (table 6), the activation temperature had the largest variance, and the largest contribution to the total variance, the impregnation ratio and activation time exhibited the second and third largest variances, while the impregnation time contributed to 2.17% of total variation for MB and 2.07% for MO. It can be seen that the results of ANOVA were consistent with the direct analysis of S/N ratio (table 2) as regards the relative significance of these processing parameters.

The *F*-ratio of the factor (*F*) is typically used to identify statistical significance of a parameter of an ANOVA. However, the degree of freedom (*DOF*) for error term was zero in this investigation (table 6). As a result, the *F*-ratio of each parameter could not be computed. In this context, a pooled ANOVA method was applied to eliminate the zero *DOF* for the error term. The process of ignoring the contribution of a non-significant factor is known as pooling. The detailed information on this method can be found in the literature [26]. Since the contribution of parameter *D* (impregnation time) was the smallest and non-significant (2.17%), this parameter can be pooled into the error term based on the pooled ANOVA methodologies. Accordingly, the *F*-ratios of the four parameters investigated were calculated, and the percentage contribution of each was readjusted, the results are presented in table 7. In addition, the confidence interval is generally set at 90% for significant and 95% for very significant levels according to statistical principle. In this case, the critical points of the *F*-ratios for both MB and MO were obtained with F (5%, 2, 2) = 19.00 and F (10%, 2, 2) = 9.00. Comparing the *F*-ratios of the four parameters and those of the critical points (table 7), it can be seen that activation temperature was the most significant parameter affecting the dye adsorptive capacities of the activated carbon, since the *F*-ratios for both MB and MO were higher than 19.00. The F_A-ratios for MB and MO were between 19.00 and 9.00, signifying that the impregnation ratio contributed significantly to both MB and MO adsorptive capacities. The activation time had no significant influence on the result of the experiment with the F_C-ratios less than 9.00.

Based on the discussion above, it can be proposed that the optimized processing combination for preparing activated carbon with an enhanced adsorption capacity for both MB and MO was *A*3-*B*2-*C*3. Parameter *D* was the least important and therefore it was exempt from the optimum combination. It should be noted that although activation time (parameter *C*) was identified to be statistically insignificant, this parameter remained for the optimum combination given its percentage contribution of up to 10.68% for MB and 11.24% for MO (see table 7).

Table 7

Pooled analysis of variance of S/N ratios for MB and MO adsorption

Source	S/N data of MB adsorption						S/N data of MO adsorption					
	DOF	*SS*	*V*	*F*	*SS*′	*P* (%)	*DOF*	*SS*	*V*	*F*	*SS*′	*P* (%)
A	2	0.92	0.46	13.64	0.86	27.41	2	0.75	0.38	16.98	0.71	33.09
B	2	1.73	0.87	25.56	1.66	53.24	2	1.06	0.53	23.88	1.02	47.39
C	2	0.40	0.20	5.92	0.33	10.68	2	0.29	0.14	6.43	0.24	11.24
D	{2}			Pooled			{2}			Pooled		
Error	2	0.07	0.03			8.67	2	0.04	0.02			8.28
Total	8	3.13				100	8	2.15				100

SS, sum of squares; *DOF*, degree of freedom; *V*, variance; *F*, *F* ratio of the factor; *SS*′, pure sum of squares; *P* (%), percentage of contribution.

3.2. EFFICIENCY PREDICTION AND CONFIRMATION

With the optimal combination obtained (*A*3-*B*2-*C*3), the theoretically predicted optimum S/N ratios can be calculated using equation (3). For MB adsorption, the predicted S/N ratio, η_{opt} (MB), is 52.17 dB, which was computed as follows:

$$\eta_{\text{opt}}(\text{MB}) = m_t + \eta_{A3} - m_t + \eta_{B2} - m_t + \eta_{C3} - m_t = \eta_{A3} + \eta_{B2} + \eta_{C3} - 2m_t$$
$$= 51.44 + 51.54 + 51.38 - 2 \times 51.09 = 52.17,$$

where m_t is the total mean S/N ratio of MB, calculated from table 2. The values of η_{A3}, η_{B2}, and η_{C3} are the mean S/N ratios for *A*3, *B*2, and *C*3, obtained from table 3.

Also, the confidence interval (*CI*), for S/N ratio of MB at the optimum condition, was calculated using equations (4) and (5)

$$n_{\text{eff}} = \frac{N}{1 + DOF_{\text{opt}}} = 1.286,$$

$$CI = \pm\left(\frac{F_\alpha(1, f_e)V_e}{n_{\text{eff}}}\right)^{0.5} = \pm 0.657,$$

where: $N = 9$, $DOF_{\text{opt}} = 6$, $f_e = 2$, $F_{0.05}$ (1, 2) = 18.51 from the *F* table for 95% of confidence level, $V_e = 0.03$. Therefore, the expected result of S/N ratio for MB at the optimum preparation condition lies between 51.52 and 52.82 dB.

In order to estimate optimum adsorption efficiency of the activated carbon, the expected results of S/N ratio were transformed into the adsorbed amounts of MB and MO using equation (2). An example of the calculation regarding the predicted amount of MB adsorbed (y_A) is expressed as follows:

$$52.17 = -10\log\left(\frac{1}{y_A^2}\right) = 20\log y_A .$$

Hence, y_A was obtained with the value of 405.98 mg/g. In the same way, the corresponding expected range of the amount of MB adsorbed at the optimum condition was calculated (table 8). Similarly, for MO adsorption efficiency, the predicted results of the S/N ratio and of the related amount of adsorbed MO were computed by the same procedure, the results are also listed in table 8.

Table 8

Predicted results of MB and MO adsorption efficiencies

	Optimal combination	Predicted value		*CI* of S/N ratio (dB)	Expected value range	
		S/N ratio (dB)	Adsorption (mg/g)		S/N ratio (dB)	Adsorption (mg/g)
MB	*A*3-*B*2-*C*3	52.17	405.98	±0.66	51.52–52.82	376.70–437.52
MO	*A*3-*B*2-*C*3	59.08	899.50	±0.54	58.54–59.62	845.28–957.19

CI denotes the confidence interval.

According to the Taguchi method, a confirmation experiment is needed to verify the predicted results. If the observed values are close enough to the corresponding predicted values, the optimum condition can be considered valid. Otherwise, if there is no agreement between the two, this indicates some main factors may be omitted or interaction effects between the selected factors may exist, and, therefore, further experimentation and analysis would be needed to reach the expected results. For this purpose, we performed a confirmation experiment by running another three replications in the optimized combination (*A*3-*B*2-*C*3). From the results shown in table 9, the mean amounts of adsorbed MB and MO, i.e. 398.74 and 894.04 mg/g, match with the predicted values and are within the expected value ranges (see table 8). Thus, it can be proposed that the optimum process combination and the corresponding predicted response values in this experiment are valid.

Table 9

Results of the confirmation experiment

$N = 3$	Adsorption (mg/g)			Mean (mg/g)	S.D	R.S.D (%)
	1	2	3			
MB	395.43	402.67	398.12	398.74	3.66	0.92
MO	890.10	895.24	896.79	894.04	3.50	0.39

N, the number of repetition for the comfirmation experiment.

The activated carbon prepared under the optimum conditions (*A*3-*B*2-*C*3) presented high adsorptive capacity for MB (approximately 400 mg/g). AVELAR et al. [27] used *piassava* fiber (a residue of the broom industry) as a precursor to prepare activated carbon by chemical activation with zinc chloride and phosphoric acid, as well as by physical activation with carbon dioxide and water vapour. The activated carbon prepared using zinc chloride exhibited the highest adsorptive capacity for MB (276.40 mg/g). However, the difference in conditions of adsorption tests, including the adsorbent amount, the adsorbate concentration and the solution volume, may result in different consequences being observed in practice or deduced theoretically using the Langmuir isotherm. Therefore, further investigation for the activated carbon is needed to verify the plausible superiority in adsorption efficiency. Moreover, it is interesting to observe that the amount of MO adsorbed was far higher than that of MB (see tables 8 and 9), regardless of the uniform preparation conditions for activated carbon. This disparity may be related to the difference in charge between MB and MO; they have similar molecular size but opposite charge. Further investigation of this disparity is needed, but it was beyond the scope of this work.

3.3. THE ANALYSIS OF THE TAGUCHI RESPONSE GRAPHS

To further explore the effects of the process parameters on the adsorption efficiency of the activated carbons from a dynamic perspective, the data of the mean S/N ratios (tables 4 and 5) were used to plot response graphs. The response graphs of MB and MO are presented in figures 1 and 2.

3.3.1. THE EFFECT OF IMPREGNATION RATIO

The S/N ratios indicating the corresponding adsorptive capacities with positive correlation increase markedly with increasing impregnation ratios from 1 to 1.5 (figures 1 and 2). Further increasing the impregnation ratio up to 2.0, however, resluts in the S/N ratios levelling off for both MB and MO, as is shown by the slopes of the lines between different levels (figures 1 and 2). Therefore, it can be proposed that the efficiency of the activated carbon in adsorbed MB and MO is less affected by an impregnation ratio whose value exceeds 1.5. Similar trends have been confirmed by an available literature [28], [29]. These results indicate that only a trifling improvement in the performance of the activated carbon is achieved at the expense of considerable amounts of activating agent. It is a challenge to maximize the technical properties and the efficiency of activated carbon, while simultaneously minimizing costs.

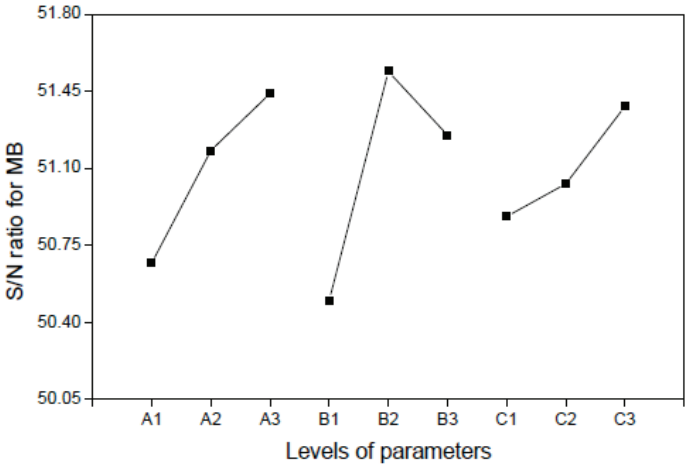

Fig. 1. Effect of operational parameters on the S/N ratio of methylene blue (MB) adsorption

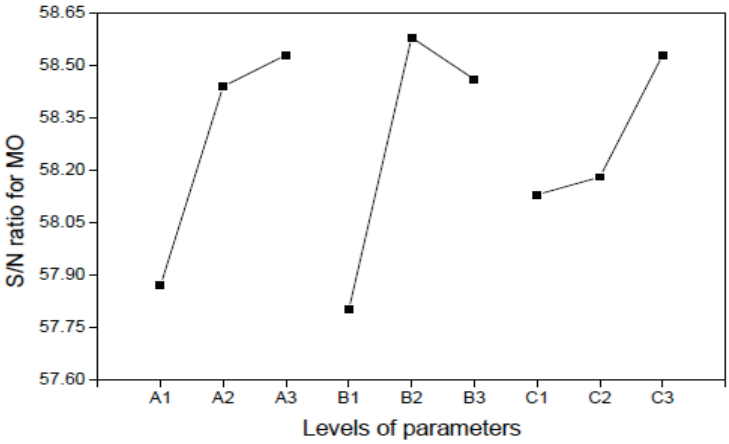

Fig. 2. Effect of operational parameters on the S/N ratio of methyl orange (MO) adsorption

3.3.2. THE EFFECT OF ACTIVATION TEMPERATURE

Figures 1 and 2 show the relationship between the S/N ratios and the activation temperature; a significant increase in the values of S/N ratios for MB and MO were observed when the activation temperature increased from 350 to 550 °C. Excessive activation with increasing temperature up to 750 °C, however, resulted in reduced S/N ratios, which indicates a reduction in ability to adsorb MB and MO. This observation is consistent with the results reported by YANG and LUA [30] and CHANDRA [31]. This may be attributed either to the sintering effect of the volatiles and a shrinkage of the carbon structure resulting from excess activation temperature, or

the possibility of over-activation accelerating surface erosion in preference to pore formation [32].

3.3.3. THE EFFECT OF ACTIVATION TIME

The results presented in figures 1 and 2 show that prolonging the activation time from 30 to 60 min increases the S/N ratios for both MB and MO and, consequently, improves adsorptive capacities for MB and MO. Different results have been identified in a previous work using $ZnCl_2$ as the activating agent for the effect of activation time on the property and efficiency of the activated carbon. A gradually reduced surface area and pore volume were observed when activation time was prolonged from 0.5 to 5 h at 400 °C activation temperature, when cattle-manure compost was used to produce activated carbon [33]. However, this result contradicts the study by MOHANTY et al. [34] who suggest surface area and pore volume first increase with prolonging carbonization time and reach their maximum at 1 h, and thereafter decrease. The discrepancy may be explained by the effect of one process parameter on the characteristics and performances of activated carbon, depending not only on the parameter and the activated carbon itself, but also on the nature of precursors and the type of activating agent – even on the magnitude and range of other process parameters.

4. CONCLUSIONS

Waste husks of Chinese Hickory were used to prepare activated carbon for dye pollutant removal. Methylene blue (MB) and methyl orange (MO) were employed as indicators to characterize the dye adsorption capacities of the activated carbon. The Taguchi experimental method, in combination with the analysis of variance (ANOVA), was applied to optimize the parameters of the activated carbon preparation, including the impregnation ratio, the activation temperature, the activation time and the impregnation time – as well as to investigate, qualitatively and quantitatively, the effects of these parameters on the adsorption efficiencies of the dye compounds.

Within the selected parameters and level values, two sets of optimized parameter combinations for maximizing the individual adsorption efficiency of the activated carbon for MB and MO were found to be similar, both included an optimum combinatiom of *A*3 (impregnation ratio of 2:1), *B*2 (activation temperature of 550 °C) and *C*3 (activation time of 60 min). Under these optimized conditions, adsorption of approximately 400 mg /g for MB and 900 mg /g for MO can be obtained, based on prediction analysis and experiment confirmation.

The most effective parameter for maximizing the capacity of activated carbon to adsorb MB and MO was found to be activation temperature with the optimal value of 550 °C. An activation temperature which is excessively low or high leads to a decrease in adsorption efficiency. The impregnation ratio has a significant effect on the

adsorption of both dyes, with the trend being higher adsorption at higher impregnation ratio. The activation time and the impregnation time were identified to be not significant parameters from a statistical point of view, but the effect of the activation time cannot be neglected considering the percentage contribution to the adsorption response value – 10.68% for MB and 11.24% for MO.

If converting Chinese Hickory husks into activated carbon to adsorb dye pollutants is, indeed, potentially one of the best methods to treat and reuse this waste, several concerns need to be addressed, and this warrants further investigation, including comparison of different preparation methods, the effects of adsorption process parameters and adsorption equilibrium and kinetics.

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AUTHOR DISCLOSURE STATEMENT

The authors declare that no conflicting financial interests exist.

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