

A comparative study of one-step and two-step activated carbon from longan seeds by dry chemical activation with NaOH



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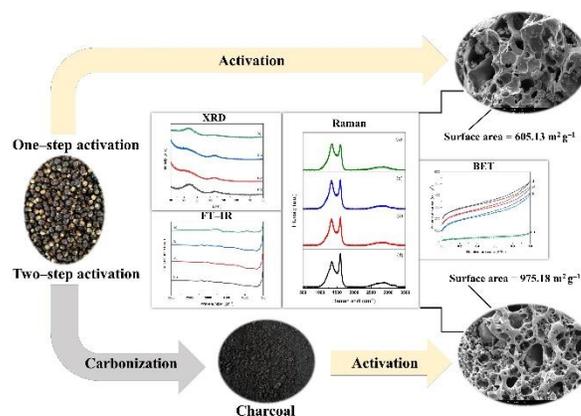
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Abstract

This research aims to study the effects of one-step and two-step activated carbon from longan seeds by dry chemical activation with NaOH. The longan seeds and their charcoal produced at carbonized temperature of 500 °C, were impregnated by dry chemical activation with NaOH at a weight ratio of 1.00:1.00, 1.00:1.50 and 1.00:2.00 at activation temperatures ranging from 500, 600 and 700 °C for 2 h. The iodine number, surface area, pore volume, functional group, crystalline phases, surface morphology and elemental composition of the activated carbons were examined. The results showed that the two-step process had the highest iodine number and BET surface area of 987.22 mg g⁻¹ and 975.18 m² g⁻¹, respectively, which is the standard measure for liquid-phase applications.



Keywords: Activated carbon; Longan seeds; NaOH; One-step; Two-step

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Introduction

Charcoal and activated carbon are two forms of carbon that have a lot of overlap, with very similar composition and methods of production. Both are prepared by the pyrolysis process, which produces a substance with a high carbon content. The main difference between charcoal and activated carbon is that charcoal is used for heating or cooking. While activated carbon, through a process known as activation, has an increased pore volume resulting in greater adsorption efficiency, which is more than ordinary charcoal can absorb odor and color. It can be used for many purposes, such as heavy metal adsorption, bleaching, deodorization, purification of gas, water purification, and in various industries [1 – 5].

From the past researches, there are many studies on preparation of activated carbon from fruits seeds, which contain high amount of lignocellulosic material, such as Lapsi seeds stone, avocado seeds, tamarind seeds, guava seeds and papaya seeds [6 – 10]. In Thailand, several economic fruits were distributed available fresh and

processed which will have a lot of leftover fruit raw materials. Especially on the north of Thailand, longan is a tropical and subtropical fruit native to Asia, which is considered to be the important economic fruit of the community. In addition, longan seeds contain high carbon, a suitable raw material for the preparation of activated carbon. Successful results gathered from multiple previous studies showed that activated carbon can be obtained from longan seeds as an appropriate adsorbent for the removal of chromium from aqueous solutions [11]. Furthermore, chemical activation by means of base reagents such as NaOH and KOH is one of the most effective methods of obtaining high porosity and surface area [12, 13].

The conventional method of chemical activation begins by soaking raw materials into a solution containing an activating agent, after this process, the raw materials are dried before continuing the activating process, however this process is very time consuming. Another tool that can be used in order to minimize the time spent is dry chemical

activation [14]. In addition, two types of dry chemical activation are available, which are one-step and two-step activation. The one-step process is a method in which dry raw materials are combined directly with a dry activating agent and then activated together into activated carbon. Whereas, the two-step is a process that has first carbonized raw materials to charcoal which is then combined directly with a dry activating agent and then activated together into activated carbon [15, 16].

In this study, one-step and two-step activated carbons were prepared by dry chemical activation with NaOH. As the iodine number, Brunauer–Emmett–Teller (BET) surface area, Fourier transform infrared spectroscopy (FT–IR), Raman spectroscopy, X–ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM) and energy-dispersive X–ray spectroscopy (EDX) are discussed.

Materials and Methods

Sample Preparation

For activated carbon precursors, the dry longan seeds were used in two separate dry chemical methods. The longan seeds powder, a one-step process, was triggered using a dry chemical method at a weight ratio of 1.00:1.00, 1.00:1.50 and 1.00:2.00 between longan seeds powder and NaOH. Consequently, at activation temperatures ranging from 500, 600 and 700 °C, the mixed samples were heated. These activation temperatures were retained for 2 h. The activated carbon was then rinsed with a 0.10 M HCl solution after cooling down at room temperature and washed with water until the pH level of the samples became neutral. The washed specimens were then dried for 24 h at 110 °C and deposited for examination. This product was branded as 1SAC (Fig. 1).

Dry longan seed powder, a two-step process, was used for the preparation of charcoal and activated carbon. The charcoal was prepared specifically for 2 h at a carbonized temperature of 500 °C followed the report of Mopoung [17]. In addition, the charcoal was then activated at the same weight ratio and activation temperatures as a one-step process using a dry chemical method. The two-step technique product was branded as 2SAC (Fig. 1).

Sample Characterization

The ASTM D4607–94 method was used for analyzing the iodine number, which is used to determine the absorption of iodine from aqueous solution [18]. In determining the iodine number, 10 ml of 5 % by weight hydrochloric acid as added to 1 g of activated carbon and was allowed to boil. After the solution was cooled to room temperature, 100 ml of 0.10 N iodine solution was added. The content was shaken vigorously and filtered. 25 ml of the filtrate was titrated with 0.10 N sodium thiosulphate in the presence of starch as

indicator.

The specific surface area of the activated carbon was obtained from N₂ adsorption–desorption isotherms on the Brunauer–Emmett–Teller (BET) apparatus at liquid nitrogen temperature (–196.15 °C). A. The functional groups of the activated carbon were analyzed using a Fourier transform infrared spectrophotometer (FT–IR) the spectra were recorded in the region of 0 – 4000 cm⁻¹. Similarly, the Raman spectra were analyzed in the same range using a single monochromatic source for spectral light. X–ray diffraction (XRD) was measured to determine the crystalline phases formed in the activated carbon. Scanning electron microscopy (SEM) and energy-dispersive X–ray spectroscopy (EDX) were used to visualize the surface morphology and elemental composition of the activated carbon.

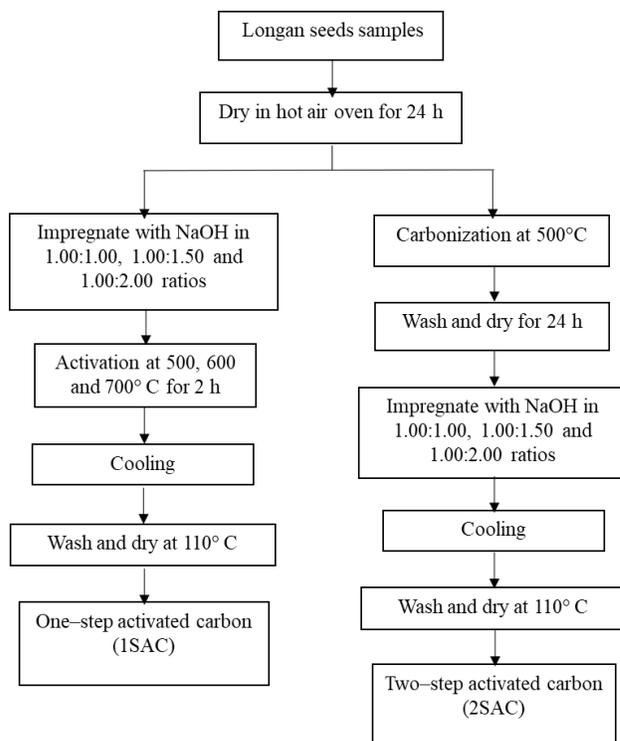


Fig. 1 Steps for preparation of activated carbon from longan seeds samples.

Results and Discussion

The iodine quantity of charcoal and activated carbon from longan seeds can be seen in Table 1. The outcome shows that the iodine number value of both 1SAC and 2SAC is greater than charcoal. The iodine number found in 1SAC ranged from 275.18 to 562.81 mg g⁻¹ and the maximum iodine number was found at 562.81 mg g⁻¹ at the activation temperature of 1.00:1.50 weight ratio of 700 °C. Whereas

2SAC was found to be between 508.35 and 987.22 mg g⁻¹ and the maximum amount of iodines was found at 987.22 mg g⁻¹ at the same activation temperature and weight ratio as 1SAC. However, it was found that the iodine number was lower when compared to commercial grade activated carbon. At the optimum temperature of 700°C, it was noted that the iodine number values were decreased by raising the weight ratio of NaOH from 1.50 – 2.00, likely due to an excess of NaOH that can react with the ash stored in longan or charcoal with this effect, the iodine values of 1SAC and

2SAC were decreased from the ideal values of about 32.25 percent and 25.71 percent respectively [19]. The findings of this analysis showed that 2SAC was less impaired than 1SAC and 2SAC also had a substantially higher iodine value than 1SAC.

From Table 2, the surface area and pore volume obtained from charcoal, 1SAC and 2SAC that were prepared under an optimum ratio of 1.00:1.50 and activation temperature of 700 °C and commercial grade activated carbon.

Table 1 Iodine number of charcoal, the activated carbon from longan seeds and commercial grade.

Product	Temperature (°C)	Weight ratio		Iodine number (mg g ⁻¹)
		Longan :	NaOH	
1SAC	500	1.00	1.00	305.57
		1.00	1.50	537.51
		1.00	2.00	431.13
	600	1.00	1.00	344.93
		1.00	1.50	369.94
		1.00	2.00	445.21
	700	1.00	1.00	275.18
		1.00	1.50	562.81
		1.00	2.00	381.30
Charcoal	500	Charcoal : NaOH		
		1.00	0.00	252.15
2SAC	500	1.00	1.00	508.35
		1.00	1.50	682.00
		1.00	2.00	539.64
	600	1.00	1.00	707.69
		1.00	1.50	801.01
		1.00	2.00	765.64
	700	1.00	1.00	731.77
		1.00	1.50	987.22
		1.00	2.00	733.38
Commercial grade	-	-	-	1,098.12

Table 2 Surface areas and pore volumes of charcoal, the activated carbon of ratio 1.00:1.50 at 700°C and commercial grade.

Product	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Charcoal	325.56	0.1655
1SAC	605.13	0.3811
2SAC	975.18	0.4537
Commercial grade	1,034.05	0.8112

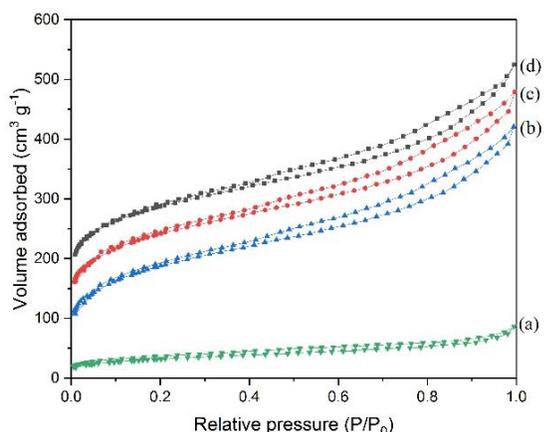


Fig. 2 Nitrogen adsorption – desorption isotherm of (a) charcoal, the activated carbon of ratio 1.00:1.50 at 700 °C (b) 1SAC, (c) 2SAC and (d) commercial grade.

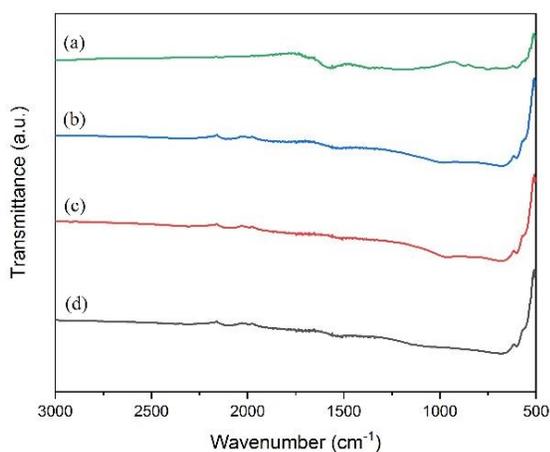


Fig. 3 FT-IR spectra of (a) charcoal, the activated carbon of ratio 1.00:1.50 at 700°C (b) 1SAC, (c) 2SAC and (d) commercial grade.

The results showed that the surface area and pore volume of activated carbon was significantly greater than that of charcoal but still lower when compared with commercial grade. Similarly, the adsorption isotherm in Fig. 2 show that the sequence of adsorption capacity is commercial grade > 2SAC > 1SAC > charcoal. This result tends to be the same surface area and pore volume as shown in Table 2. Moreover, the iodine number was also directly correlated with the pore volume, since the pore are accessed preferentially by the iodine molecules due to their size. For this reason, commercial grade has the highest iodine value, followed by 2SAC, 1SAC and charcoal, respectively. It's well known that iodine number is the most fundamental

parameter used to characterize activated carbon performance. From this research, it was found that at the mass ratio of 1.00:1.50 at 700 °C, the iodine number from 2SAC appeared maximum at 987.22 mg g⁻¹ (typical range 500 – 1200 mg g⁻¹), which is the standard measure for liquid-phase applications such as water treatment, groundwater remediation, and water filters.

Figure 3 (a) presented the FT-IR spectra of charcoal before activation process shows the absorption peak at 1580, 1245 and 720 cm⁻¹ of C=C, C-O and C-C groups respectively. Whereas, for the spectra of activated carbon after activation process and commercial grade, the peak was found at ~ 680 cm⁻¹ meaning that the increasing of C-C group.

Raman spectra for charcoal, activated carbon and commercial grade are shown in Fig. 4. Two bands are clearly observed D band at ~ 1,340 cm⁻¹, which corresponds to the disordered carbon structure and G band at ~ 1,600 cm⁻¹, which is related to the graphitic structure of carbon. Hence, D band represents a highly defective carbon structure, whereas G band represents a high of graphitic structure. As seen in Fig. 4, commercial grade has the highest G band, followed by 2SAC, 1SAC and charcoal, respectively.

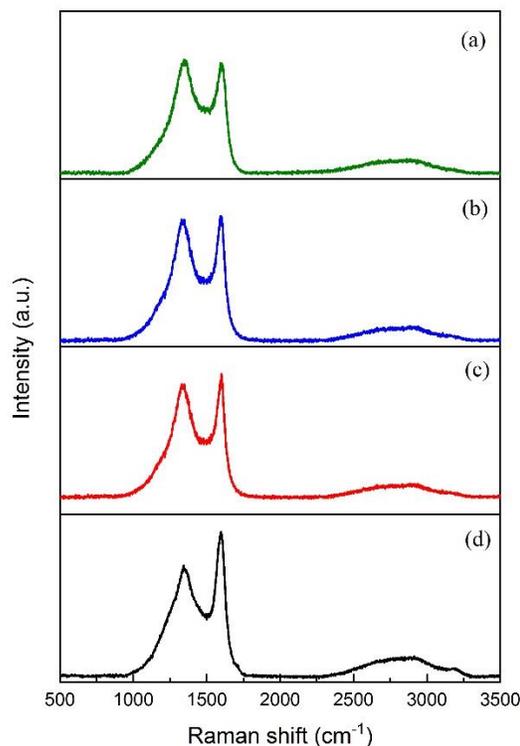


Fig. 4 Raman spectra of (a) charcoal, the activated carbon of ratio 1.00:1.50 at 700 °C (b) 1SAC, (c) 2SAC and (d) commercial grade.

Figure 5 shows the XRD patterns of charcoal, activated carbon and commercial grade. As seen in Fig. 5, the diffraction peaks located at $2\theta = \sim 24$ and $\sim 43^\circ$ corresponds to (002) and (100) plane, respectively. The diffraction peaks at $2\theta = \sim 24^\circ$ (002) represents a combination of graphitic and amorphous structure in samples, and the diffraction peaks at $2\theta = \sim 43^\circ$ (001) correspond to the growth of graphitic carbon phase [20]. In comparison with 1SAC, 2SAC and commercial grade the diffraction peaks of charcoal are much lower in the intensity of the graphitic carbon phase. This results demonstrated an improvement in the graphitic carbon phase of activated carbon.

SEM was visualized by the surface morphology of charcoal, the activated carbon at the optimum ratio and activation temperature and commercial grade, as shown in Fig. 6. SEM images revealed that the external surface of activated carbon (Fig. 6(b) and (c)) was very irregular and full of cavities with different shapes and sizes comparing to that of the charcoal (Fig. 6(a)). This can be a consequence of the gasification and release of volatile matter produced during the activation process. Especially in the case of 2SAC, many small pores were found, while the commercial grade has a porous structure similar to that of capillary (Fig. 6(d)). In addition, EDX analysis indicated the presence of C and O in the optimization of NaOH mass ratio and activation temperature (2SAC). The weight percentage of C and O calculated from the quantification of the peaks, gave the value of about 76.40 and 9.42, respectively. This relatively high carbon content presented better experimental results compared to 1SAC.

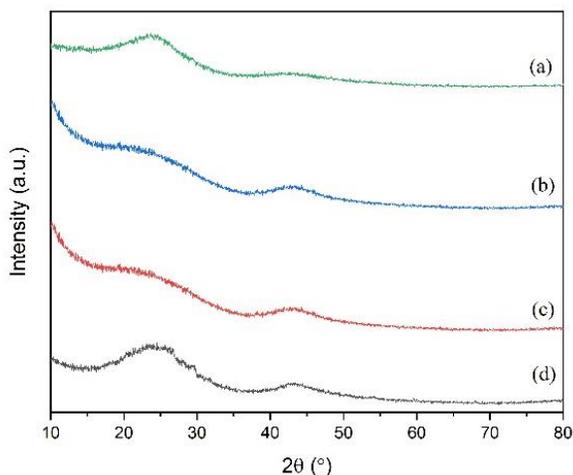


Fig. 5 XRD patterns of (a) charcoal, the activated carbon of ratio 1.00:1.50 at 700°C (b) 1SAC, (c) 2SAC and (d) commercial grade.

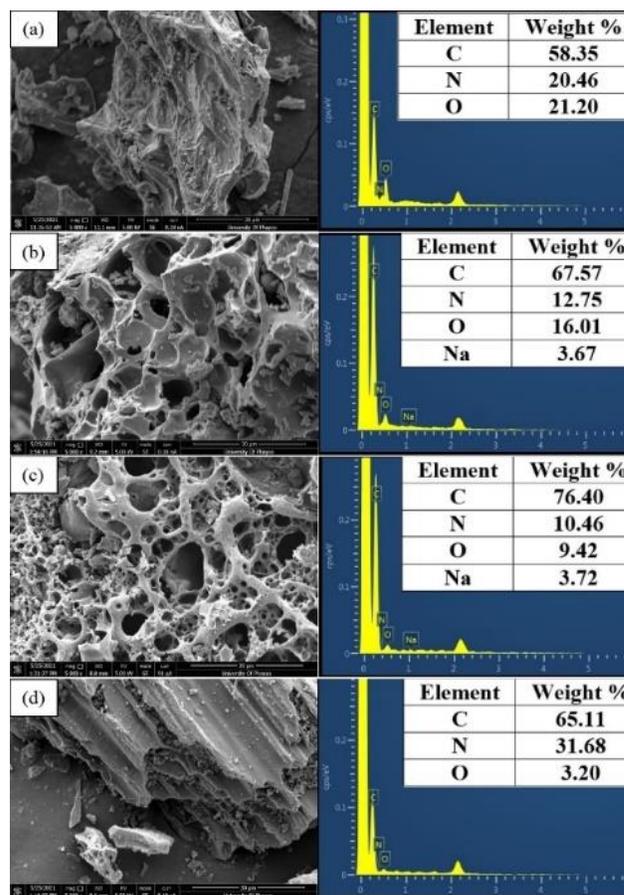


Fig. 6 SEM micrographs and EDX analysis of (a) charcoal, the activated carbon of ratio 1.00:1.50 at 700°C (b) 1SAC, (c) 2SAC and (d) commercial grade.

Conclusion

From this research, the dry chemical activation indicated improved efficiency of activated carbon prepared from longan seeds, it was found that the mass ratio of 1.00:1.50 at 700 °C from 2SAC presented better experimental results compared to 1SAC. The NaOH reactions in the carbon pores at the micropore development were observed with SEM. Although the results are still lower when compared to the commercial grade activated carbon, these results indicate that preparation of activated carbon from longan seeds with high specific surface area is a promising approach for high value conversion of abundant agricultural waste.

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