Optimization of Activated Carbons Production from Sesame Stalks Using Response Surface Methodology

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Abstract—The use of relatively expensive and nonrenewable precursors such as natural coal is the main reasons for the high cost of commercial activated carbons. Agricultural wastes are considered as promising precursors for low cost and high surface area activated carbons due to their high volatile matter and lignocellulosic contents and their renewable natures. To recycle agricultural wastes and decrease activated carbon(AC) production cost, in this study, AC from sesame stalks were prepared by sodium hydroxide activation. Activation temperature, activation time and impregnation ratio (IR) were optimized by Response surface methodology (RSM) in AC preparation. Results showed that temperature at 640°C, time 1.45h and IR 1.93, methylene blue(MB) adsorption capacity and yield of AC reached 224.11 mg/g and 18.29%, respectively. Furthermore, surface characteristics of AC were studied using BET surface area analysis and scanning electron microscopy (SEM).

Keywords-Sesame stalks; Activated carbon; Response surface methodology; Optimization

I. INTRODUCTION

In recent years, solid waste management ranked equal to water and air pollution as the most intricate environmental turmoil in China. With circular economy legislation being introduced in China, desired direction of solid waste management was oriented towards waste minimization, resource and materials reuse. All strategies adopted were aimed to decrease quantity of solid wastes needing disposal and create available products. China as one of the largest agricultural country, its vast agricultural wastes were produced annually. However, these wastes were underutilized and often burned in open field, thus causing heavily environmental pollution. Accordingly, use of agricultural wastes for fabrication of value-added materials seems very attractive and promising from environmentally and economically viable view.

Activated carbon (AC), as a well-known multiporous material, was widely used in various fields, such as separation and concentration of useful or harmful components from mixed liquids or gases, and catalyst support [1-6]. However, the manufactures costs of commercial AC are in fact rather high [7, 8]. As such, it is urgent to produce AC from cheaper, renewable and readily available materials. Recently, some agricultural wastes, such as rambutan peel [1], oil palm fiber [2], bamboo waste [3], cotton stalks [4], mangosteen peel [9] and artichoke leaves [10] were commonly used to prepare AC.

Sesame as one of major economy crops in China, up to 0.36 million tones of stalks were generated annually and usually burned in open fields, thus leading to heavily air pollution. As well known, sesame stalks possess high carbon and volatile contents, low ash, and reasonable hardness. Tragically, up to date, there was no report on preparing AC from sesame stalks (SS).

Consequently, in this study, SS was used as raw materials to prepare AC. Initially, effects of parameters (activation temperature, activation time and impregnation ratio) on adsorptive property and yield of AC were investigated and optimized by RSM. Then, the prepared AC was characterized by BET surface area analysis and SEM.

II. MATERIALS AND METHODS

A .Preparation of activated carbon

SS used in this study was obtained from a village in Xuzhou city, jiangsu Province, China. SS was initially washed twice with pure water to remove dust and subsequently dried at 105°Cfor 24 h to remove moisture content. Then, dried SS were ground and sieved to size of 1-2mm. Afterwards, 4g sieved particles was selected to mix with NaOH pellets with different impregnation ratio (IR), respectively, and (50ml) deionized water was added to dissolve all NaOH pellets.

The IR was estimated from following equation:

$$IR = \frac{\text{weight of NaOH}}{\text{weight of sesame stalks}} \quad (1)$$

The mixture was left overnight at room temperature and then dried at 110°C for 24 h. The dried material was set on a ceramic boat which was then inserted in a stainless tube (i.d.40 mm) and pyrolyzed in furnace with nitrogen (N2) flow rate of 30mLmin−1 and heating rate of 5°Cmin−1 . Temperatures and times were based on design of RSM shown in TABLE1. After pyrolysis, furnace was cooled to room temperature in flowing N_2 overnight. Afterwards, obtained samples were washed with 1 M HCl, and then with distilled water to make effluent pH close to 7. Then, AC samples were dried at 120°Cfor 24 h, sieved and stored in plastic containers for measurement.

B . Experimental design

RSM was employed to optimize operating conditions of AC manufacturing process. The parameters of activation temperature(A), activation time(B)and IR(C)were optimized by Central Composite Design(CCD). The ranges of three factors to be evaluated were: 532≦A≦868°C, 532≦B≦868°C, and 532≦B≦868°C. Response Y values were MB adsorption capacity (Y_1) and yield (Y_2) of AC.

TABLE1 CODED AND ACTUAL LEVEL FOR INDEPENDENT FACTORS USED IN THE EXPERIMENTAL DESIGN

Factors	Code	Units	Coded variable levels				
			-α	-1	0	+1	+α
activation temperature	A	°C	532	600	700	800	868
activation time	B	h	0.66	1	1.5	2	2.34
IR	C	-	0.32	1	2	3	3.68

C.Measurement of MB and yield of activated carbon

Because of its size (1.43nm×0.61nm×0.40 nm), the well known methylene blue cationic dye ($[C_{16}H_{18}N_3S]^+$, Cl^-) is commonly used to probe mesoporous volume of AC by adsorption experiments [11]. Thus, adsorptive properties of AC were studied by using Methylene blue (MB) as adsorbate. Adsorption studies were carried out according to GB/T12496.10-1999 (testing standard of activated carbon in China). The concentration of MB was determined using a double beam UV–vis spectrophotometer (America Varian Pty.Ltd) at 665 nm.

The yield of AC was estimated from following equation:

$$\text{Yield of AC (wt\%)} = \frac{\text{weight of activaed carbon}}{\text{weight of sesame stalks}} \quad (2)$$

D. Characterization of activated carbon

Characterizations of AC were determined by nitrogen adsorption at 77K using a Micromeritics ASAP2010C surface area analyzer (USA).The BET surface area was calculated from N_2 adsorption isotherms by using Brunauer-Emmett-Teller (BET) equation based on the assumption area of nitrogen molecule to be 0.162nm^2. The total pore volume (Vp_j) was estimated from volume of N_2 (as liquid) held at a relative pressure (P/P_0) of 0.95. The pore size distribution (PSD) of AC prepared was calculated from adsorption isotherms using BJH method. The morphology of AC was examined by scanning electron microscopy (Hitachi Co., model S - 3400NⅡ).

III. RESULTS AND DISCUSSION

A.Optimization of activation temperature and time and impregnation ratio (IR) by response surface methodology (RSM)

Statistical experimental design, as an efficient way to improve experimental works, has been widely used in chemistry, food and environmental engineering[12-14]. Among these design methods, RSM is considered as a powerful technique for testing multiple process variables and identifying interactions between these variables, and a combination of factors generating an optimal response can be identified by this technique[15]. Besides raw materials, external parameters of activation temperature, activation time and impregnation ratio (IR) play key roles in AC preparation, Accordingly, to determine optimal preparation conditions, RSM experiment was applied and MB adsorption capacity (Y_1)and yield total (Y_2) was analyzed as response values. Based on previous single-factor test results (data not shown), activation temperature, activation time and IR were set in the range of 532 to 868°C, 0.66 to 2.34h and 0.32 to 3.68, respectively.

Variable design and experiment results were shown in TABLE1 and TABLE2. Each factor has three levels and corresponding twenty experiments were designed. Each experiment was carried out in triplicate and repeated twice and the average of experimental results was used. As shown in TABLE2, highest experimental value of MB (326.4mg/g) was obtained under conditions of 800°C, 1h and IR3. In contrast, total AC yield reached the highest value of 23.3 under 600°C, 1h and IR1. It was evident that two values of MB and AC yield can not reach the maximal values simultaneously at the same prepared conditions. Consequently, design-Expert software version7.0.0 was used to obtain the relatively optimal values of MB and AC yield under fixed conditions.

TABLE 2 EXPERIMENTAL DESIGN MATRIX AND RESULTS

Run no	A	B	C IR(-)	Y_1(mg/g)	Y_2 (%)
1	700	1.5	2	272.32	18.82
2	800	1	3	326.44	15.83
3	700	1.5	2	259.61	18.63
4	600	1	1	70.2	23.32
5	700	1.5	2	269.43	17.96
6	700	1.5	2	270.81	18.05
7	600	2	1	114.34	21.65
8	868.1793	1.5	2	280.03	15.05
9	700	1.5	0.318207	89.4	19.34
10	800	2	1	109.03	17.92
11	700	0.659104	2	219.09	19
12	800	2	3	320.87	16.12
13	600	2	3	312.56	16.64
14	700	1.5	2	230.93	17.94
15	700	2.340896	2	224.31	17.73
16	531.8207	1.5	2	143.02	18.57
17	700	1.5	3.681793	306.45	14.78
18	600	1	3	238.78	17.58
19	800	1	1	102.77	18.52
20	700	1.5	2	273.64	18.11

Regression coefficients for $Y_1$and Y_2 were shown in TABLE 3 and TABLE 4 respectively. Then regression equations of MB and AC yield can be achieved according to these coefficients. Correlation coefficient of regression

models of MB and AC were 93.6% and 88.4%, which meant a high fitting accuracy. From TABLE 3 and 4, F-values of 16.31and16.52 implied that the models are significant. There is only a 0.01% chance in both models occurring due to noise. Moreover, values of "Prob > F" less than 0.0500 indicate that model terms are significant. For TABLE 3, A, C, A_2, C_2 are significant, whereas B, AB, AC,BC and B_2 were insignificant to the response. For TABLE 4, A, C, AC are significant while B, AB, and BC were insignificant to the response. Accordingly, it was concluded that activation temperature and IR influenced AC preparation significantly, but activation time showed relatively less significant effect, which was consistent with the previous conclusion [1, 16, 17].

As indicated in Fig.1, MB adsorption capacity(Y_1) was affected by both IR and activation temperature. Moreover, compared to temperature, IR had a higher effect. For instance, MB adsorption capacity decreased from 306 to 89 as IR changed from 3.68 to 0.32. In contrast, corresponding value changed from 280 to 143 with activation temperature changing from 868 to 532°C.

TABLE 3 ANALYSIS OF VARIANCE (ANOVA) FOT RESPONSE SURFACE QUADRATIC MODEL FOR Y1

Source	Sum of Squares	df	Mean Square	F Value
Model	1.277E+005	9	14192.71	16.31305
A	9158.042	1	9158.042	10.52622
B	1188.264	1	1188.264	1.365787
C	99780.66	1	99780.66	114.6876
AB	1717.859	1	1717.859	1.974502
AC	590.133	1	590.133	0.678297
BC	39.64951	1	39.64951	0.045573
A^2	5636.887	1	5636.887	6.47902
B^2	3772.743	1	3772.743	4.336379
C^2	8710.988	1	8710.988	10.01238
Residual	8700.217	10	870.0217	

TABLE 4 ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE $2F_I$ MODEL FOR Y_2

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	66.65859	6	11.10976	16.51701	< 0.0001
A	20.46997	1	20.46997	30.43293	< 0.0001
B	1.871726	1	1.871726	2.782716	0.1192
C	38.42914	1	38.42914	57.13303	< 0.0001
AB	0.66125	1	0.66125	0.983088	0.3395
AC	4.89845	1	4.89845	7.28258	0.0182
BC	0.32805	1	0.32805	0.487716	0.4973
Residual	8.744133	13	0.672626		

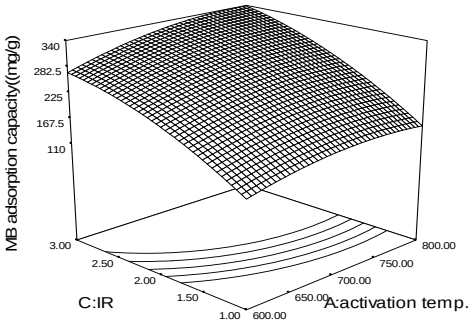


Figure1. Three dimensional response surface plot of the MB adsorption capacity (effect of activation temperature and IR,for t = 1.5h)

Generally, the reaction mechanism of NaOH activation for AC preparation can be expained by following equation[18,19]:

$$6NaOH+2C \leftarrow 2Na + 2Na_2CO_3 + 3H_2 \quad (3)$$

According to Eq. (3), stoichiometric ratio of NaOH/ char is 3:1, indicating greater quantity of NaOH needed to form AC. It was showed that higher IR was favorable for widening of micropores to mesopores, thus increasing MB adsorption capacity [20]. In addition, Lillo-Ródenas [21]found that micropore volume and surface area increased as the ratios of NaOH/ char changed from 1/1 to 3/1, however, as the ratio exceeded 3/1, increase degrees of these two values decreased. Moreover, as NaOH/ char ratios increased from from 3/1 to 4/1, surface oxide groups increased markedly[22], which shows negative effect on adsorption capacity [23].

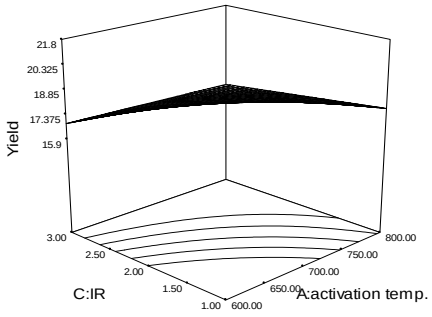


Figure2.Three dimensional response surface plot of activated carbon yield (effect of activation temperature and IR,for t = 1.5h).

Meanwhile, Fig.2 indicated that both activation temperature and IR significantly affected AC yield (Y_2). It was observed that AC yield decreased with an increase in IR and activation temperature , which is contrary to MB adsorption capacity. The reason can be attributed to certain prepared AC being consumed by IR. As a result, AC yield was decreased, which can be further explained by following equation.

Based on above Eq. (3), elemental Na was generated, and part of which was further turned into NaOH through oxidation and hydration that can be described by Eq. (4) reported by Lillo-Ródenas [19]. Evidently, NaOH from Na further consumed prepared AC, thus leading to relatively lower yield. Meanwhile, it was reported that Na+ can

promote oxidation of carbon atoms on AC surface, resulting in increased consumption of AC[24].

$$2Na \xrightarrow{oxidation} Na_2O \xrightarrow{hydration} NaOH \quad (4)$$

In addition, the effect of activation temperature on AC yield was similar to IR while activation time had an insignificant effect(data not shown), which was in agreement with the previous works[1,17,25]

In short, among three tested external factors, both IR and activation temperature showed an important influence on MB adsorption and AC yield, while activation time did not show a significant effect.

B. Effects of optimized external conditions on AC preparation

In following equation (5) and (6), Y1and Y2 represent MB adsorption capacity and total AC yield respectively.A, B and C represent activation temperature, activation time and IR, respectively.

$$Y_1=263.04+25.90\times A+9.33\times B+85.48\times C-14.65\times AB+8.59\times AC+2.23\times BC-19.78\times A_2-16.18B_2-24.59\times C_2 \quad (5)$$

$$Y_2=18.08-1.22\times A-0.37\times B-1.68\times C+0.29\times AB+0.78\times AC+0.20\times BC \quad (6)$$

Based on achieving relative maximum MB and AC yield, optimal preparation conditions of activation temperature, activation time and IR were calculated by design-Expert software version7.0.0. As shown in TABLE 5, under conditions of 640°C, 1.45h and IR1.93, MB and AC yield reached the relatively highest values of 233.2 and 19% respectively. Furthermore, to test accuracy of the value achieved by above model, optimized experimental conditions for AC preparation were carried out. It was evident that, shown in TABLE 5, MB adsorption and AC yield reached 224.11mg/g and 18.29%, respectively, which was only 3.89% and 3.74% in decrease as compared to the predicated value. It was suggested that the RSM is effective and practical in optimizing conditions for AC preparation.

TABLE 5 COMPARATION OF PREDICTED AND EXPERIMENTAL RESULTS ON MB ADSORPTION CAPACITY AND YIELD

operating conditions	MB adsorption capacity (mg /g)		
	Experimental	Predicted	Error (%)
T=640°C, t=1.45h, IR=1.93	224.11	233.18	3.89
	yield(%)		
	Experimental	Predicted	Error (%)
	18.29	19.00	3.74

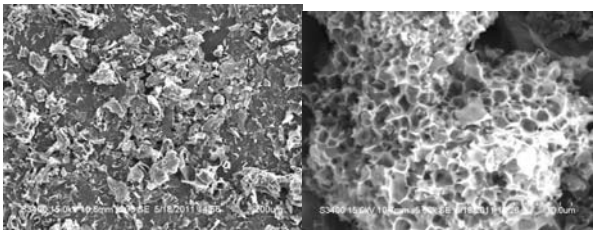
C. Characterization of prepared AC using BET and SEM

To further confirm property of AC prepared under above optimal conditions, some sesame stalk AC(SSAC) samples and commercial AC(CAC) were randomly selected to obtain surface area, total pore volume and average pore diameter by surface area analyzer. As shown in TABLE 6, BET surface area, total pore volume and average pore diameter of SSAC were 1254.01 m^2/g, 0.43 m^3/g and 2.32nm, respectively; and correspoding values were 1524.23 m^2/g , 0.51 m^3/g and 1.04nm for CAC. It was evident that surface area and total pore volume of SSAC were similar to CAC, indicating an excellent adsorptance capacity. However, there is a significant difference in average pore diameter between two AC, which suggests that pores of SSAC belongs to mesopore region .

TABLE 6 CHARACTERISTICS COMPARISION OF PREPARED AC WITH COMMERCIAL ONE

Parameters	surface area (m^2/g)	totalpore volume (cm^3/g)	average pore diameter (nm)
SSAC	1254.01±3.2	0.43±0.02	2.32±0.2
CAC	1524.23±2.1	0.51±0.03	1.04±0.1

Furthermore, to test status of pore shape and distribution on AC, raw material and SSAC were observed under SEM. As indicated in Fig.3, there was no hole or cavity on surface of raw materials. In comparison, external surface of SSAC was full of homogeneous hole and cavities. It seems that the cavities were resulted from removal of impregnated NaOH and its derivatives, thus leaving the space previously occupied by the compounds.



(a) (b)

Figure 3. SEM photographs of raw material(a) and SSACop(b)

IV. CONCLUSIONS

Sodium hydroxide was a suitable activating agent for AC preparation from sesame stalks (SS). Compared to IR and activation temperature which significantly influenced AC production, activation times did not show a significant effect. The prepared AC was filled with homogeneous cavities and their sizes belonged to mesopore region.

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