The Effect of Parameter Combinations (Carbonization Temperature - Chemical Activator) on Degree of Graphitization, Aromaticity, and Fungsional Group of Rose Petal (*Rosa sp*) Based-Activated Carbon

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The Effect of Parameter Combinations (Carbonization Temperature - Chemical Activator) on Degree of Graphitization, Aromaticity, and Fungsional Group of Rose Petal (*Rosa sp*) Based-Activated Carbon

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Abstract. Activated carbon is a porous material which is produced from the carbonization of organic compounds by involving the activation process. Activated carbon can be used as an absorbent of heavy metal cations, anions, and organic compounds. Quality of activated carbon is determined by the crystal structure, aromaticity, and its surface functional group. Activated carbon consists of amorphous and graphite structures. The graphite structure in activated carbon is important because it determines its thermal stability. Content of graphite structure in the activated carbon is stated as degree of graphitization (DOG). Aromaticity (f_a) is related to amount of carbon atoms which form graphene layers in the activated carbon. The oxygenated functional groups of the activated carbon determines its hydrophilic / hydrophobic nature. Purpose of this research is to learn effect of carbonization temperature - chemical activator ($ZnCl_2$) combination on degree of graphitization, aromaticity, and functional group on activated carbon. This research was conducted by using a pink rose flower precursor, at activator/precursor mass ratio of 0.1 at carbonization temperature of 400, 600 and 800°C for two hours under nitrogen gas stream. Characterization was carried out with FTIR spectrophotometry and X-ray diffraction. The DOG and aromaticity were calculated based on intensity of the difractograms. The characterization with FTIR spectra related to –OH and aromatics C=C bond vibrations. The highest DOG was obtained by the activated carbon resulted at 400°C,i.e. 92.31%. However, no significant different of the aromaticity, about 0.42 to 0.50.
Keywords*:* activated carbon, rose, degree of graphitization, aromaticity, carbonization temperature, activator

1. Introduction

Activated carbon is a porous material that widely applied in various fields. Based on literature studies, activated carbon can be applied as adsorbent of organic subtance such as methylene blue [1], heavy metal removal such as lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), and zinc (Zn) from water [2], catalyst [3], electrode [4], adsorbent of water purification [5], and many other applications. Activated carbon can be synthesized from biomass. Biomass is widely used as precursor of activated carbon because of its large abundance, low price, and renewable material.

Previous studies have explained various biomass that can be synthesized into activated carbon, such as coconut shells [6], rice husks [7], orange peels [8], and cherry blossoms [9]. In the process, synthesis of activated carbon includes activation process. There are two types of activation processes, namely physical activation and chemical activation. Chemical activation has advantages over physical activation, because the calcination process can be conducted at lower temperatures and more carbon produced [10]. In the chemical activation process chemicals such as KOH, NaOH, K_2CO_3, Na_2CO_3, H_3PO_4, $ZnCl_2$ [11], $CaCl_2$, Na_2SO_4 [12] are used. From these chemical reagents, $ZnCl_2$ is the most preferred reagent because $ZnCl_2$ is efficient to produce pores during the calcination process [12].

Quality of activated carbon is influenced by degree of graphitization (DOG) and aromaticity (f_a). XRD Diffractogram can provide data to calculate both characteristics. The degree of graphitization can be calculated using peak area [13] or peak intensity [14]. In this research, the later was used to calculate the degree of graphitization [14]:

$$g = \frac{I_{002}/I_{10}}{14.3} \text{ x } 100\% \quad (1)$$

Where, I_{002} and I_{10} are the intensities of corresponding XRD patterns, the empirical constant 14.3 is derived for the completely graphitized pyrolytic carbon without amorphous phase. The equation for calculating aromaticity is [15]:

$$f_a = \frac{C_{ar}}{C_{ar}+C_{al}} = \frac{A_{002}}{A_{002}+A_{\gamma}} \quad (2)$$

Where, f_a is the degree of aromaticity and A is the area under the curve of the peak. f_a is the ratio between C aromatic and total C (C aromatic + C aliphatic). Theoretically, the area under the curve of the peak d_{002} or π (26°) is equivalent to the number of aromatic carbon atoms (C_{ar}) and and the area under the curve of the peak γ (20°) is equivalent to the aliphatic carbon atom (C_{al}). Assuming that the baseline length of π and γ peak are same, A can be replaced with peak intensity (I), to be:

$$f_a = \frac{I_{002}}{I_{002}+I_{\gamma}} \quad (3)$$

2. Experiment

2.1. Chemical and Instrumentations

The precursor used in this research is fresh pink rose's petal. The chemical compounds used are zinc chloride, iron(III) chloride, and hydrochloric acid, all supplied by Merck. The instruments for synthesis were used during the research are analytical balance (Ohaus Pioneer PA214), glasswares (pyrex), oven (Memmert type U30), and homemade furnace. Activated carbon are characterized by FTIR spectrophotometry (Shimadzu FTIR 8400S) and X-ray Diffraction (PANalytical Minipal 4).

2.2. Synthesis procedure

The activated carbon synthesis procedure is follows of work of Ray et al. [16] and Purkait [17] with temperature range modification and activator used. First, amount 40 grams of precursor was washed with distilled water to remove impurities. Then it placed in a 500 mL beaker and soaked in 150 mL of activator solution ($ZnCl_2$) 0.2 M for two hours then drained. Precursors ware dried with an oven at 110°C for three hours. Furthermore, dried precursor was heated using a furnace at temperatures of 400°C, 600°C, and 800°C for 120 minutes with N_2 gas flowing. The product was washed with 100 mL 0.2 M HCl, and distilled water. Finally, the activated carbon was dried at 110°C for 6 hours. Table 1 presents codes of the activated carbons.

Table 1. Active carbon synthesis code

	400°C	600°C	800°C
Without activator	C28-[CAM-4]	C29-[CAM-6]	C30-[CAM-8]
Using $ZnCl_2$	C34-[CAM-Zn4]	C35-[CAM-Zn6]	C36-[CAM-Zn8]

3. Result and Discussion

Figure 1. show the images of the products which were obtained with and without $ZnCl_2$ activator at different temperatures. No significant difference of their appearances are shown.

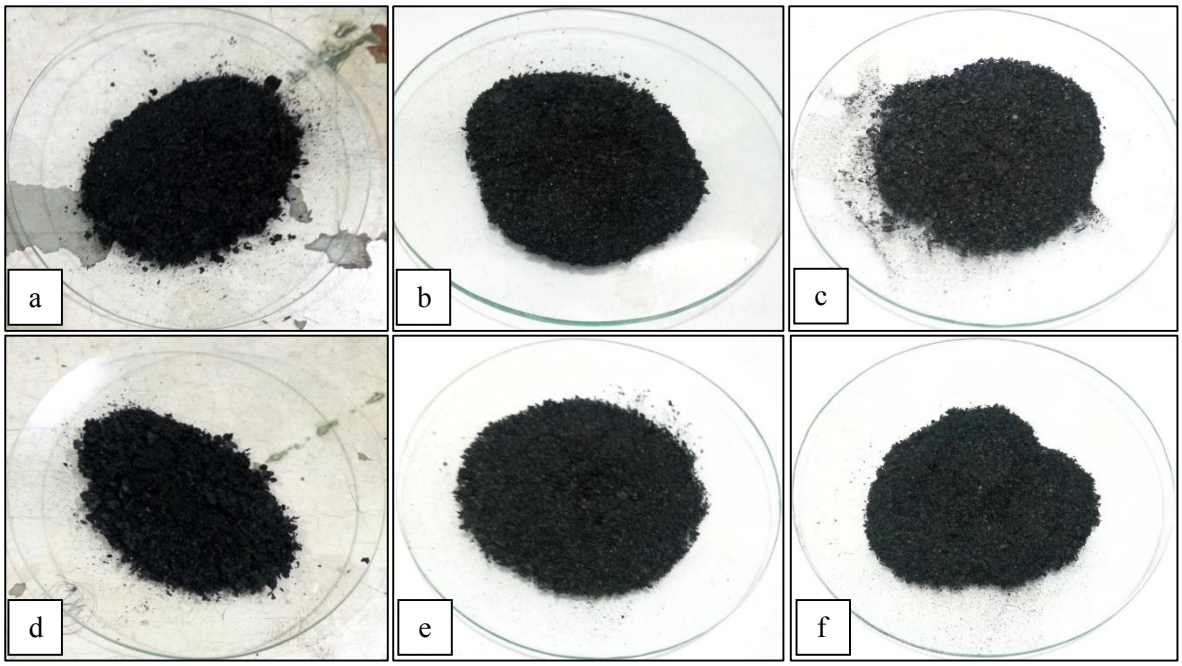

Figure 1. Images of activated carbon synthesized without activator at (a) 400°C, (b) 600°C, (c) 800°C, with $ZnCl_2$ activator at (d) 400°C, (e) 600°C, (f) 800°C

3.1. Functional groups of the activated carbon

The functional groups of the precursor and activated carbon products were analyzed using FTIR spectrometers. A broad peak around 3000 to 3500 cm^{-1} is stretching vibrations of –OH which may be connected to hydrate or hydroxil groups of the carbon. The band in the area of 2950 to 2800 cm^{-1} is stretching vibration of C-H in the methyl functional group. The sharp band at 1645 cm^{-1} indicated stretching vibration C = C aromatic ring. The band under area 1300-1000 cm^{-1} is stretcing vibration of C-O. Related to the spectra of rose petal, those functional groups indicate structure tannin, geraniol, nerol, citronellol, terpene, vanilin, farnesol, and eugenol.

Without activator, several functional group in 3000-3500 (-OH), 2950-2800 (aliphatic C-H), 1655 (C=O), 1371 (-OH bending), 1645 (aromatic C=C), 1300-1000 cm^{-1} (C-O) show lower intensities after carbonization due to thermal reaction in pyrolisis process. With activator, peak of -OH in 3000-3500 (strechings) and 1371 cm^{-1} (bending) are sharper than the same peaks of the activated carbon without activator. It indicated that $ZnCl_2$ activator support formation of –OH of the surface functional group.

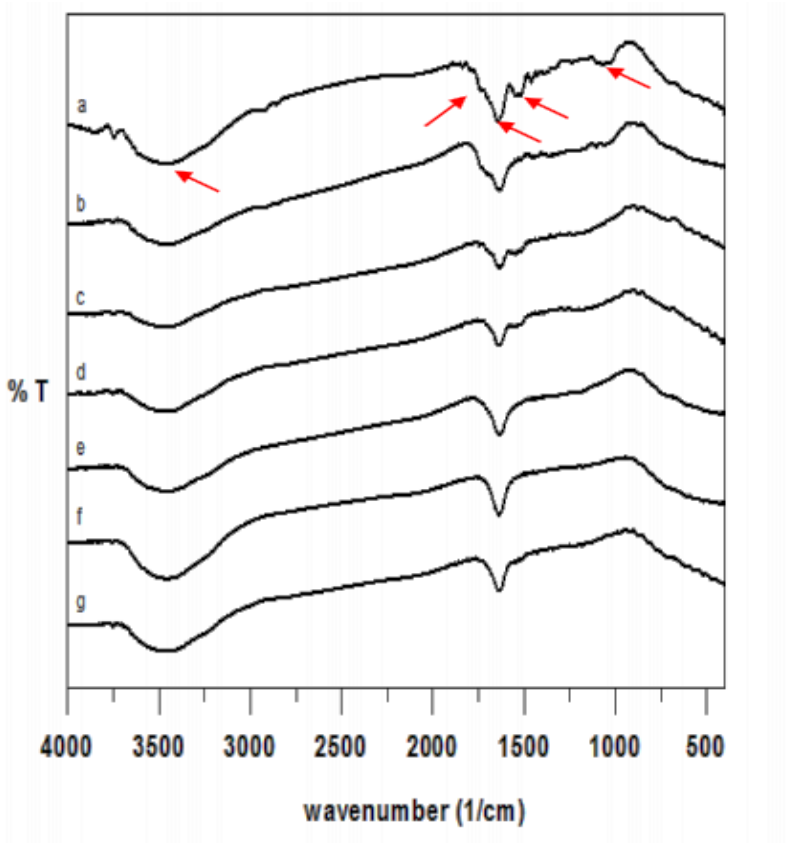

Figure 2. IR spectra of (a) rose petal precursor, (b,c,d) are activated carbon without activator at calcination temperature of 400, 600, 800°C (e,f,g) are activated carbon with $ZnCl_2$ activator at calcination temperature of 400, 600, 800°C

3.2. XRD Difractograms Analysis

The diffractograms shows wide peaks at 2θ 26° and 43°. Based on comparation to other research [18], they indicate patterns of turbostatic structure of the activated carbon. The calculated DOG and aromaticity were presented in figure 4a and 4b.

The calculation results show that the highest DOG value is obtained by C34-[CAM-Zn4] which reaches 92.31%. The lowest DOG is found in C30-[CAM-8], which is 35.79%. The DOG value of each activated carbon; C28-[CAM-4] is 87.41%, C29-[CAM-6] is 42.54%, C35-[CAM-Zn6] is 45.84%, and C36-[CAM-Zn8] is 37.46%. It means that activated carbon products have different graphite content. The remaining percentage in activated carbon products is amorphous phase. The high DOG value of the C34-[CAM-Zn4] sample caused by the role of activator during the synthesis process [12]. $ZnCl_2$ is an activator which works actively at low temperature.

Figure 5b shows a graph of the relationship between temperature and f_a. Blue line is a graph for activated carbon without activator and red one for activated carbon with activator. The figure show that f_a of activated carbon is little higher by increasing of temperature and by usage of activator. It means that high temperatures and activators can play an important role in improving the amount of carbon atoms which form graphene layers in the activated carbon. The highest f_a is 0.5, while the lower is 0.4

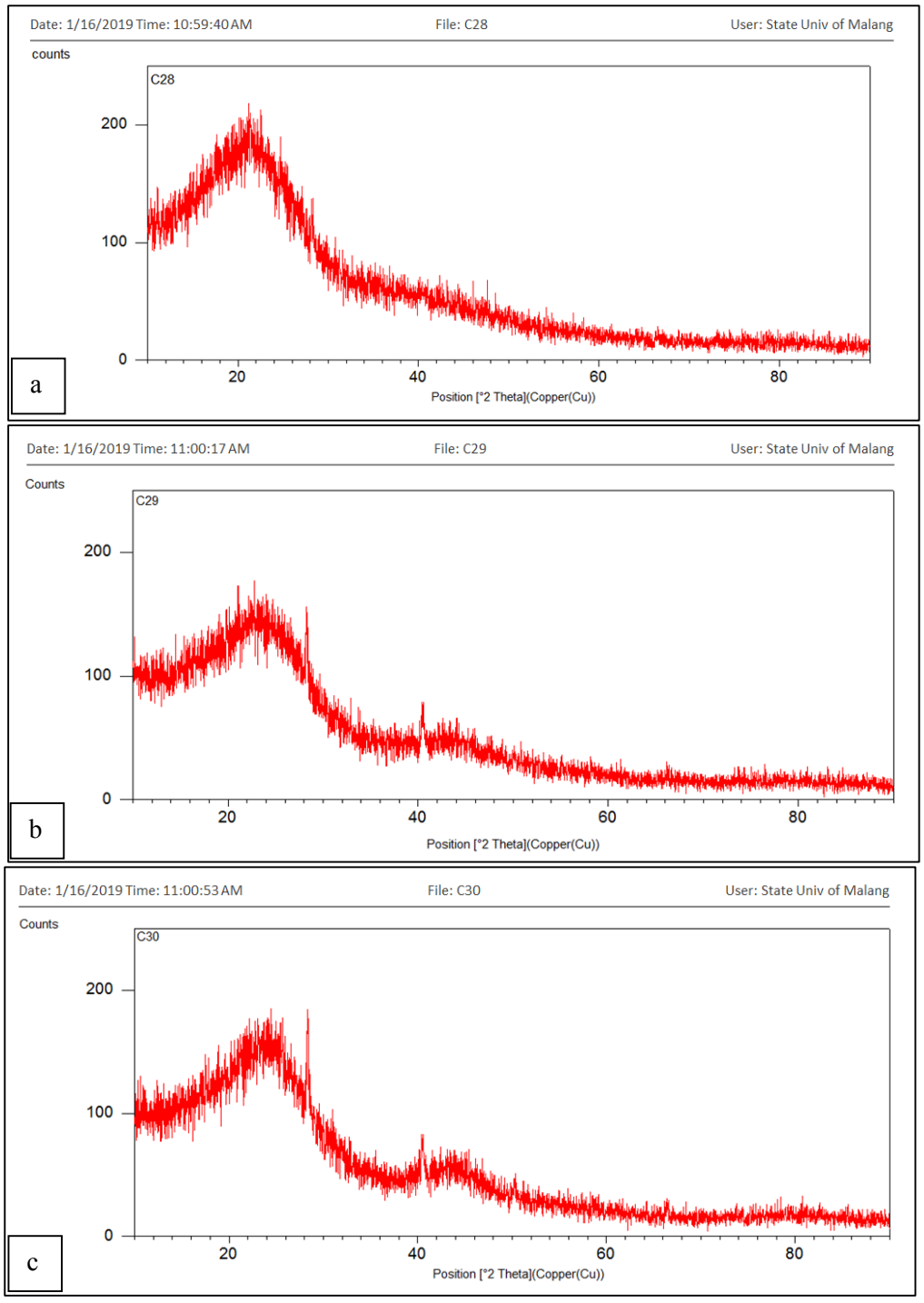

Figure 3. XRD Difractograms of activated carbon without activator at calcination temperature of (**a)** 400°C, **(b)** 600°C, **(c)** 800°C

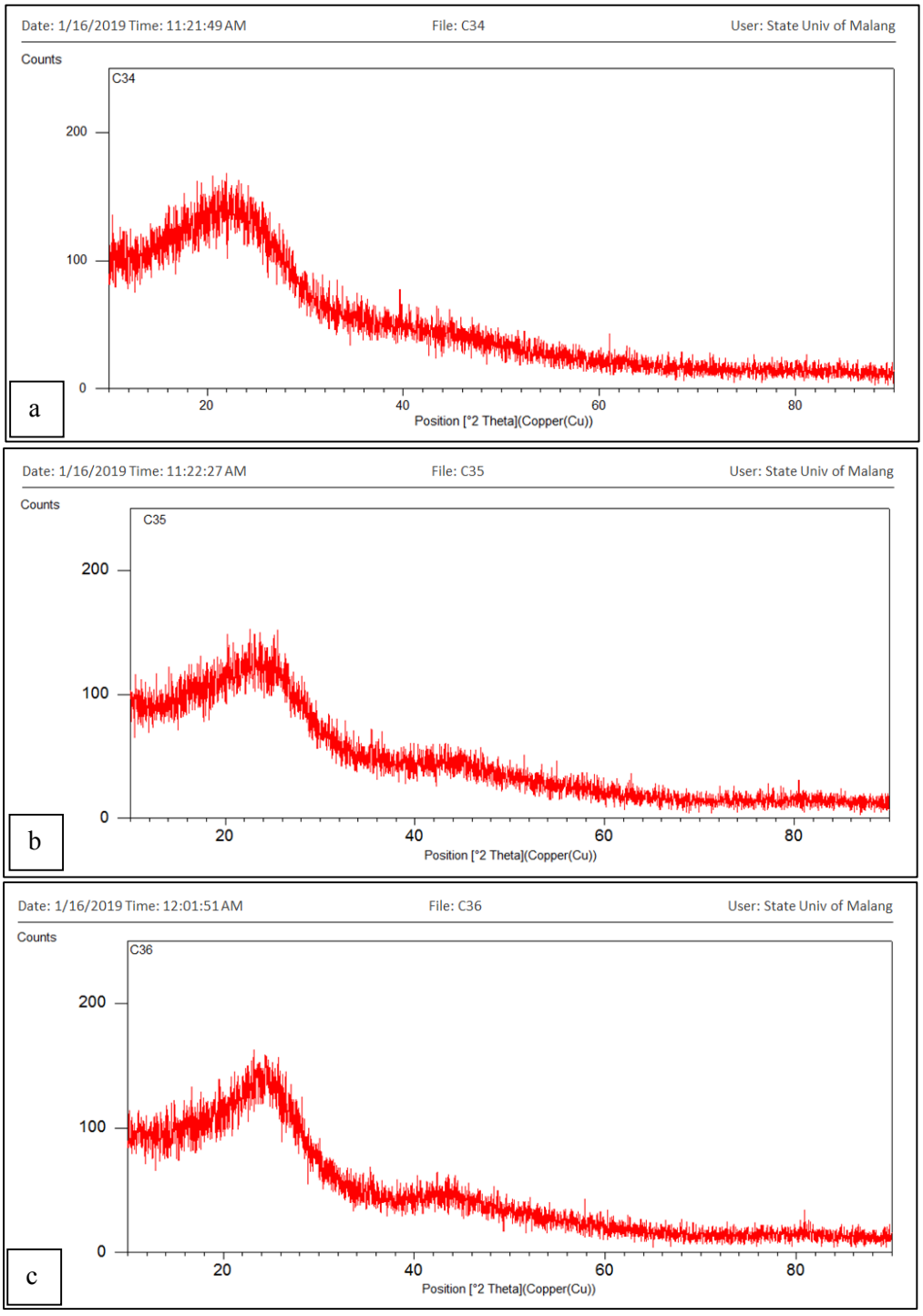

Figure 4. XRD Difractograms of activated carbon with $ZnCl_2$ activator at calcination temperature of (**a)** 400°C, **(b)** 600°C, **(c)** 800°C.

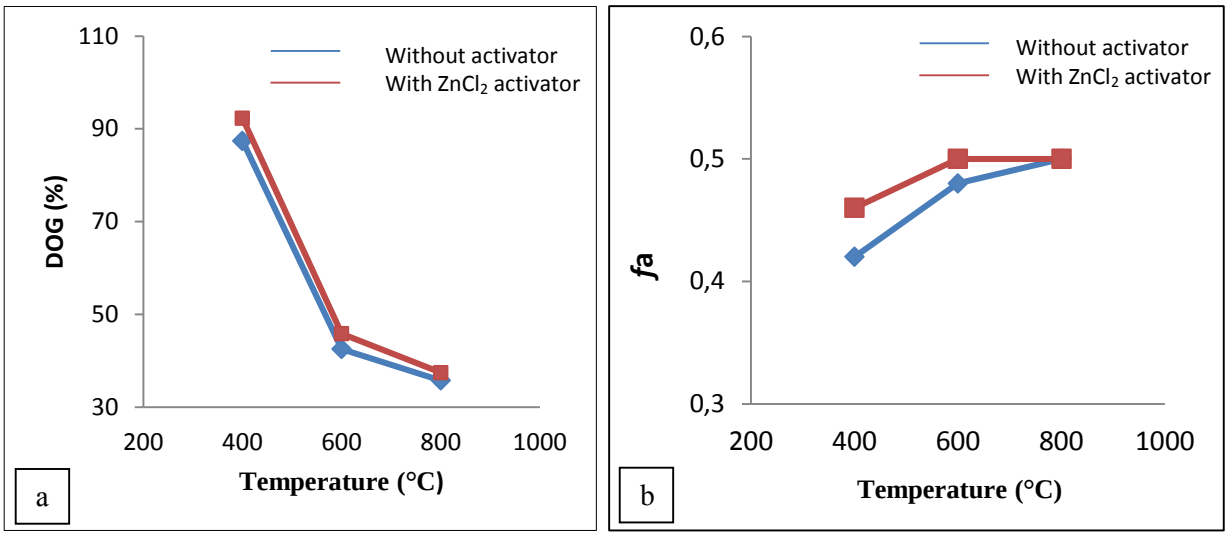

Figure 5. The relationship graph between Temperature and (a) DOG, (b) f_a

4. Conclusion

Activated carbon with a ratio of 0.1 activator / precursor of mass at calcination temperatures of 400, 600 and 800°C was synthesized successfully. The results of the analysis show the effect of parameter combination on Degree Of Graphitization (DOG) and aromaticity. The highest DOG is achieved by the combination parameter of 400°C – $ZnCl_2$ with degree of graphitization of 92.31%. The highest aromaticity (f_a) of the activated carbon is obtained by parameter combination of 600°C - $ZnCl_2$, 800°C - $ZnCl_2$, and 800°C - non activator, i.e. 0.5.

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