Synthesis of potassium hydroxide-treated activated carbon via one-step activation method

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Abstract. Physicochemical activation has been popular currently due to the incredible surface area of activated carbon produced. In the process, the step of activation has a significant role in influencing the characteristics of activated carbon. Previously, several studies conducted one-step activation in which potassium hydroxide (KOH) was impregnated with the precursors derived from agricultural biomass and wastes. Currently, the materials have been interesting due to their renewable and low-cost properties. This paper reviews the recent studies regarding the variables and the effect of one-step activation towards properties of KOH-impregnated adsorbents which were synthesized from agricultural biomass and wastes. The variables of one-step activation and pore development are compared in this paper. It was found that the increase of pore characteristics follows the increased amount of KOH concentration, ratio, carbonizing temperature and time until reaching the optimum level of variables. One-step activation has been proved by the studies to the successful activation of activated carbon with different excellent surface area, even up to approximately 2800 m^2/g. In the future, it will be a great challenge to develop the efficient processes of synthesizing activated carbon with improved optimization to achieve incredible and maximum results of the surface area.

Keywords: activated carbon; one-step activation; biochar; biomass; KOH.

1. Introduction

In recent years, raw materials derived from agricultural biomass and wastes have been treated as commercialized products due to their renewable, low-cost and abundant materials in nature. Nevertheless, a lot of materials are still generally to be thrown away to the environment which results in contamination in water bodies and ends as natural fertilizers or heaps of rubbish at landfill sites. In fact, the abundant renewable biomass can be treated to be a high valuable material, such as activated carbon or activated biochar.

The advantage of synthesizing activated carbon from agricultural biomass and wastes is the production of highly porous carbon due to the lignocellulosic components in the materials. Activated carbon has been proved in achieving high adsorption capacity in water purification, such as dyes (1-3), phenol groups (4, 5), palm oil mill effluent (6-8) and heavy metals (9, 10). This is all due to the large surface area of carbon that could adsorb a large number of adsorbate particles. Furthermore, activated carbon is also used in other applications, such as air purification (11), gas storage (12) and supercapacitor (13-15).

Production of activated carbon depends on the processes that are used, such as physical, chemical, and physicochemical activation. Physical activation occurs when carbonisation takes place, which uses heat or thermal as the activator. On the other hand, chemical activation involves the chemical agents to destroy the carbon walls, opening the pores and form the active sites on the activated carbon. The combination of both processes that are called physicochemical activation has been popular due to the incredible surface area of activated carbon as the result. The process of physicochemical activation relates to the steps that are used, such as one-step and two-step activation.

The step of activation has a significant role in producing the activated carbon. It influences the characteristics of activated carbon, depending on the characteristics of biomass used. Several studies conducted one-step activation in which indicating good achievements related to the pore characteristics of activated carbon (16, 17). Moreover, KOH as an activator has been highly used due to its strong basic properties to produce incredible surface area in line with the increase of temperature of carbonisation (18). One-step activation using KOH has been conducted by a lot of studies yet there is a lack in reviewing the effect of variables on the pore characteristics in the recent literature. Herein, the recent studies of one-step activation in treating biomass to become valuable activated carbon are reviewed. The objective is to compare the variables used to synthesize activated carbon and the pore development of potassium hydroxide (KOH)-treated activated carbon as an expansion toward knowledge.

2. Mechanism of KOH activation

As a carbon activator, KOH has been commonly used and compared with other chemicals. According to a study conducted by Elmouwahidi *et al* (2017), KOH activation produced activated carbon with higher surface area and porosity than phosphoric acid (H_3PO_4) activation (19). This was also similar in comparison with sodium hydroxide (NaOH) activation (20) on which KOH activation produced incredibly higher BET surface area. However, KOH activation resulted in lower yield compared to zinc chloride ($ZnCl_2$) activation due to violent chemical reaction happened during heat treatment (21). The mechanism of KOH reaction with carbon is as indicated in equation (1)-(4) (22).

$$6\ KOH + 2\ C \rightarrow 2\ K + 3\ H_2 + 2\ K_2CO_3 \tag{1}$$

$$K_2CO_3 + 2\ C \rightarrow K_2O + 2\ CO \tag{2}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{3}$$

$$2\ K + CO_2 \rightarrow K_2O + CO \tag{4}$$

When KOH is added to the carbon precursor, the formation of K_2CO_3 occurs at around 400°C which then KOH is fully transformed to K_2CO_3 at around 600°C (23). K_2CO_3 then decomposes and produces K_2O along with CO and CO_2 around 700°C. However, CO and CO_2 evolution are generated slightly at lower temperatures until it is significantly observed above 800°C (24). The reaction between KOH and precursor results in pore development with excellent surface area, consisting of micropores and mesopores. KOH is a popular activator due to its strong basic properties to destroy the carbon walls which then produces a lot of micropores. However, the number of micropores formed depends on the composition of precursors and conditions during chemical impregnation and carbonisation of materials.

3. One-step activation with different variables of synthesis

In terms of one-step activation, chemical impregnation is commonly conducted before carbonisation. During the processes, the concentration of KOH, the ratio between KOH and material, the activation temperature and time are very essential to obtain the best characteristic of activated carbon. When KOH concentration is used exceedingly, excessive activation takes place in which the formed microporous carbon is destroyed and turned to be larger pores (25). The same also applies to the activation ratio.

Table 1 indicates the previous studies of various activated carbon production derived from agricultural biomass and wastes by using one-step KOH activation. The amount of concentration and ratio of KOH:precursor affects the surface area and the major pores formed on the activated carbon, whether they are mesopores or micropores. Okman *et al* (2014) varied KOH concentrations such as 25, 50 and 100wt% (26). It was reported that the higher KOH concentration used, the smaller surface area and the lower micropores volume were then formed at 800°C of carbonisation temperature. It was also found that the decrease of surface area was in line with the reduction of micropore volume (27). Giraldo and Carlos (2018) studied the activated carbon production using mangosteen peel with different activating agent/charcoal ratios (28). The increase of surface area and pore volume followed the raise of the ratio from 0.5 to 1.5. However, the addition of excessive KOH at ratio 2.0 diminished the surface area and pore volume due to the additional reaction between KOH and microporous carbon which destroyed the as-formed structure. Bhomick *et al* (2019) found out that the maximum surface area and total pore volume were obtained with ratio of 1:2 and carbonisation temperature at 600°C (29). Besides, the yield percentage decreased as opposed to the increase of KOH ratio.

The combination of both chemical activation and carbonisation is very supportive to produce high adsorptive porous on activated carbon. The production of activated carbon with carbonisation only requires more energy to produce similar surface area and thus, showing less effectiveness compared to the physicochemical activation. In one-step activation, the carbonisation is only conducted once and so, the step requires less energy for activation temperature and shorter activation time than the two-step activation. Wang *et al* (2019) varied carbonizing temperatures ranging from 600°C to 700°C and found that the best adsorption capacity was obtained by activated carbon with the highest temperature (700°C) (30). Borhan *et al* (2019) also yielded the highest surface area at temperature of 700°C within 120 min of carbonization (31). Nevertheless, the increasing time (180 min) at the same temperature decreased the surface area produced. This is due to the excessive thermal which broke down the porous carbon wall and turned out the micropores into mesopores. Activation temperatures and time are frequently varied in various studies to find the best conditions to synthesize activated carbon. Moreover, Oginni *et al* (2019) found that synthesis via one-step activation resulted in better surface area than using two-step activation, along with the larger number of mesopores and pore volume formed (32). Overall, the incredibility of the surface area is affected not only by the composition of precursors but also by both chemical and physical activation.

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Table 1. One-step activation using KOH with different precursors and variables used

Precursors	Chemical Impregnation			Pyrolysis/Carbonisation				Surface Area (m^2/g)	Vtotal (cm^3/g)	Vmicro (cm^3/g)	References
	Weight Ratio (KOH:P)	Time	KOH Concentration	Time (min)	Temperature (°C)	Heating Gas	mL/min				
Trichosanthes kirilowii maxim shell	1:1	48h	10%	45	700	N_2	300	657	0.45	0.14	(30)
Kanlow switchgrass	1:1	24h	100 wt%	60	900	N_2	-	1271	0.63	0.28	(32)
Public miscanthus	1:1	24h	100 wt%	60	900	N_2	-	1596	0.89	0.23	
Rubber seed shell	2:1	Overnight	-	120	700	N_2	-	1129	0.412	-	(31)
Spent coffee ground	1.5:1	-	-	30	850	N_2	150	2265	1.17	1.07	(17)
Yellow mombin fruit stones	1:1	-	-	60	500	N_2	50	167	-	0.027	(33)
Casuarina fruit waste	1:4	Overnight	10%	60	600	-	-	217	0.189	-	(34)
Rice husk	-	-	1M	120	800	CO_2	-	1836	1.126	0.805	(35)
Bamboo waste	2:5	Overnight	-	60	800	NH_3	200	2892	1.533	-	(16)
Posidonia oceanica seagrass	-	Overnight	500 mg/10 mL	120	800	Ar	-	1563	0.736	0.742	(36)

4. Conclusion and future challenge

To sum up, the level of KOH concentration and ratio, as well as the temperature and time of carbonisation, are in line with the number of surface area, total pore volume and micropore volume until the optimum level of each variable is achieved. One-step activation has been studied and resulted in the successful activation of activated carbon with different excellent surface area, even up to approximately 2800 m^2/g. It is envisaged that the synthesis of activated carbon will be a great challenge in developing efficient processes with improved optimization to achieve excellent and maximum results of the surface area.

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