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Optimization of Conditions for Preparation of Activated Carbon from Coconut Husk Fiber Using Responses from Measurements of Surface Area and Adsorption

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Coconut husk fiber-based activated carbon was synthesized using $ZnCl_2$. Analytical technique such as SEM was used for the characterization of the developed activated carbon obtained from the carbon husk. Effects of various influential parameters are optimized using the Taguchi experimental design. The optimization of S_{BET} with the percentage removal of 4-nitrophenol, methylene blue and acid red-27 dye were applied as standard responses, the optimized parameters for S_{BET} were activation temperature of 800 °C, concentration of $ZnCl_2$ of 50 % w/v, nitrogen flow rate of 100 cm^3/min, activation time of 2 h and carbonization temperature of 300 °C. 4-Nitrophenol optimized conditions were: carbonization at 400 °C, impregnation with 5 % w/v $ZnCl_2$ solution and activation at 700 °C for 2 h with nitrogen flow rate of 200 cm^3/min. Except for the impregnation ratio, nitrogen flow rate and activation time in the case of methylene blue, the ideal conditions of the percentage removals of methylene blue and acid red-27 are almost equal to that of the S_{BET}. The surface characteristics of the samples produced under optimal conditions were examined. There are no pores available in the surface of the coconut fiber compared to the surface of the other two samples prepared under ideal conditions. Moreover, the activated carbons prepared under these optimized conditions contain small amounts of oxygen and have neutral surfaces.

Keywords: Taguchi method, Coconut husk fiber, ANOVA analysis, S_{BET}, Methylene blue, Acid red-27.

INTRODUCTION

Rapid removal and fast adsorption of various noxious impurities from the aqueous source by commercial activated carbons was one of the most widely used efficient techniques in wastewater treatment. Adsorption using various forms *i.e.* powder form and granulated forms provide us the efficient results. This is due to the ability of these adsorbents to adsorb a wide range of pollutants with their higher adsorption capacities [1]. Despite the excellent adsorptive properties of these two forms of activated carbons, their use still has some disadvantages, for example, the raw materials commonly used for production of these adsorbents are non-renewable and relatively expensive [1]. Therefore, various studies were carried out for the production of commercial activated carbons using renewable and low-cost precursors. Many conventional methods have been used for the rapid removal of noxious impurities from aqueous solutions, it includes sedimentation, chemical treatment, oxidation, electrochemical methodology [2-10], biological treatment, reduction, precipitation, membrane filtration, ion exchange and adsorption [11]. Among all the techniques, adsorption was found to be superior over other traditional techniques for water purification and decontamination in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [12]. It also does not result in the formation of any other harmful secondary pollutant [12]. So far, researchers have tested many different types of developed adsorbents such as carbon nanotubes [13-20], MWCNTs [21,22], nanoparticles and nanocomposites [23-27], rubber tyre [28,29], Corn grain [30], olive husk [31], sewage sludge [32], flamboyant pods [33], coconut shells [34], rubber seed coats [35] and pecan shells [36] and other low cost adsorbents [37-42] *etc.* are used for the removal of noxious impurities from the aqueous solution. Granulated and powdered activated carbons have slow intra-particular diffusion and difficulties in handling, respectively [43]. Moreover, the regeneration of these two forms of activated carbon is expensive [44]. In addition, the powder use generates fine carbons [45].

In contrast, activated carbon fiber has a high surface area, excellent mechanical stability, fast adsorption and desorption rates [35,45]. Furthermore, it is simple to carry out a batch adsorption [35,45]. Therefore, activated carbon fibers have attracted keen attention of many researchers as a new adsorbent for the treatment of polluted gaseous and liquid phases [46].

Fibrous activated carbons were mostly resulted from the carbonization and activation of various types of manufactured fibers [47-53]. These industrial fibers are commonly expensive [45]. Thus, one of the main negative aspects of the activated carbon fibers is its elevated price compared to commercial activated carbons [53]. Therefore, to increase the functionality and application capabilities of activated carbon fibers, it is recommended that we use low cost materials like natural fibers as precursors for production of activated carbon fibers. According to previous studies, fibrous activated carbons have been produced from piassava fibers [54], kenaf fibers [53,55], cotton stalk [56,57], coconut shell fibers [58], jute and coconut fibers [45] and oil palm fibers [59]. These activated carbons with their surface areas are summarized in Table-1.

TABLE-1
BET SURFACE AREA FOR ACTIVATED CARBON FIBERS PREPARED FROM DIFFERENT NATURAL RAW MATERIALS

Precursors	S_{BET} (m^2/g)	Ref.
Jute and coconut fibers	959, 1303	[12]
Kenaf	45	[20]
Piassava	1190	[21]
Kenaf	490	[22]
Oil palm fibers	1118	[22]
Cotton stalk	1520, 1570	[23,24]
Coconut sell fibers	512	[25]
Coconut	5435	This work

Coconut fibers cause serious disposal problems for the environment [58]. It is found in excess in the tropical countries like Malaysia [45]. It possesses a low ash content and low cost in comparison with industrial fibers [45]. The conversion of coconut fibers to activated carbon with a BET surface area of about 512-1303 m^2/g reported previously [45,58]. Despite these studies, there has been no attempt to carry out, under the optimized conditions required, for production of a superior adsorptive properties and a high-surface-area activated carbon from coconut fibers. Therefore, one of the main aims of this work was to produce activated carbon fibers with high surface area and desired adsorption efficiency from coconut husk fibers.

The adsorption performance normally depends on the morphological, textural and anatomical characteristics of the adsorbent. These properties are affected by the method used during their synthesis, conditions of production and the nature of the used raw materials [53]. Physical and chemical methods are the most widely used method for activated carbon production. Chemical methods have some advantages over physical methods in terms of its lower activation temperature and higher yield [53,60]. Activation by steam or carbon dioxide increases the oxygen content in the product [61-63]. The existence of high amounts of oxygen in activated carbon supports oligomerization of phenols on the surface of the used adsorbent [64]. It is reported that oligomerization of phenolic compounds on any adsorbent surface reduces its regeneration efficiency [64]. Therefore, to avoid an increase in oxygen content in the structure of samples produced, a chemical method was selected for this work.

Pradhan and Sandle [65] used HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$ as activation agents for the production of activated carbons. They concluded that the amount of oxygen content on the final product depends on the type and concentration of the oxidizing agent.

Chemical activation by H_2SO_4 develops acidic functional groups on the surface of the samples produced [66]. In contrast, basic agents such as potassium hydroxide lead to improving the basic functional groups [67]. Acidic functional groups on the surface of any adsorbent have a negative effect on the adsorption capacity to phenols [68]. Oligomerization of phenol and its derivatives can be improved by the surface alkaline groups [68]. For these reasons, acidic or basic agents were avoided in this work.

Ioannidou and Zabaniotou [60] elicited from the previous studies that the activated carbons prepared from nut shells and peanut hulls by activation with potassium hydroxide at 800 °C for 1 h and 500-700 °C for 3 h, respectively. These have fewer adsorption efficiencies than that of those produced when, $ZnCl_2$ was used as a chemical agent. Moreover, they also found that the surface area of activated carbon produced from almond shell activated with H_3PO_4 is less than those mixed with $ZnCl_2$. Thus, $ZnCl_2$ was selected as a chemical agent in this study.

The effect of influential parameters on the characteristics and adsorption efficiency of the prepared activated carbon can be estimated and optimized by using a central composite design or by the Taguchi experimental design method. The Taguchi method has some successful points over the others. For example, in Taguchi method only a small number of experiments are required to investigate a large number of variables. Therefore, the second aim of this study was to determine the ideal conditions for production of coconut husk fibers-based activated carbon using the Taguchi method. The optimal parameters were selected in terms of the highest surface area and adsorption affinity to 4-nitrophenol, methylene blue and acid red-27 dye. The Taguchi method was applied to optimize the experimental parameters for the production of activated carbon from kenaf fibers [55] and cotton stalks [57]. This method was applied here for the first time to investigate the effects of five experimental parameters on the surface area and adsorption performance of the produced coconut husk fiber-based activated carbon.

EXPERIMENTAL

Coconut fibers were obtained as brooms from a local market in Selangor, Malaysia. A 4-nitrophenol (4-NP) (purity of ≥ 99 %), hydrochloric acid, methylene blue (MB) (purity of ≥ 95 %), acid red-27 dye (AR-27) (purity of ≥ 97 %) and zinc chloride were supplied by Sigma-Aldrich, USA. These chemicals were used as-received.

Preparation of activated carbon fibers: Coconut fiber was repeatedly washed using cold deionized water and boiled for 15 min by deionized to remove dissolved dirt. The sample was dried at 120 °C in an oven for 24 h. 40 g of the dried sample was placed in the quartz tube (length 500 mm, internal diameter 44 mm) which was located at the center of the ceramic horizontal tubular furnace (length 900 mm, internal diameter 500 mm). An inert stream of high purity nitrogen gas was initially allowed to flow through the furnace for 20 min with a flow rate of 100 cm^3 min^{-1} to remove oxygen from inside the tube furnace. Carbonization of the dried coconut fiber was then conducted under the high-purity nitrogen flow of 100 cm^3 min^{-1} by elevating the temperature at a rate of 5 °C min^{-1} until various carbonization-temperatures (250, 300, 400 or 500 °C). The samples were kept at this temperature for 1 h and cooled to room temperature under the nitrogen environment. In activation step, the cooled carbonized samples were soaked for 24 h in a solution of $ZnCl_2$ with various concentrations (5, 15, 30 or 50 % w/v). These samples were dried at 120 °C in an oven for 24 h. The samples were again placed in the furnace and kept for 20 min at room temperature under nitrogen atmosphere with the flow rate of 100 cm^3 min^{-1}. The furnace was heated with the temperature rising at the rate of 5 °C min^{-1} until the required activation temperatures (500, 600, 700 or 800 °C) were reached with nitrogen flow rates of 100, 200, 300 and 400 cm^3 min^{-1}. The samples were kept at this temperature for 0.5, 1, 2 or 4 h and cooled in an inert atmosphere until samples reached room temperature. The activated samples were washed once with 1.5 M of HCl solution to dissolve the $ZnCl_2$ and several times with deionized water until the pH of the washing effluent reached 6-7. Finally, the samples were dried at 110 °C over night in an oven. The investigated levels of the experimental parameters were proposed by Taguchi method.

Experimental conditions for the optimization of activated carbon fibers production: The Taguchi experimental design method was applied to optimize the preparation conditions of the activated carbon fiber. In order to determine the consequent optimal values, an L_{16} orthogonal array with five operational parameters each in four levels (L1- L4) were used. 500, 600, 700 and 800 °C are the four levels for the activation temperature (parameter A). 5, 15, 30 and 50 % w/v are the four levels for concentration of the activation agent (parameter B). The four levels of the nitrogen flow rate (parameter C) are 100, 200, 300 and 400 cm^3 min^{-1}. The four levels of the activation time (parameter D) and carbonization temperature (parameter E) are (0.5, 1, 2 and 4 h) and (250, 300, 400 and 500 °C), respectively.

According to L_{16}, an orthogonal array design of Taguchi method, 16 samples of activated carbon fiber were prepared as shown in Table-2. ANOVA analysis was used to determine the optimal experimental conditions for production of activated carbon with the highest BET surface area, percentage removal of 4-nitrophenol, methylene blue and acid red-27 dye. ANOVA analysis was also used to estimate the significant factors affecting these four standard responses and to investigate the impacts of the experimental parameters on these responses.

Surface analyzer: The surface area and the porosity of the 16 prepared activated carbon samples were measured by adsorption and desorption of nitrogen at 77 K in a Sorptomatic Automated Gas Sorption System (Sorptomatic Thermo Finnigan 1990, U.S.A.). The surface areas were calculated using a Brunauer Emmet Teller (BET) model. These parameters were determined automatically by using the software available with the Sorptomatic 1990 instrument. To find an acceptable explanation for the results obtained, micropores %, mesopores % and the number of pores for each sample was calculated using the following equations:

$$\text{Micropores }(\%) = \frac{V_{mic}}{V_T} \times 100 \tag{1}$$

$$\text{Mesopores }(\%) = \frac{(V_T - V_{mic})}{V_T} \times 100 \tag{2}$$

$$\text{No. of pores} = \frac{S_{BET}}{\text{Average pore diameter}} \tag{3}$$

where, V_T and V_{mic} are the total pore volume and micropores volume, respectively.

TABLE-2
L_{16} ORTHOGONAL ARRAY OF DESIGNED EXPERIMENTS AND THE VALUES OF S_{BET}, 4-NITROPHENOL, METHYLENE BLUE AND ACID-RED-27 FOR EACH SAMPLE OF THE PREPARED ACTIVATED CARBON FIBERS

Run	A (°C)	B (%)	C (mL/min)	D (h)	E (°C)	S_{BET} (m^2/g)	4-Nitrophenol (%)	Methylene blue (%)	Acid red-27 (%)
1	1	1	1	1	1	64.87	93.17	36.06	3.34
2	1	2	2	2	2	1472	92.64	92.92	16.46
3	1	3	3	3	3	1878	93.25	78.65	13.25
4	1	4	4	4	4	612.5	85.80	4.57	2.46
5	2	1	2	3	4	730	96.88	25.70	1.70
6	2	2	1	4	3	2102	94.26	80.43	12.75
7	2	3	4	2	2	2740	94.24	95.13	17.03
8	2	4	3	2	1	2317	89.91	95.10	24.80
9	3	1	3	4	2	503.1	97.87	32.31	1.70
10	3	2	4	3	1	1354	99.14	63.10	4.93
11	3	3	1	2	4	1016	96.31	18.72	0.49
12	3	4	2	1	3	2104	95.29	76.15	15.25
13	4	1	4	2	3	582.1	97.71	76.63	7.25
14	4	2	3	1	4	947.7	93.11	2.87	1.06
15	4	3	2	4	1	4092	94.46	86.44	22.94
16	4	4	1	3	2	5435	94.22	99.63	32.82

(Highlighted line demonstrates that the sample 10 has the highest percentage removal towards 4-nitrophenol, whereas, the green line is for sample 16 that has the highest surface area and the highest % removal for methylene blue and acid red)

The effects of some other experimental parameters on the porosity of the prepared activated carbon were also carried out here.

Chemical composition: To investigate the effect of experimental conditions on the percentage of oxygen which has significant effect on the adsorption performances of the adsorbent, the chemical composition of prepared activated carbon fiber samples were examined using EDX-analyzer (INCA Energy, Oxford Inst).

Characterization of the activated carbon fibers prepared under optimal conditions: The surface morphology of the raw coconut fiber and two selected samples of the prepared activated carbon fiber as well as activated carbon granular (ACG) were examined at magnification in the range of 1000-2000x by scanning electron microscopy (SEM) (LEO 1455 VP, England).

Percentage removal study: 25 mL of solutions of 4-nitrophenol, methylene blue or acid red-27 dye with known concentrations were added to 30 mL amber bottles, each one containing 0.03 g of the prepared samples. The bottles were placed in a shaker and shaken (150 rpm) at room temperature (30 ± 1 °C) for three days to reach the adsorption equilibrium. Then the samples were filtered and the residual concentrations of these compounds in the filtrates were measured by an UV-visible spectrophotometer (Shimadzu, Japan) at 317, 618 and 420 nm for 4-nitrophenol; methylene blue and acid red-27 dye, respectively. The percentage removals of these pollutants were calculated using eqn. 4.

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4)$$

where, C_0 and C_e are the initial and final concentration of these selected organic compounds.

RESULTS AND DISCUSSION

BET surface area: The surface area values of all the 16 samples of activated carbon fiber prepared according to the L_{16} array designed by the Taguchi method are listed in Table-2. It can be observed from this table that the sample number 16 of activated carbon fiber has the highest surface area (5435 m^2/g). This high surface area has been obtained for the first time in this work.

Adsorption efficiency: Adsorption performance of the prepared samples were measured by the values of the percentage removal of 4-nitrophenol, methylene blue and acid red-27 dye on the prepared sample of activated carbon fiber. These values are also represented in Table-2.

As shown in Table-2, sample 10 of activated carbon fiber has the highest percentage removal for 4-nitrophenol (99.14), whereas the highest percentage removals of methylene blue (99.63) and acid red-27 (32.82) were achieved by sample 16. The lower percentage removal of acid red-27 (32.82) by sample 16 was due to the higher initial concentration of acid red-27 (600 mg/L) used in this work. Samples 10 and 16 of the prepared activated carbon fiber were named as ACF-10 and ACF-16, respectively.

Pore characteristics: The number of pores, average pore diameter, micropores % and mesopores % have significant effects on the surface area and adsorption ability of activated carbon. Therefore, these variables were calculated for the 16 samples of activated carbon fiber and listed in Table-3. This table demonstrates that sample 10 of activated carbon fiber has the largest micropores %. This is a reasonable explanation for the highest percentage removal of 4-nitrophenol by this sample. Micropores are more effective for adsorption of phenols [68]. It can be seen from the table that the prepared ACF-16 has a significant mesopores % which are preferred for adsorption of large compound such as dyes and humic acid [68]. The superior mesopores % with the highest surface area (5435 m^2/g) of the prepared ACF-16 explains the highest percentage removal of this sample for methylene blue and acid red-27 dyes. Though samples ACF-7, ACF-8 and ACF-12 have 100 % mesopores, its % methylene blue and % AR-27 removals are not as high as ACF-16 as their surface areas are not high (2104 to 2740 m^2/g).

TABLE-3

L_{16} ORTHOGONAL ARRAYS OF DESIGNED EXPERIMENTS AND VALUES OF NUMBER OF PORES, AVERAGE PORE DIAMETER (Å), MICROPORES %, MESOPORES % AND OXYGEN % FOR EACH SAMPLE OF PREPARED ACTIVATED CARBON FIBER

Run	A (°C)	B (%)	C (L/min)	D (h)	E (°C)	No. of pores	Pore diameter (Å)	Micropores (%)	Mesopores (%)	O_2 (%)
1	1	1	1	1	1	1.37	9.59	23.30	76.70	17.33
2	1	2	2	2	2	65.72	19.98	10.58	89.43	8.56
3	1	3	3	3	3	80.38	18.35	24.69	75.31	8.38
4	1	4	4	4	4	12.70	16.97	61.28	38.72	9.50
5	2	1	2	3	4	18.10	16.09	52.62	47.38	13.76
6	2	2	1	4	3	99.90	20.45	4.96	95.04	7.61
7	2	3	4	2	2	108.60	25.24	0.00	100.00	9.63
8	2	4	3	2	1	62.40	37.13	0.00	100.00	10.42
9	3	1	3	4	2	9.47	16.88	59.42	40.58	13.15
10	3	2	4	3	1	63.68	19.52	91.09	8.91	6.15
11	3	3	1	2	4	9.78	17.10	60.42	39.58	4.64
12	3	4	2	1	3	230.5	9.130	0.00	100.00	7.54
13	4	1	4	2	3	14.71	16.03	57.05	42.95	13.49
14	4	2	3	1	4	19.20	16.43	64.91	35.09	7.22
15	4	3	2	4	1	43.07	26.63	36.83	63.17	9.78
16	4	4	1	3	2	56.35	29.76	18.29	81.71	8.68

(Highlighted lines demonstrate samples have the highest value of % mesopores)

ANOVA analysis was also applied to investigate the effects of some important preparation parameters on the pore structure of the prepared activated carbon fiber. The ANOVA graphs of the impact of some selected experimental conditions on the number of pores, average pore diameters, micropore % and mesopores % are represented in the Figs. 1-4, respectively. These figures will be used to explain the experimental parameters on the selected responses in the following sections.

Amount of oxygen content: The amount of oxygen content in the adsorbent plays an important role in the adsorption of phenolic compounds [68]. Therefore, the percentages of oxygen in the chemical composition of prepared samples of activated carbon fiber were measured by EDX-analyzer and summarized in Table-3. These results will be used to explain the effect of preparation parameters on the adsorption ability of the prepared activated carbon fiber towards 4-nitrophenol.

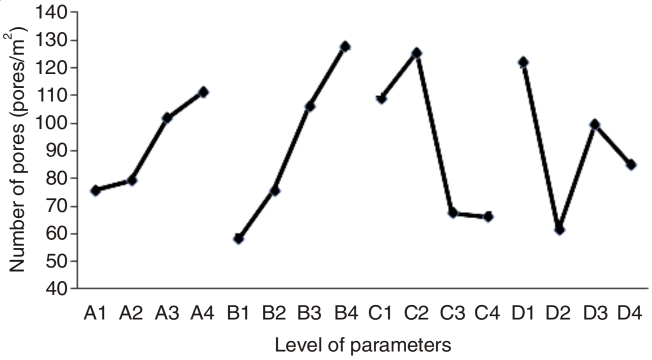

Fig. 1. Effect of experimental parameters (A, B, C and D) on the number of pores

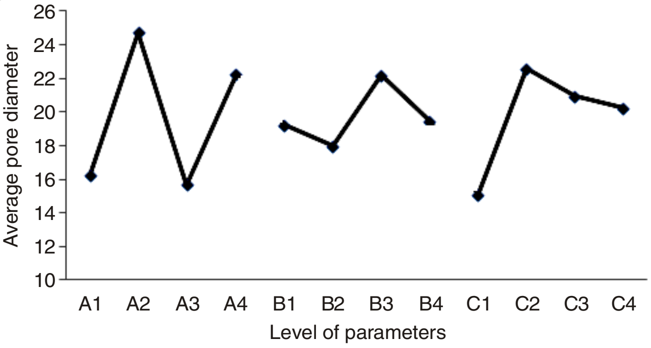

Fig. 2. Effect of experimental parameters (A, B and C) on average pore diameter of the prepared activated carbon fiber

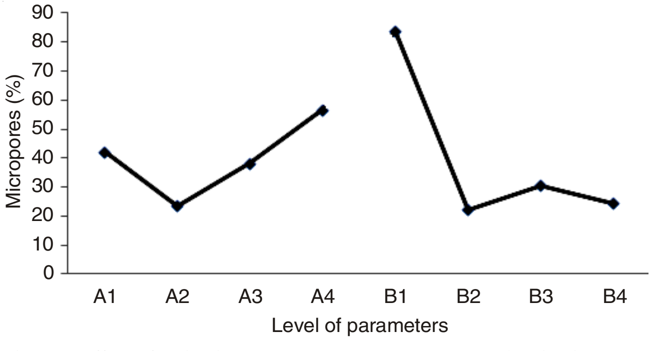

Fig. 3. Effect of activation temperature (parameter A) and activation agent (parameter B) on micropores %

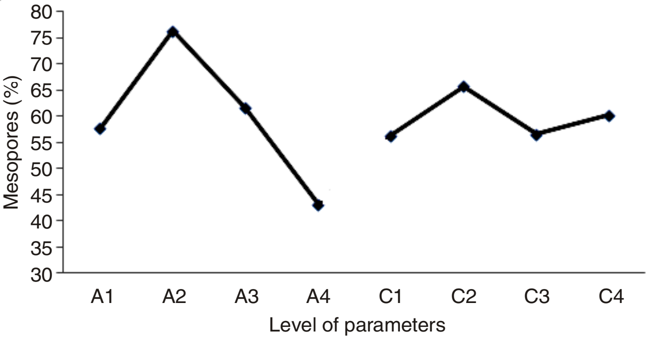

Fig. 4. Effect of activation temperature (parameter A) nitrogen gas flow rate (parameter C) on mesopores %

The effect of some operation factors on the amount of oxygen content on the prepared activated carbon fiber was investigated and illustrated in Fig. 5, this figure will be used to explain the effect of experimental parameters on the percentage removal of 4-nitrophenol on the prepared activated carbon fiber samples.

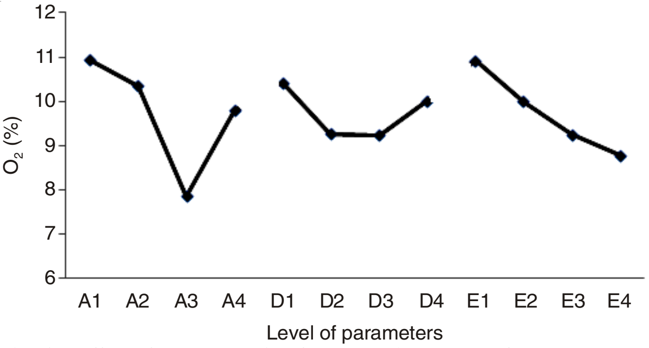

Fig. 5. Effect of some operation factors on the amount of oxygen content on activated carbon fibre

Optimization of activated carbon fiber preparation with the highest surface area: The results of ANOVA analysis for the effects of operation parameters on the surface area of the prepared activated carbon fiber are presented in Table-4 and Fig. 6. The P value obtained designates whether the parameter will affect the response of activated carbon fiber or not. If the P-value is lower than 0.05, it means that this factor is significant to the response [69]. It can be observed from this table that only the concentration of the chemical agent (P = 0.007) and carbonization temperature (P = 0.028) were significant factors for the surface area of the prepared activated carbon fiber and the most important parameter was the concentration of $ZnCl_2$. Activation time, activation temperature and the nitrogen flow rate have less influence than concentration of the chemical agent and carbonization temperature.

Fig. 6 showed that the increasing activation temperature up to 600 °C increases the surface area. This is due to increasing the number of pores and mesopore % since elevated activation temperature from 500 to 600 °C creates new pores and converts the old micropores to mesopores as illustrated in Figs. 1, 3 and 4 (parameter A).

In contrast, increasing the activation temperature until 700 °C decreases the surface area. This comes from the collapsing of the mesopores, when the activation temperature is increased

TABLE-4
ANOVA ANALYSIS OF S_{BET} FOR PREPARED ACTIVATED CARBON FIBER SAMPLES

Factor	Sum of square	Degree of freedom	Mean square	F	P	Contribution (%)
A	3520402	1	3520402	4.848	0.052	17.926
B	8258759	1	8258759	11.372	0.007	42.056
C	2497301	1	2497301	3.439	0.093	12.717
D	542341	1	542341	0.747	0.408	2.762
E	4818920	1	4818920	6.636	0.028	24.539
Residuals	7262133	10	726213.3			
Total	26899856	15	20363936.3			100

(Highlighted lines refer to the significant factors for preparation activated carbon fiber with highest surface area)

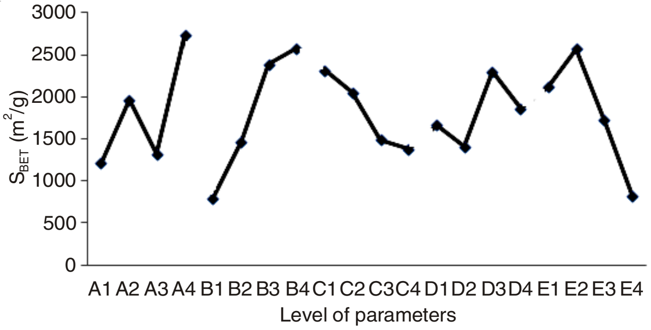

Fig. 6. Effect of operational parameters on S_{BET} of the prepared activated carbon fiber samples [(A) activation temperature, (B) activation agent concentration, (C) N_2 follow rate, (D) activation time and (E) carbonization temperature]

over 600 °C as observed in Fig. 4, which represents the impact of the activation temperature on mesopores %. Further increasing this parameter up to 800 °C, increases the porosity of the prepared samples.

Fig. 1 (parameter A) represents the relationship between activation temperature and number of pores whereas Fig. 3 (parameter A) presents the effect of this parameter on micropores %. This leads to an increase in the surface area (Fig. 6). The results obtained in our work are almost in agreement with the results observed by Tay *et al.* [70]. However, it can be observed from Table-2 and Fig. 6 that the optimum activation temperature with respect to the highest surface area is 800 °C.

Fig. 6 shows that raising the concentration of $ZnCl_2$ from 5 to 50 % w/v increases the surface area of the prepared activated carbon. This is due to increasing the porosity of the samples produced as can be observed in Fig. 1 (parameter B).

Fig. 1 (parameter B) shows that the number of pores on the surface of the prepared activated carbon increased with increasing concentration of $ZnCl_2$. Moreover, the increase of activation agent concentration improves the adsorbent surface area because the role of the chemical agent is to reduce the formation of tars and any other liquid that could block the pores and inhibit the porous structure development within the adsorbent [63]. It was reported that the surface area of the activated carbon prepared from sewage sludge increased with increasing the concentration of the activation agent [32]. Tay *et al.* [70] found the same results in their work on activated carbon prepared from digested sewage sludge and coconut husk. Table-2 and Fig. 6 show that the optimum value of $ZnCl_2$ concentration is 50 % w/v.

Fig. 6 illustrates that the enhancement of nitrogen flow rate decreases the surface area of the resulting samples. This may be due to the collapse of the wall of the mesopores [22]. The optimum value for this factor is found to be 100 mL/min. Fig. 6 (parameter D) indicates that the surface area of the samples slightly decreases when activation time is increased from 30 until 60 min. This response sharply increases when this variable is increased up to 120 min. Increase in activation time over 120 min reduces the surface area of the products. This is due to some of the mesopores collapsing. Therefore, the number of pores decreases, which leads to decreasing surface area of the prepared samples' (Fig. 1 parameter D). Furthermore, in Fig. 1 (parameter D) activation until 120 min is shown to enhance the porosity of the resulting samples. Similar results were observed previously by other researchers [45,69]. The optimum value of activation time is 120 min.

Fig. 6 (parameter E) demonstrates the ANOVA results regarding the effect of carbonization temperature on the surface area of the prepared activated carbon fiber. The results show that the surface area of the prepared activated carbon increases with increasing this factor from 250 to 300 °C. The obtained increase in the surface area perhaps comes from the separation of volatile materials from the coconut. This creates additional pores leading to increasing the surface area [45]. In contrast, this response decreases when the carbonization temperature is increased over 300 °C. This is due to shrinkage of carbonized char structure. Similar results were also reported [45]. The optimized value for this factor is found to be 300 °C.

Optimization of activated carbon fiber preparation with superior adsorption of 4-nitrophenol: Values of the sum square, F, P and contribution percentage are summarized in Table-5. These values indicate that both activation temperature and concentration of the agent have significant influences on the adsorption efficiency of the prepared activated carbon fiber to 4-nitrophenol. Similar results were reported by previous workers [1,69,70]. The nitrogen flow rate, activation time and carbonization temperature have negligible effects on the adsorption ability of the samples produced. Tan *et al.* [1] and Tay *et al.* [70] found that the activation time has an insignificant effect on the adsorption affinity of their products to phenol. The most significant factor affecting the adsorption ability of the prepared activated carbon fiber towards 4-nitrophenol is the concentration of the activation agent (parameter B).

The average pore diameter and the amount of oxygen of the activated carbon play an important role in the adsorption process. Therefore, the effects of some preparation conditions on these two responses were also investigated and represented in the Figs. 2 and 5.

The ANOVA graph of the effects of experimental parameters on the percentage removal of 4-nitrophenol is demonstrated in Fig. 7. As illustrated from Fig. 7, that increasing

TABLE-5
ANOVA ANALYSIS OF % REMOVAL OF 4-NITROPHENOL ON THE PREPARED ACTIVATED CARBON FIBER

Factor	Sum of square	Degree of freedom	Mean square	F	P	Contribution (%)
A	46.879	1	46.879	8.289	0.016	45.39
B	54.648	1	54.648	9.663	0.011	52.91
C	0.869	1	0.869	0.154	0.703	0.84
D	0.673	1	0.673	0.119	0.737	0.65
E	0.221	1	0.221	0.039	0.847	0.21
Residuals	56.557	10	5.656			
Total	159.847	15	108.946			100

(Highlighted lines refer to the significant factors for preparation activated carbon fiber with highest % removal of 4-nitrophenol on the prepared activated carbon fiber)

the activation temperature up to 700 °C, lead to increase in the percentage removal of the activated carbon fiber for 4-nitrophenol. On the other hand, excessive increase in this parameter over 700 °C decreases the performance of the prepared samples for this compound. The presence of oxygen in the structure of the activated carbons has a negative effect on their adsorption to phenols [66].

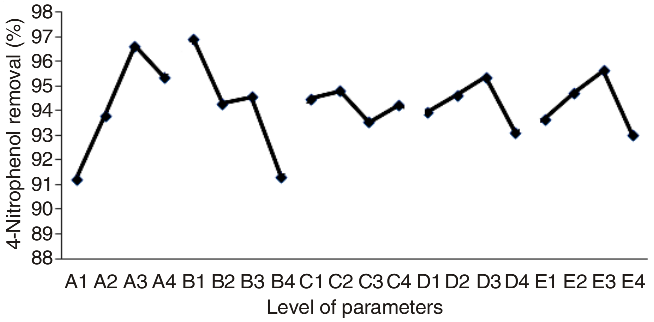

Fig. 7. Effect of operational parameters on 4-nitrophenol percentage removal of the prepared activated carbon fiber [(A) activation temperature, (B) activation agent concentration, (C) N_2 follow rate, (D) activation time and (E) carbonization temperature]

From Fig. 5 (parameter A) the percentage of oxygen content in the samples produced is shown to decrease and then increase when the activation temperature is increased in the range of 500-700 °C and 700-800 °C respectively. Therefore, it can be suggested that the results demonstrated in Fig. 5 represented the main reason for the increase and decrease in the percentage removal of 4-nitrophenol on the prepared activated carbon fiber samples when activation temperature is changed in the above mentioned range.

As shown in Fig. 7, adsorption of the samples to 4-nitrophenol sharply decreases when the concentration of the chemical agent is raised from 5 to 15 % w/v and slightly increases when this parameter is increased up to 30 % w/v. On the other hand, increasing the chemical activation agent over 30 % w/v stridently decreases adsorption efficiency of the samples produced. This can be explained by the results represented in Fig. 7 (parameter B) where the percentage of micropores, which have a positive effect on the adsorption of 4-nitrophenol decreased when the concentration of $ZnCl_2$ is increased to 15 % w/v, while the % of micropores increased with increase of this factor up to 30 % w/v. It is also demonstrated in Fig. 3 (parameter B) that the raising of the activation agent concentration to 50 % w/v reduced the percentage of the micropores in the prepared samples.

Values of the sum square, F, P and percentage contribution are summarized in Table-5. The nitrogen flow rate has no significant effects on the adsorption of the samples produced for 4-nitrophenol. Fig. 7 illustrates that a slight enhancement in the adsorption is obtained when nitrogen flow rate was raised up to 200 mL/min. It can also be observed that this ability is sharply decreased with increasing this factor to 300 mL/min. Nevertheless, increasing the nitrogen flow rate over 300 mL/min improved this response for the samples produced. The effect of the nitrogen flow rate on the average pores diameter was investigated and the results of this investigation were presented in Fig. 2 (parameter C). From this figure it has been shown that increase in this parameter up to 200 mL/min reduced the average pores diameter, which has negative effect on 4-nitrophenol adsorption. This response is sharply increased, when this factor was raised to 300 mL/min. It can also be observed from Fig. 6 (parameter C) that increasing this parameter up to 400 mL/min led to decreasing the average pores diameter.

Results of the ANOVA analysis are summarized in Table-5, demonstrating that the activation time has negligible effect on the adsorption of activated carbon fiber. Similar observations were reported previously [1,70].

Fig. 7 illustrates that enhancing the activation time up to 2 h led to improvement on the adsorption performance of the prepared samples. While, increasing this variable over 2 h reduced the 4-nitrophenol adsorption affinity on the activated carbon fiber. The influence of activation time on the amount of oxygen content in the samples produced were also investigated and represented in Fig. 5 (parameter D). Since the efficiency of the adsorbent to 4-nitrophenol adsorption decreased with increasing oxygen content. Fig. 5 (parameter D) gives a reasonable explanation for increasing and decreasing the adsorption ability of the activated carbons observed when the activation time was increased up to and over 2 h. The results observed throughout this work are in agreement with the work of Phan *et al.* [45].

Results of the ANOVA analysis in Table-5 indicate that the carbonization temperature parameter had no significant influences on the adsorption of the prepared samples for 4-nitrophenol. As shown in Fig. 7, adsorption affinity of the samples is increased when the carbonization temperature was increased up to 400 °C. In contrast, it can also be seen that this response is reduced at temperatures over 400 °C. The consequential increase in this response came from decreasing amount of oxygen content in the resulting char, Fig. 5 (parameter E). A decrease in the adsorption performance at over 400 °C is explained by the decrease in the surface area of the prepared samples (Fig. 6).

Fig. 7 demonstrates that the optimization of the activated carbon fiber preparation with highest percentage removal for 4-nitrophenol was found to be 700 °C as activation temperature, 50 % chemical agent concentration, 200 mL/min nitrogen gas flow rate, 2 h activation time and 400 °C carbonization temperature.

Optimization of activated carbon fiber preparation with superior adsorption of methylene blue: Values of F, P and percentage contribution are listed in Table-6, which show that the percentage removal of methylene blue is significantly affected by carbonization temperature and the concentration of the chemical activator. Meanwhile, nitrogen flow rate, activation temperature and activation time have the least effect on the adsorption of the prepared activated carbon fiber.

Tan *et al*. [1] reported that the efficiency of the prepared adsorbent was considerably affected by the concentration of the chemical activator and was not affected by the activation time. Fig. 8 illustrates the effects of the experimental variables on the percentage removal of methylene blue from aqueous solution.

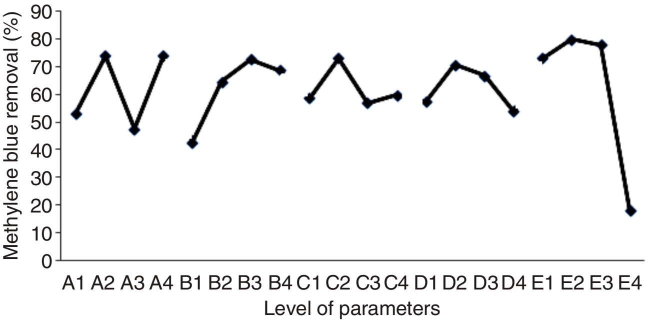

Fig. 8. Effect of operational parameters on the methylene blue percentage removals of the prepared activated carbon fiber samples [(A) activation temperature, (B) activation agent concentration, (C) N_2 follow rate, (D) activation time and (E) carbonization temperature]

It can be seen from Fig. 8 that the percentage removal of methylene blue increases, decreases and increases when activation temperature is raised in the range of 500-600, 600-700 and 700-800 °C, respectively. This can be explained by the similar changes obtained for surface area and average pore diameter when activation temperature is increased in the above-mentioned ranges. Effects of activation temperature on average pores diameter and surface area are illustrated in Figs. 2 and 6 (parameter A), respectively. It has been reported previously that the methylene blue adsorption is strongly affected by adsorbent surface area and average pore diameter [71]. From Fig. 8, the optimum value for activation temperature is 800 °C.

Fig. 8 demonstrates that adsorption of methylene blue on the activated carbon fiber samples increases as the concentration of the activation agent is increased. This is due to the increase in surface area (Fig. 6) which has a significant effect in the adsorption process. Optimum value of $ZnCl_2$ concentration used in this work is 50 % w/v. It was also reported that adsorption of methylene blue increases with increase in activation agent concentration [1].

Fig. 8 shows the results of ANOVA analysis for the effect of the nitrogen flow rate on the adsorption performance of the activated carbon fiber samples. Enhancing the nitrogen flow rate from 100 to 200 mL/min increases the adsorption efficiency of the produced samples. This response decreases as the nitrogen flow rate is increased up to 300 mL/min. On the other hand, raising this factor more than 300 mL/min increases the adsorption ability of the prepared activated carbon fiber. These results can be explained by the results presented in Fig. 4 (parameter C), where parameter C demonstrated that the effect of nitrogen flow rate on the percentage of mesopores which has a significant effect on the adsorption of methylene blue.

The results of ANOVA analysis for the effect of activation time on the percentage removal of methylene blue by the activated carbon fiber are presented in Fig. 8. The results demonstrate that the methylene blue uptake improves with increasing activation time of up to 1 h. Additional increase in this parameter over 1 h decreases the percentage removal of methylene blue. From Fig. 2 the parameter D which illustrates the effect of activation time on the average pores-diameter, indicated that activation until 1 h enhanced the average pores-diameter, which has significant effect in adsorption of methylene blue. Meanwhile the average pores-diameter is reduced when activation time was extended to 4 h. The ideal value for this parameter is shown to be 2 h.

Results presented in Fig. 9 indicate that increasing carbonization temperature from 250 to 300 °C increases the adsorption ability of activated carbon fiber samples towards methylene blue. The increase in surface area of the prepared samples has resulted in more efficient adsorption process as shown in Fig. 6. Carbonization temperature exceeding to 500 °C decreases the methylene blue adsorption. This is due to a decrease in the surface area of the activated carbon fiber samples when this parameter was increased to over 300 °C as demonstrated in Fig. 6.

TABLE-6
ANOVA ANALYSIS OF % REMOVALS OF METHYLENE BLUE ON THE PREPARED ACTIVATED CARBON FIBER SAMPLES

Factor	Sum of square	Degree of freedom	Mean square	F	P	Contribution (%)
A	269.562	1	269.562	0.298	0.597	3.60
B	1499.306	1	1499.306	1.657	0.227	20.02
C	32.474	1	32.474	0.036	0.854	0.43
D	42.472	1	42.472	0.047	0.833	0.57
E	5645.304	1	5645.304	6.239	0.032	75.38
Residuals	9048.553	10	904.855			
Total	16537.671	15	8393.973			100

(Highlighted line refers to the significant factor for preparation activated carbon fiber with highest % removal of methylene blue on the prepared activated carbon fiber)

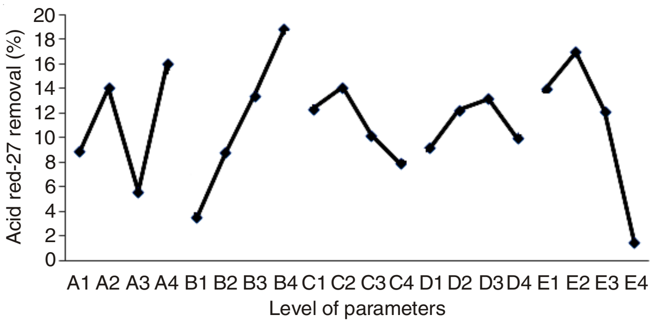

Fig. 9. Effect of operational parameters on acid red-27 dye percentage removals of the prepared activated carbon fiber samples [(A) activation temperature, (B) activation agent concentration, (C) N_2 follow rate, (D) activation time and (E) carbonization temperature]

Optimization of activated carbon fiber preparation with superior adsorption of acid red-27: Results of the ANOVA analysis for the adsorption of acid red-27 dye (AR-27) on the 16 activated carbon fiber samples are shown in Table-7 and Fig. 9. Table-7 confirms that the concentration of the chemical activator and carbonization temperature contributed 52.83 and 37.42 %, respectively, thus having considerable effects on the adsorption of acid red-27 by the prepared activated carbon fiber. Nitrogen flow rate, activation temperature and activation time have insignificant effects. From Fig. 9, increasing the activation temperature up to 600 °C increases the adsorption ability of the prepared activated carbon fiber samples. This is due to the increase in the surface area and average pore diameters that have significant effects on the adsorption process as illustrated in Figs. 6 and 2 (parameter A). On the other hand, increasing activation temperature up to 700 °C reduces the adsorption ability of the prepared activated carbon fiber samples as a result of decrease in the average pores diameter and surface area of these samples. For additional rise in activation temperature of up to 800 °C, the uptake of acid red-27 dye is improved.

Fig. 9 shows that an increase in the concentration of $ZnCl_2$ from 5 to 50 % w/v causes improvement in the percentage removal of acid red-27 by the activated carbon fiber samples. This is as a result of the increment in the surface area which contributes to the efficient adsorption process as presented in Fig. 6.

Increasing the nitrogen flow rate until 200 mL/min increases the adsorption ability of the prepared activated carbon fiber samples. This increase is attributed to the enhanced porosity of the adsorbents prepared which has a significant effect in the adsorption process, as demonstrated in Fig. 1 (parameter C). Exceeding this factor to over 200 mL/min reduces the adsorption ability. Since an increase in the nitrogen flow rate in the range of 200-400 mL/min decreases the number of pores on the surface of activated carbons as illustrated in Fig. 1 (parameter C).

Results presented in Fig. 9 illustrate that the adsorption ability of the prepared activated carbon fiber samples increases with exceeding the activation time to 2 h. This is due to increasing the surface area which resulted in more effective adsorption as presented in Fig. 6. Increasing this factor up to 4 h diminishes the adsorption ability of the activated carbon fiber samples. A larger increase in this parameter reduces the surface area of the produced activated carbon fiber as shown in Fig. 6.

Fig. 9 shows that increasing the carbonization temperature up to 300 °C increases the adsorption ability of the prepared activated carbon fiber samples. This is due to an increase in the surface area, thus enhancing the adsorption process as shown in Fig. 6. A further increase in this factor up to 500 °C decreases the adsorption ability of the prepared activated carbon fiber samples as a result of decreasing surface area of the produced activated carbon as demonstrated in Fig. 6. The results obtained in this work are in agreement with the reported results [45].

Fig. 9 illustrates that the optimized activated carbon fiber for removal of acid red-27 from aqueous solutions can be prepared at 800 °C activation temperature, for 2 h activation time, 50 % activation agent concentration, 200 mL/min nitrogen gas flow rate and 300 °C carbonization temperature.

Surface morphology: Scanning electron microscope (SEM) images of the precursor (coconut raw fiber), ACG, ACF-16 and ACF-10 are illustrated in Fig. 10. It can be seen from Fig. 10(a) that no pores are observed on the surface of the precursor.

Fig. 10(b) demonstrates that ACG surface contains macropores, while in Fig. 10(c) a number of large pores in a honeycomb shape can be observed on the surface of the ACF-16. Fig. 10(d) shows the pores on the surface of ACF-10. Similar results have been reported previously with activated carbon prepared from coconut husk [1].

Conclusion

The Taguchi experimental design method can be used to optimize the conditions of the preparation of activated carbon fiber from coconut husk using $ZnCl_2$ as activator. Concentrations of $ZnCl_2$ and carbonization temperature were significant factors for the surface area. The % removal of 4-nitrophenol

TABLE-7
ANOVA ANALYSIS OF % REMOVALS OF ACID RED-27 DYES ON THE PREPARED ACTIVATED CARBON FIBER

Factor	Sum of square	Degree of freedom	Mean square	F	P	Contribution (%)
A	33.502	1	33.502	0.676	0.430	3.45
B	512.730	1	512.730	10.348	0.009	52.83
C	59.048	1	59.048	1.192	0.301	6.08
D	2.181	1	2.181	0.044	0.838	0.22
E	362.995	1	362.995	7.326	0.022	37.42
Residuals	495.468	10	49.547			
Total	1465.924	15	1020.003			100

(Highlighted lines refer to the significant factors for preparation activated carbon fiber with highest % removal of acid red-27 dye on the prepared activated carbon fiber)

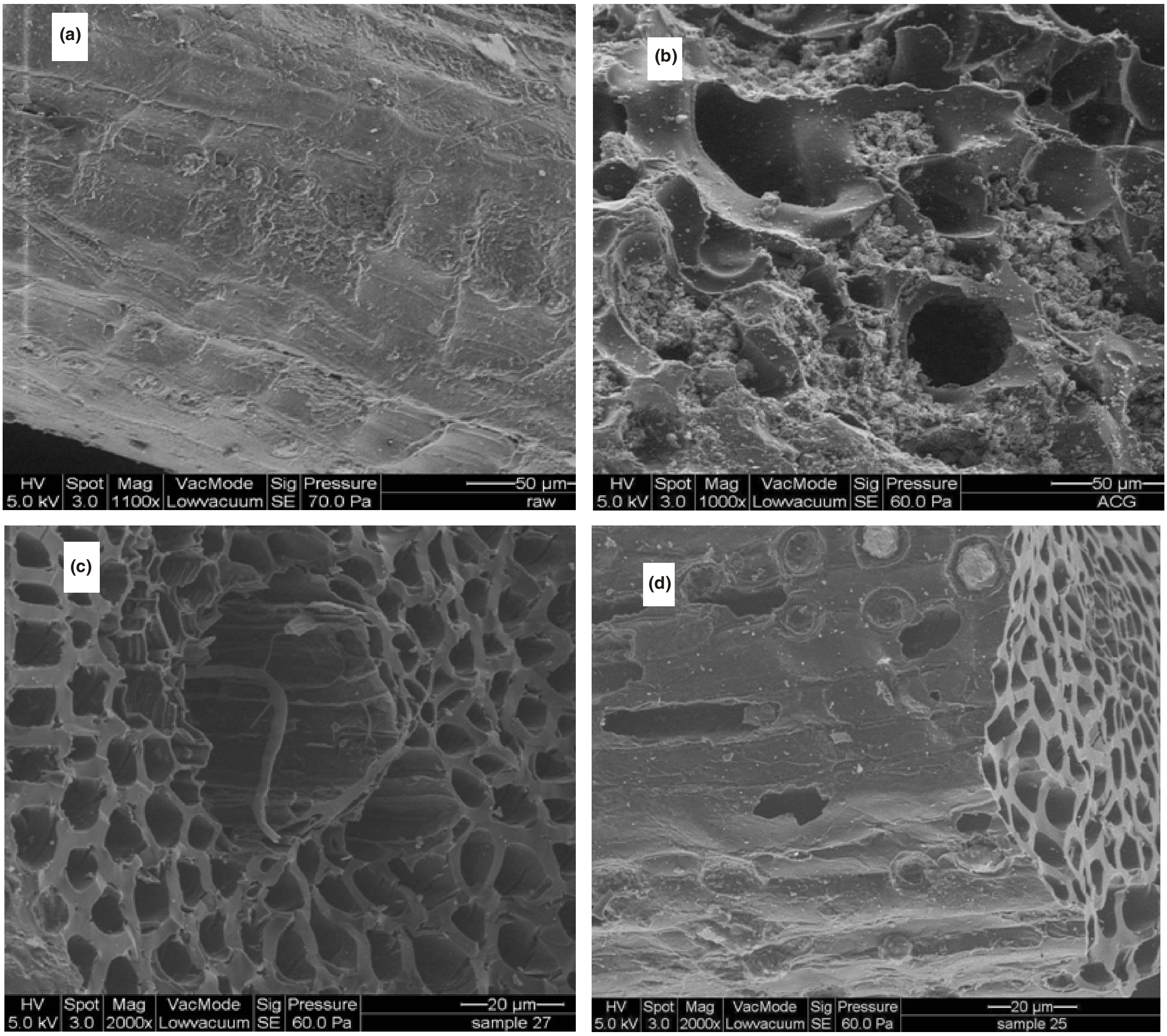

Fig. 10. SEM image of (a) raw coconut, (b) ACG, (c) ACF-16 and (d) ACF-10

was significantly influenced by the concentration of zinc chloride and activation temperature. Carbonization temperature had the largest impact on the percentage removal of methylene blue by the prepared activated carbon. While the most effective parameter in the case of acid red-27 dye adsorption was concentration of $ZnCl_2$. Both nitrogen flow rate and activation time have a negligent effect on the above mentioned four responses. According to our best knowledge, the highest surface area (5435 m^2/g) for the first time has been obtained in this work. Activated carbon fiber prepared under optimization conditions in this study presented adsorption ability with significant values to 4-nitrophenol, methylene blue and acid red-27 dye.

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