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Synergistic Studies on the Removal of Dyes by Waste (*Metroxylon sagu*) Based Activated Carbon: an Optimization Study

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Abstract. Physically activated carbon prepared from untreated *(Metroxylon sagu)* waste was used as adsorbents for the adsorption studies of methylene blue (MB) and gentian violet (GV) dye in aqueous solution. Response Surface Methodology (RSM) was employed to investigate the different operating parameters on the uptake of the dye molecule. The adsorbent before and after activation process were characterized to determine the specific surface area, iodine value, textural structure, and surface functional group. The results predicted using CCD model showed high values of regression coefficients R^2 (MB= 0.9944 and GV= 0.9845) indicating good agreement with experimental data. Characterization of PAC produced also showed that the activation conditions would find good-quality adsorbent with the highest BET surface area of 1423.5 m^2/g, iodine value of 1275.2 mg/g and well-forming pores distribution.

1.   Introduction

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons for the fact that the adverse effect of these dyes may be responsible for permanent injury to humans and animals because they are found to be a mitotic poisoning agent, which is recalcitrant and carcinogenic, and thus regarded as a biohazard [1], [2]. Thus, the removal of these dyes from effluents is essential not only to protect human health but also for the protection of water resources. Hence attempts are made in this study to develop an inexpensive adsorbent for removal of MB and GV from aqueous solutions using low cost activated carbon produced from agricultural waste.

There are basically two methods for preparing activated carbon, namely physical and chemical activation. Generally, physical activation which involves carbonization of a carbonaceous material followed by activation of the resulting char at elevated temperature in the presence of suitable oxidizing gasses such as carbon dioxide, steam, air or their mixtures. The chemical activation is performed by the thermal decomposition of the raw material impregnated with certain chemicals such as $ZnCl_2$, NaOH, KOH, H_2SO_4, and H_3PO_4. Then, heat treatment at moderate temperatures (400–600 ^{o}C) in a one-step process [3], [4].

Application of physical activation using steam has shown the best potential for producing activated carbons with high surface area and good pore ratio [5]. The main advantage of physical activation over chemical activation is that it avoids the incorporation of impurities coming from the activating agent, it's cheap, eco-friendly and economical for production. Although various agricultural wastes have been
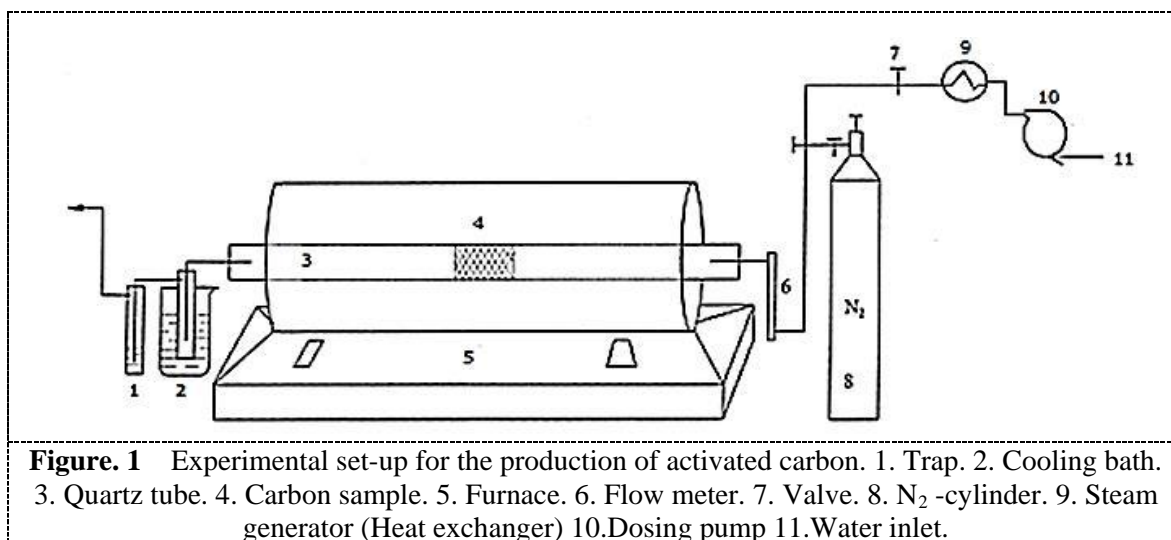
used for preparing activated carbons by other chemical methods, the major concerns resulting from secondary pollution and chemical consumption must be considered. However, there are no reports up to date related to the production of activated carbon from *(Metroxylon spp)* waste by one step thermal activation using steam as an oxidizing agent. This method is hoped to enhance the absorption properties of the obtained activated carbons.

The aim of this paper was first to prepare the activated carbons from sago waste and to measure their physicochemical properties such as the yield, iodine number, BET surface area, pore size distribution, total pore volume, surface morphology and the elemental analysis. The environmentally friendly steam as an oxidizing agent was used in this work for activation processes. The amounts and rates of adsorption of dyes using the activated carbon from *(Metroxylon spp)* waste were then measured to investigate various parameters viz: agitation speed, pH, temperature on the removal of MB and GV using a two-level 3 factor (2^3) Central Composite Design (CCD) with the help of Design Expert 6.0.8 (Stat-Ease, USA).

2.   Materials and methods

2.1.   *Production of porous carbon by steam activation*
Precursor, *(Metroxylon sagu)* waste also known as sago waste was used for the production of PAC by thermal pyrolysis and in the presence of steam by one step activation. A known amount of raw material was carbonized and activated in a cylindrical quartz tube (OD: 95 mm, ID: 90 mm, L: 1,100 mm) using a rectangular horizontal high-temperature CSC— Split furnace (Lenton Thermal Design, UK). The system setup is shown in Figure 1. Once the tube furnace was switched on and set at required temperatures 900 ^{o}C, nitrogen gas (N_2) was supplied to the system at 2.5 l/min [6]. This was continued for one hour at a heating rate of 23 ^{o}C/min. During this process, the impurities purged was passed through and trapped in a container of water in the fume hood.

Figure. 1   Experimental set-up for the production of activated carbon. 1. Trap. 2. Cooling bath. 3. Quartz tube. 4. Carbon sample. 5. Furnace. 6. Flow meter. 7. Valve. 8. N_2 -cylinder. 9. Steam generator (Heat exchanger) 10.Dosing pump 11.Water inlet.

Upon the completion of carbonization, the N_2 gas flow was stopped and steam was introduced for activation of 15 min according to [6]. At the end of the operation, the steam generator was stopped to terminate the activation and switched back to the inert gas and the system was allowed to cool to below 50 ^{o}C before removing the AC from the quartz tube inside the furnace. The AC produced was ground and sieved to size fractions less than 250 µm [7]. The weights of samples were taken before and after production and the AC yield was calculated by the following expression:

$$Y_{Ch} (\%) = \frac{Weight\ of\ Activated\ Carbon}{Weight\ of\ Precusor} \times 100 \qquad (1)$$

2.2. Characterization of activated carbons

The iodine number of activated carbon was obtained on the basis of the Standard Test Method, by titration with sodium thiosulphate (ASTM, D 4607-94) [8]. The concentration of iodine solution was thus calculated from the total volume of sodium thiosulphate used and volume dilution factor. The BET surface area (SBET) and pore features of PAC, and sago waste were measured under N_2 adsorption/desorption isotherms at 77 K using a surface area analyzer (Quantachrome Corporation, USA). The surface morphology of the PAC based sago waste adsorbents before and after activation was observed by scanning electron microscopy (SEM) (Hitachi S-520, Japan). Functional groups present in the raw material i.e. SW and PAC were evaluated by FTIR spectra, which were recorded between 4000 and 400 cm^{-1} (resolution of 4 cm^{-1} and acquisition rate of 32 scan min^{-1}) using an IR prestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan).

2.3. Design of experiments

In order to develop an adsorption process for the design of the experiment, a number of factors influencing this process such as pH, agitation speed, and temperature are to be studied. CCD via face-centered was selected to model the effects of the methylene blue and gentian violet onto PAC based sago waste preparation variables; pH (5-9), agitation speed (100-400 rpm), temperature (35- 55 $^{\circ}$C) towards their responses; MB (Y_1) and GV (Y_2) adsorption value. These three variables together with their respective ranges were chosen based on preliminary studies as given in Table 3. CCD requires three variables; 8 factorial points, 6 axial points and 6 replicates at the center points, indicating that altogether 20 experiments for this procedure, as calculated from Eq. (2) [9]:

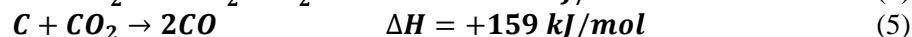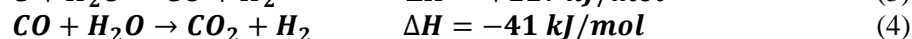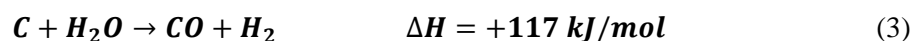$$N = 2^n + 2n + n_c = 2^3 + 2(3) + 6 = 20 \qquad (2)$$

where N is the total number of experiments required. A weighed amount (0.1 g) of activated carbon and 500 ppm of dyes concentration solution was used for all experiment

3. Results and discussion

3.1. Characteristics of the activated carbon produced

3.1.1. The effect of activation mechanism

The mechanism of preparation process for the carbon by steam activation can be explained as follows: (1) carbonization is a strong phase of chemical reaction which enhances organic matter degradation; (2) steam activation is a multiple reaction in gas/solid phase system and is divided into two processes: physical and chemical phase. These are water vapor spreading into the surface of granule, gasification reaction on the surface of carbon, decomposition of intermediate product and stripping of the reaction product. As an activating agent, steam can enter into the carbon particulate and react with it. The activation reaction mechanism of a carbon atom with steam as an activating agent has been illustrated below:

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = +117 \ kJ/mol \qquad (3)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41 \ kJ/mol \qquad (4)$$
$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +159 \ kJ/mol \qquad (5)$$

In the above equations, C is the carbon atom activation sites. Steam activation was undergone under inert condition and temperature greater than 700 $^{\circ}$C, and the prepared activated carbon can avoid the erosion of oxygen. The reaction of Eq. (3) will produce carbon monoxide, which will then react with H_2O to form CO_2. Then the CO_2 will react with carbon and consume more carbon and hence higher burn-off [10], [11]. Maximum yield of 12.6 % was recorded for PAC at an activation temperature of 900 $^{\circ}$C, carbonization time of 1hour in the presence of steam flow for 15 mins. In general, greater the aromaticity and molecular weight of the precursor, greater will be the char yield. The low carbon yield

in the case of cellulose is due to the fact that significant amount of carbon is lost from the glucose derivatives due to volatilization and as a result, the char yield is low.

3.1.2. Surface area and pore size distribution of the PAC

The N_2 adsorption-desorption isotherms and the pore size distribution by Barret, Joyner, and Halenda (BJH) method for PAC was shown in Fig. 2(a) and 2(b). As can be seen from Figure 2(a), increasing the relative pressure led to the appearance of a hysteresis loop as a result of capillary condensation, signifying a substantial development of mesoporosity. The total pore volumes were estimated to be the liquid volume of adsorbate (N_2) at a relative pressure of 0.98. All surface areas were calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule to be 0.162 nm [12]. Total surface area of 1432.5 m^2/g, micropore surface area (1524 m^2g^{-1}), total pore volume (0.906 cm^3g^{-1}), micropore volume (0.542 cmg^{-1}) and average pore radius (1.72 nm) respectively was obtained after production. The BET surface area and pore volume of the PAC based SW were greater than that of the untreated sago waste as indicated in Table 1.
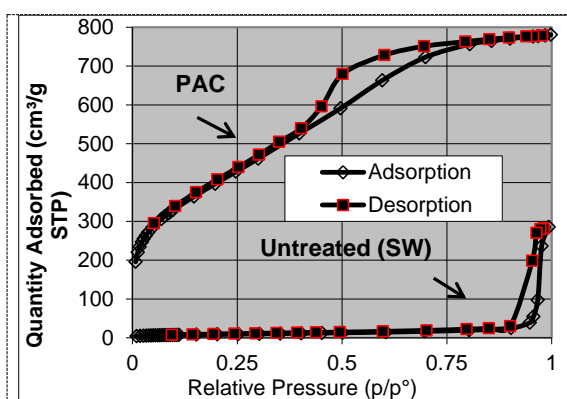

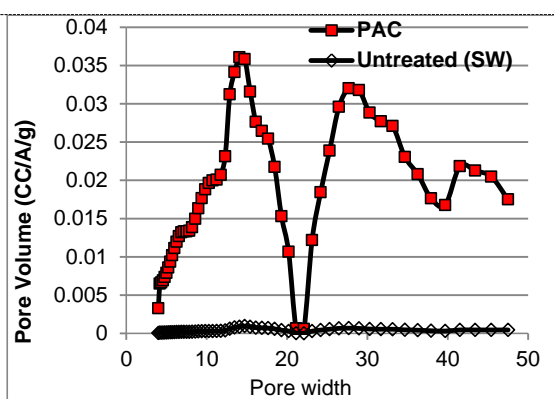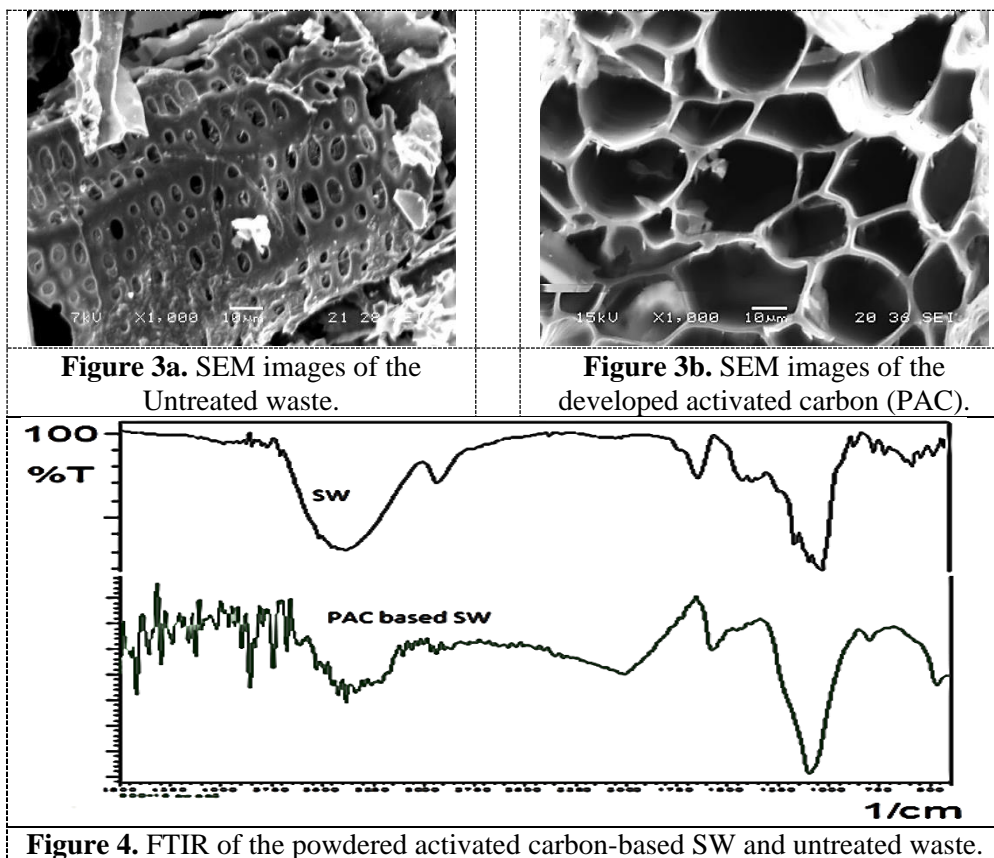| **Figure 2(a).** Nitrogen adsorption/desorption isotherms for PAC and untreated waste. | **Figure 2(b).** Size distributions for PAC and untreated waste. |

Table 1. Physiochemical characteristics of PAC based sago waste and raw sago waste

	Iodine Value (mg/g)	Total Surface Area (BET) (m^2g^{-1})	Micropore Surface Area (m^2g^{-1})	Total Pore Volume (cm^3g^{-1})	Micropore Volume (cm^3g^{-1})	Average pore radius (nm)
PAC based SW	1275.2	1423.5	1524.1	0.906	0.542	1.724
Untreated	83.7	32.01	39.48	0.151	0.014	-

The AC development porosity is associated with gasification reaction. The pore size distribution is shown in Fig. 2(b), substantiate that the PAC comprise micro-mesopores with 2 sharp peaks pointing to pore diameters of 14.08 and 27.7 nm for the micropore and mesopores size ranges, respectively.

Each 1.0mg of iodine adsorbed is ideally considered to represent 1.0m^2 of the activated carbon internal area [13]. The iodine number of 1275.2 mg/g was obtained for PAC after production. Activated carbons with iodine numbers of about 550 mg/g can be attractive for wastewater treatment from the user's viewpoint [13]. The iodine number value is an indication of the surface area of the activated carbon [14].

Fig. 3 (a), and (b), respectively shows the SEM micrographs obtained before and after activation at an accelerating voltage of ~10 kV and $1000\times$ magnification. At such magnification, distinct differences in the surface structure and porosity were clearly identifiable. It is evident that the novel activated carbon and its raw state affects the number of charged functional groups on the adsorbent surface. The

microporosity is opened and widened with even a shift to meso- and macro-porosity as the removal of the exterior of the particle is significant at high burn-offs. This shows that steam was effective in creating well-developed pores on the surfaces of the precursor, hence leading to the activated carbon with large surface area and porous structure which had high adsorption capacity on dyes. The surface of the raw material was dense and planar without any cracks and crevices [6]. Due to these well-developed pores, the activated carbon possessed high surface area and adsorptive capacity. The pore size distribution of the activated carbon indicated that the diameter of the pores is greater than 2 μm which show that mesopores developed in the activated carbons.

| **Figure 3a.** SEM images of the Untreated waste. | **Figure 3b.** SEM images of the developed activated carbon (PAC). |

Figure 4. FTIR of the powdered activated carbon-based SW and untreated waste.

The changes in the spectrum in Figure 4 clearly indicate the possible involvement of carbonization and steam activation to amend the surface chemistry of the prepared activated carbon than the raw precursor. The new broadband at 3855 - 3423 cm^{-1} respectively found in the spectrum of the activated carbon can be assigned to O-H stretching vibration of hydroxyl functional groups including hydrogen bonding. Other peaks detected on the sago waste after activation with steam were located at 2934, 2005.5, 1574.4, 1093.0, 795.6, 651.5 cm^{-1} and 462.92 cm^{-1}, respectively assigned to C-H stretching in alkanes/alkyl groups, C-N stretching, C-O-C stretching, C-H out-of-plane bending in benzene derivatives, C-O stretching and O-H bending modes of alcoholic, phenolic, carboxylic groups, O-H stretching and C-O-H twist. C-H out-of-plane bending in benzene derivatives was commonly found on the surface of various activated carbons [15].

3.2. Statistical analysis

The complete design matrices together with both the response values obtained from the experimental work are shown in Table 2. Adsorption capacity value low and high of MB and GV were found to range from 216.1 to 253.1 mg/g and 104.9 to 250.7 mg/g, respectively.

The results of the surface quadratic model in the form of analysis of variance (ANOVA) for MB and GV adsorption capacity value respectively are given in Table 3. ANOVA is required to justify the significance and adequacy of the models. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. For the linear and quadratic models of MB and GV adsorption capacity were suggested by the software. However, the quadratic model was selected in this case due to the higher order polynomial.

Table 2. Experimental design matrix for dye adsorption using activated carbon

Std	A:pH	B:Agitat.Speed (rpm)	C:Temperature (^{o}C)	Y_1: MB (mg/g)		Y_2: GV (mg/g)	
				Actual	Predicted	Actual	Predicted
1	5.0	100.0	35.0	220.23	220.18	222.29	227.37
2	9.0	100.0	35.0	218.45	217.75	107.53	109.15
3	5.0	400.0	35.0	247.78	248.28	154.82	161.83
4	9.0	400.0	35.0	240.56	240.59	111	112.6
5	5.0	100.0	55.0	220.85	220.38	173.86	175.11
6	9.0	100.0	55.0	216.11	215.17	104.91	100.76
7	5.0	400.0	55.0	241.26	241.52	201.34	202.57
8	9.0	400.0	55.0	231.44	231.05	199.45	197.22
9	5.0	250.0	45.0	244.23	244	228.2	213.62
10	9.0	250.0	45.0	235.56	237.56	148.67	151.83
11	7.0	100.0	45.0	228.56	230.73	215.92	212.12
12	7.0	400.0	45.0	253.12	252.72	235.18	227.57
13	7.0	250.0	35.0	245.55	245.77	250.69	235.38
14	7.0	250.0	55.0	239.56	241.1	247.66	251.56
15	7.0	250.0	45.0	248.88	248.29	238.8	242.61
16	7.0	250.0	45.0	248.87	248.29	238.8	242.61
17	7.0	250.0	45.0	248.88	248.29	238.81	242.61
18	7.0	250.0	45.0	248.88	248.29	238.79	242.61
19	7.0	250.0	45.0	248.88	248.29	238.79	242.61
20	7.0	250.0	45.0	248.87	248.29	238.82	242.61

Table 3. Analysis of variance (ANOVA) for response surface quadratic models of MB and GV

Source	Sum of Squares (Y_1)	(Y_2)	DF	Mean Square (Y_1)	(Y_2)	F Value (Y_1)	(Y_2)	Prob > F (Y_1)	(Y_2)
Model	2729.76	46737.05	9	303.31	5193.01	196.06	70.48	< 0.0001*	< 0.0001*
A	103.88	9545.01	1	103.88	9545.01	67.15	129.55	< 0.0001*	< 0.0001*
B	1209.12	597.22	1	1209.12	597.22	781.6	8.11	< 0.0001*	0.0173*
C	54.52	654.32	1	54.52	654.32	35.24	8.88	0.0001*	0.0138*
A^2	155.08	9859.84	1	155.08	9859.84	100.25	133.83	< 0.0001*	< 0.0001*
B^2	118.51	1424.95	1	118.51	1424.95	76.6	19.34	< 0.0001*	0.0013*
C^2	64.67	2.04	1	64.67	2.04	41.81	0.028	< 0.0001*	0.8711
AB	13.83	2380.5	1	13.83	2380.5	8.94	32.31	0.0136*	0.0002*
AC	3.86	962.29	1	3.86	962.29	2.5	13.06	0.1451	0.0047*
BC	24.22	4325.43	1	24.22	4325.43	15.66	58.71	0.0027*	< 0.0001*
Residual	15.47	736.76	10	1.55	73.68				
Lack of Fit	15.47	15.06	5	3.09	3.01	1.16E+05	1078182	< 0.0001	< 0.0001
Pure Error	1.33E-04	6.83E-04	5	2.67E-05	1.37E-04				
Cor Total	2745.23	47473.8	19						

DF; Degree of Freedom, * Significant

The mean squares were obtained by dividing the sum of the squares of each of the variation sources, the model, and the error variance, by the respective degrees of freedom. Values greater than 0.1000 indicate the model terms are not significant. If the value of Prob. > F less than 0.05, the model terms are considered as significant. From Table 3, for Y_1 the model F-value of 196.06 and Prob. > F of <0.0001 implied that this model was significant. In this case, A, B, C, A^2, B^2, C^2, AB and BC factors were significant model terms whereas AC is insignificant to the response. In addition, Y_2 response model F-value of 70.48 and Prob. > F of <0.0001indicated that the model was significant. In this case, A, B, C, A^2, B^2, AB, AC and BC factors were significant model terms whereas C^2 is insignificant to the response. The non-significant value of lack of fit showed that the quadratic model was valid for the present study.

3.3.   Development of regression model equation

The final empirical formula models for the (Y_1) and (Y_2) in terms of coded factors are represented in Table 4 were adequate to predict the Y_1 and Y_2 adsorption capacity value within the range of variables studied. The coefficients with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between two factors and quadratic effect, respectively.

Table 4. Terms of Coded factors

	Modified equations with significant terms	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision	Standard Deviation	Mean	C.V.[1]	PRESS[2]
(Y_1)	= +248.29 -3.22 A+11.00 B-2.33 C-7.51 A^2 -6.56 B^2 -4.85 C^2 -1.32 AB -0.70 AC -1.74 BC	0.9944	0.9893	0.9655	42.69	1.24	238.83	0.52	94.68
(Y_2)	= +242.61 -30.90 A+7.73 B+8.09 C-59.88 A^2-22.76 B^2+0.86 C^2+17.25 AB+10.97 AC +23.25 BC	0.9845	0.9705	0.9015	24.85	8.58	201.72	4.26	4677.4

A: Initial Solution, B: Agitation speed (rpm), C: Temperature (^{o}C),
[1]: Coefficient of variation,
[2]: Predicted residual error sum of squares

The quality of the models developed was evaluated based on the correlation coefficients, R-value. In fact, the models developed seems to be the best at high R^2 statistics which is closer to unity as it will give predicted value closer to the actual value for the responses [12]. In addition, the R^2 and adjusted R^2 values for Y_1 and Y_2 were 0.994 and 0.9844, 0.989 and 0.9705 respectively. This indicated that 99.4 and 98.4% of the total variation in the MB and GV adsorption value respectively, were attributed to the experimental variables studied. Both R^2 values were considered relatively high, indicating that the predicted values 0.9655 and 0.9014 for MB and GV removal were accurate and closer to its actual value. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 42.69 (Y_1) and 24.85 (Y_2) indicates an adequate signal. Therefore, these model can be used to navigate the design space. At the same time, a relatively lower value of the coefficient of variance (C.V. = 0.52 and 4.26 %) indicates a better precision and reliability of the experiments carried out.

4.   Conclusions

The results of this study demonstrated that low-cost activated carbon can be prepared from *(Metroxylon sagu)* waste by physical activation with steam for MB and GV adsorption. PAC with the maximum BET surface area of 1423.5 m^2 /g was obtained under the following conditions: carbonization temperature 900 ^{o}C; carbonization time 60 min; activation temperature 900 ^{o}C and activation time 15 min. The analysis of results carried out by using central composite design idea was to avoid the traditional one-factor-at-a-time experiments and the model developed resulted in an improved response, reduced process variability, a time-saving approach for studying the combined

influence of process parameters on the response factor and closer confirmation of response to targeted requirements. The agitation speed, initial solution pH, and temperature significantly influenced the dye removal efficiency. The corresponding adsorptive efficiency in optimum conditions was found to be (244.5 and 239.86 mg/g) and their desirability was 0.997 and 0.991 for MB and GV respectively. The PAC based SW prepared demonstrated high iodine value, surface area, and well-developed porosity. Taking into consideration all the above-obtained results, PAC based SW showed a good potential and can be used as an effective sorbent for removal of MB and GV from aqueous systems.

5.   References

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