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Research Article
Preparation and Characterization of Hydrothermal Activated Carbon from Banana Empty Fruit Bunch with $ZnCl_2$ Activation for Removal of Phenol in Aqueous Solution

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Abstract

Background and Objective: Banana empty fruit bunch is a solid waste. It was easily found in large quantity and good for activated carbon precursor. The activated carbon banana empty fruit bunch was characterized and used for removal of phenol in solution. This study was conducted to produce activated carbon from banana empty fruit bunch. **Materials and Methods:** Preparation of activated carbon was conducted using zinc chloride activation under hydrothermal carbonization at 200°C. Its application was used for removal of phenol with different adsorption factors such as pH, contact time, concentration and adsorbent dosage. **Results:** Nitrogen adsorption desorption isotherm curve clearly showed Type IV with hysteresis loop relating with the presence of mesopores. The BET and Langmuir surface area were 46.304 and 69.166 $m^2 g^{-1}$, respectively. Surface chemistry exhibited more oxygen functional groups. Morphology exposed irregular pores and most of them were closed by the presence of zinc, silicon and other elements. The equilibrium adsorption were calculated by the Langmuir and Freundlich isotherm models. The Freundlich isotherm value showed a goodness-of-fit line with a correlation coefficient, R^2 value 0.9958 which was more favorable adsorption than those in the Langmuir adsorption. **Conclusion:** The banana empty fruit bunch activated carbon exhibited predominantly heterogeneous surfaces with multisite pores and was effective for removal of phenol.

Key words: Banana empty fruit bunch, activated carbon, zinc chloride, hydrothermal

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

World consumption of activated carbon was expected to rise with increasing the demand of industries. The largest applications of activated carbon were used in industries for purification and separation process such as removal of organic compounds, heavy metals, improving water treatments and raising the environmental standards[1-4]. Activated carbon has been a popular choice used as adsorbent compared to zeolites or other adsorbent types because it has well-developed pore structure, high adsorptive capacity and available in large quantity. Activated carbon can be manufactured from many types of raw materials which have high carbonaceous compound. In recent years, biomass waste materials with high cellulose and lignocellulose promise a well-started material for preparation of bio-activated carbon[5]. Type of raw material can affect the efficiency of adsorption capacity of activated carbon[6]. Previous works reported that biomass wastes such as oil palm shell showed the best physical characteristics such as high pore structures including large surfaced area, high pore volume and homogeneously pore size distributions[7,8]. However, the preparation of activated carbon can be separated into two categories, physical and chemical processes. In physical process, raw material is carbonized at high temperatures (700-1100°C) while flowing gaseous agents such as carbon dioxide, steam or nitrogen. In general, this process is unfavorable because of high energy, low pore structure production and lose surface functional group during carbonization. For chemical process, raw materials are impregnated with chemical agent such as potassium hydroxide, phosphorous acid, zinc chloride and then carbonized at moderate temperature to high temperatures. This process is usually more popular compared with physical process because it produces high quality of pore structure, consume low energy and has high surface functional groups.

Nowadays, a high quality of activated carbon is requested. It is necessary to find the alternative method and raw material for preparation of activated carbon. This research was suggested to use hydrothermal carbonization. The advantages of this method are low-energy consumption and more environmentally friendly[9-11].This study discovers the banana empty fruit bunch as alternative precursor using chemical activation under hydrothermal carbonization that can be beneficial for activated carbon production. This study will help researchers to reveal the critical areas of raw materials that many researchers were not able to explore. There are many agriculture waste can be considered as new source of raw materials due to low-cost raw material and available in large quantity. Exploration of activated carbon from biomass waste encouraged a growing research interest to find alternative resources. Thus a new method on the preparation such as hydrothermal carbonization using low energy composition may be arrived it. Resulted activated carbon may be used for multiplications in separation and purification methods[12].

The main objective of this research was to produce activated carbon from banana empty fruit bunch. The resulted activated carbon was applied as adsorbent and studied its applicability for removal of phenol in solution. Equilibrium adsorption was evaluated from different adsorption factors such as contact times, adsorbent dosage, pH solution and concentration. The amount of adsorptive capacity was evaluated for determination of equilibrium adsorption of phenol using the Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Materials: Banana empty fruit bunch was collected from the banana farmers at Yogyakarta, Indonesia. Sample was considered as an alternative raw material for manufacture of activated carbon. Hydrothermal reactor was designed from stainless steel with the highest temperature 500°C. The chemicals such as zinc chloride ($ZnCl_2$), nitric acid (HNO_3), buffer solution, phenol was obtained from E-Merck and used without further purification. This research was started from collecting sample, chemicals, preparation and its application for removal of phenol. This study was completed between August 10, 2016 and April 30, 2017.

Preparation activated carbon from banana empty fruit bunch: Banana empty fruit bunch was cut down into small pieces, vigorously washed with distilled water to remove the surface husk and dirt and then dried into oven at 110°C for 48 h. In order to obtain homogeneous particles, dried sample was ground and segregated to powder.

Hydrothermal activated carbon was prepared according to the following procedures. About 250 g of dried sample was impregnated into 500 mL of 10% $ZnCl_2$ solution and then refluxed at 80°C for 6 h. Thereafter, the mixture was filtered and washed for few times to reduce the chemical contents and then dried in oven at 105°C. Approximately, 200 g of dried sample was immersed into 100 mL distilled water and then it was transferred into hydrothermal reactor. The reactor

was set up inside graphite furnace and moderately carbonized at 200°C for 6 h. After cooling down, the result was activated carbon. Activated carbon was washed with nitric acid of 2.0 M and dried in oven at 150°C. The activated carbon was kept in desiccator for further analysis.

Characteristics of activated carbon: Pore size structure involving surface area, pore volume and pore size distribution was determined from the nitrogen adsorption, desorption isotherms data which were obtained by surface area analysis quantachrome. Surface morphology was imaged by Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). Surface functional groups of activated carbon were determined by Fourier Transform Spectroscopy Infrared (FTIR). Amount of phenol removal was determined by the UV/Vis spectrophotometry at maximum wavenumber 269.5 nm.

Moisture content of activated carbon: Thermal drying method was applied to calculate the moisture content of activated carbon. Approximately, 0.5 g of initial weight of activated carbon was placed in clean, dried and weight crucible. Sample was dried into an oven at 120°C for 3 h to a constant weight. The different weight between the initial and final weight of activated carbon indicated the moisture content using the Eq. 1:

$$\text{Moisture content } (\%) = \frac{\text{Final weight (g)} - \text{Initial weight(g)}}{\text{Initial weight(g)}} \times 100 \quad (1)$$

Ash content of activated carbon: Thermal drying method was also used to determine of the ash content of activated carbon. About 0.5 g of activated carbon was placed in clean and dried crucible and then it was moderately heated up to 600°C for 3 h. Thereafter, sample was cooled down into dedicator for 30 min and it was reweighed[13]. The ash content was determined by the different weight between before and after heating as Eq. 2:

$$\text{Ash content}(\%) = \frac{\text{Ash weight(g)}}{\text{Initial dry weight (g)}} \times 100 \quad (2)$$

Adsorption capacity of activated carbon: Adsorption capacity was determined from the removal phenol in aqueous solution. Different parameters involving pH (pH = 4, 5, 7, 8) adsorbent dosage (0.5, 1.0, 1.5, 2.0 g) contact times (15, 30, 45, 60 min) and initial concentration of adsorbate (50.0, 100.0, 150.0, 200.0 mg L^{-1}) were applied to the activated carbon. The amount of phenol removal was calculated using UV-Vis spectrophotometer at wavelength of 267 nm, respectively. Equilibrium adsorption isotherm was evaluated at room temperature using Langmuir and Freundlich isotherm models[14,15]. The adsorption capacity (q_e) and the phenol removal % (R, %) were evaluated using the Eq. 3 and 4:

$$qe = \frac{(Co - Ce)V}{m} \quad (3)$$

$$R(\%) = \frac{(Co - Ce)}{Co} \times 100 \quad (4)$$

where, Co and Ce are the initial and the equilibrium concentrations (mg L^{-1}) of phenol and 2 chlorophenol. The V is volume of the solution (L) and m is the mass of adsorbent (g).

Adsorption isotherm of activated carbon: Equilibrium adsorption for removal of phenol can be studied from Langmuir isotherm model and Freundlich isotherm model. Langmuir isotherm model is considered as monolayer adsorption on the surface occurring on the homogeneous micropore with no transmigration of adsorbate in plane of surface. While the Freundlich isotherm model occurs on the multilayer on the heterogeneous pores involving mesopores. For Langmuir isotherm model is expressed from linear based as Eq. 5:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (5)$$

The value of q_e is the removal efficiency of metals at equilibrium (mg g^{-1}). The values of Q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constant related to the maximum adsorption and energy adsorption, respectively. The Langmuir isotherm model was calculated from linear plot of specific adsorption (C_e/q_e) versus equilibrium concentration (C_e)[16].

The Freundlich isotherm model is expressed Eq. 6:

$$qe = K_F C_e^{\frac{1}{n}} \quad (6)$$

Linear parameter can be expressed by taking logarithms for determination of K_F and n by the following Eq. 7:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (7)$$

A plot of loq q_e versus log C_e gives a straight line. The values of K_F and 1/n are the Freundlich constant related to the removal capacity and adsorption intensity which can be estimated from the intercept and slop, respectively.

RESULTS AND DISCUSSION

Proximate of the activated carbon: Proximate analysis in term of ash and moisture content ash content were obtained. Resulted activated carbon has a relatively small ash and moisture content which indicated the presence of high fix carbon and mechanical strength. These properties may improve the quality of adsorbent and increase the adsorption capacity. The results of moisture and ash contents were 0.94 and 9.01%, respectively which were consistent with the previous study[12].

Nitrogen adsorption desorption isotherm of activated carbon: The plot of nitrogen adsorption desorption isotherm at 77 K of activated carbon was shown in Fig. 1. The curve of N_2 isotherm showed the type IV isotherm with well-define hysteresis loop. The hysteresis loop indicated the presence of mesopore accompanied to the multilayer or capillary condensation. Unfortunately, desorption line at the lower end of hysteresis loop did not reach closed position at relative pressure below 0.4. It indicated that there is disorder isotherm of desorption isotherm of hysteresis. This reason was assumed that activated carbon is heterogeneous pore materials or the pore shrinkage occurred during carbonization[17]. The result indicated that activated carbon has a large number of mesopores instead of microporous structure.

The pore size distribution of activated carbon according to the BJH plot was shown in Fig. 2. Pore size distribution is separated into three categories: Micropore (pore diameter <20Å), mesopore (pore diameter 20-500Å) and macropore (pore diameter >500Å). The result showed that the pores were heterogeneous structure distributed in form of micropore to mesopore.

Textural properties of activated carbon involving the surface area, the BET and Langmuir methods were shown in Table 1. Determination of BET surface area was carried out based on relative pressure in range of 0.05-0.03, while the Langmuir surface area was obtained at relative pressure ranging from 0.001-0.05. The BET surface area was 46.30 m^2 g^{-1}. This result showed a higher BET surface area compared to the previous research[12].

Surface functional group of activated carbon: The distribution of functional groups on the surface of activated carbon was shown in Fig. 3. The weak band at 3059 cm^{-1} was assigned to O-H stretching vibration in hydroxyl groups. The strong band at 1572 cm^{-1} was attributed to C = C stretching in aromatic rings. The band at 1410 cm^{-1} was ascribed to C-O stretching vibration in carboxylate groups. The band at 1030 cm^{-1} was as ascribed to C-O-C stretching vibrations. The bands at 451-413 cm^{-1} indicated the presence of Zn-O stretching. The result indicated that the activated carbon might have more oxygen functional groups attached on surface carbon.

Morphology of activated carbon: The Scanning Electron Microscopy (SEM) graph of the surface morphology of activated carbon was illustrated in Fig. 4. The microstructure showed the irregular cavities and pores on the external surfaces. Most of pores were blocked by particles as rest of hydrothermal carbonization such as zinc, silicon and other

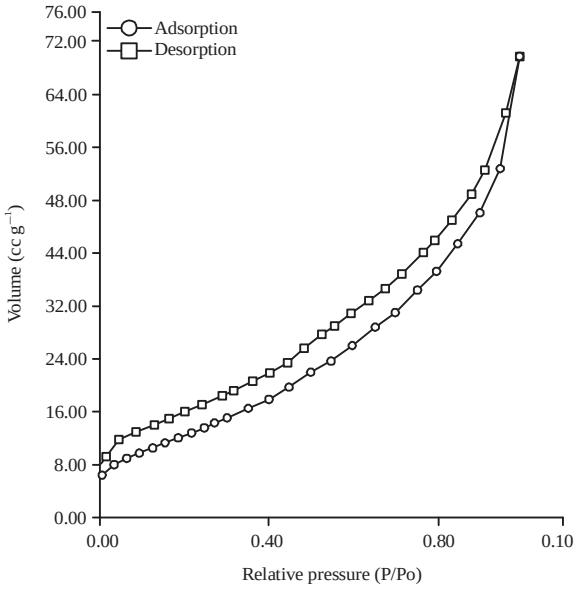


Fig. 1: Nitrogen adsorption-desorption of activated carbon

Table 1: Textural characteristics of activated carbon derived from banana empty fruit bunch

Langmuir surface area (m^2 g^{-1})	BET multipoint surface area (m^2 g^{-1})	DR micropore volume (cc g^{-1})	BJH cumulative adsorption pore volume (cc g^{-1})	BJH adsorption pore radius (Å)	DA pore radius (Å)	Average pore radius (Å)
69.17	46.30	0.02	0.10	17.01	9.20	46.19

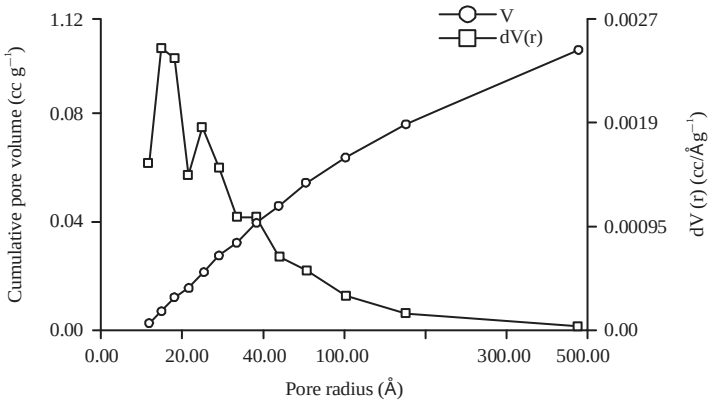


Fig. 2: BJH plot of activated carbon

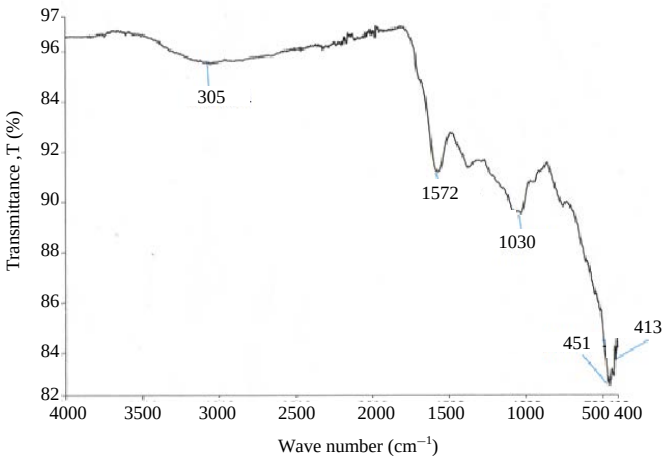


Fig. 3: FTIR spectra of activated carbon

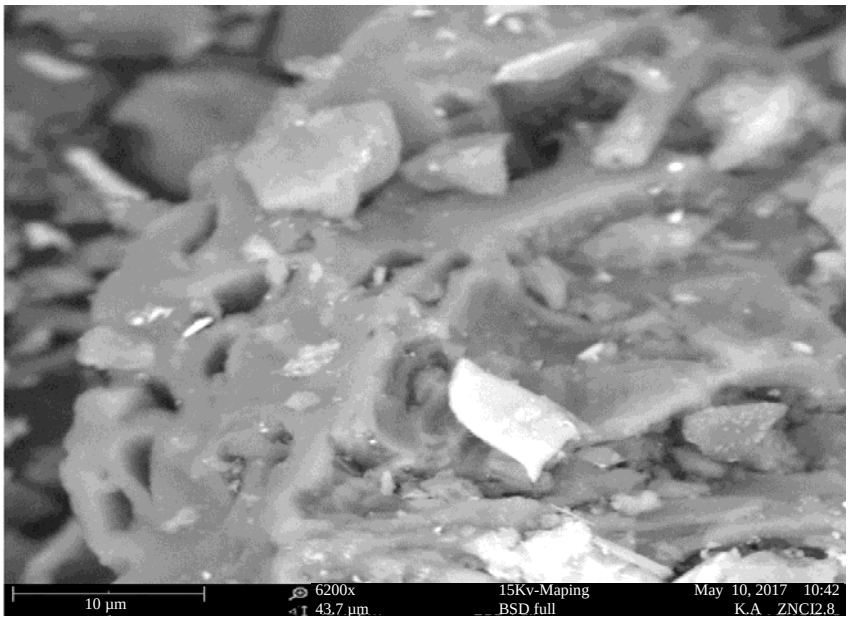
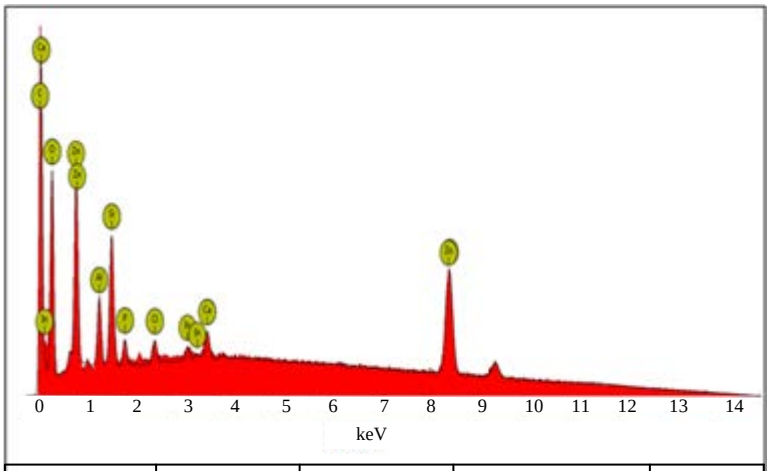


Fig. 4: Morphology structure of activated carbon prepared from banana empty fruit bunch



Element number	Element symbol	Element name	Atomic concentration	Error
6	C	Carbon	20.0	0.7
30	Zn	Zinc	22.1	0.1
8	O	Oxygen	43.8	0.2
14	Si	Silicon	6.0	0.0
13	Al	Aluminium	4.3	0.0
20	Ca	Calcium	1.0	0.6
15	P	Phosphorus	1.4	0.8
17	CI	Chlorine	0.9	3.4
49	In	Indium	0.5	1.0

Fig. 5: Elemental analysis of activated carbon by Energy Dispersive X-Ray (EDX)

elements. These pores were created from hydrothermal process which was initiated by the presence of zinc chloride as chemical agent. The formations of pores were followed with the degradation of chemical bonding, evaporation chemical reagents by leaving the empty and rearrangement to form cavities. However, at low hydrothermal temperature, zinc ion was not easy to remove from the surface of activated carbon. This result was supported by the elemental analysis by Energy Dispersive X-Ray (EDX). The relative compositions were obtained 43.8% of oxygen, 22.1% of zinc, 20.0% of carbon and the rest elements were contaminants including silicon, aluminum, calcium, chlorine as shown in Fig. 5. In addition, the presence of zinc was also confirmed from the FTIR analysis at band ranging from 451-413 cm^{-1}.

Adsorption studies for the removal efficiency of phenol: The pH is one the most important parameters that can influence the equilibrium adsorption isotherm of phenol. The effects of pH in the range of pH 3-8 were shown in Fig. 6. The obtained results showed that there exist significant effects of pH solution change. The isotherm adsorption of phenol

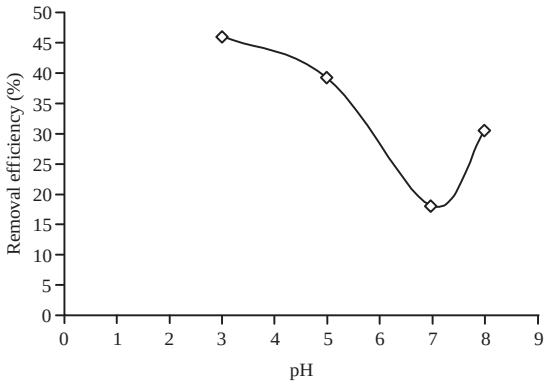


Fig. 6: Effect of pH on the removal of phenol

removal decrease as the pH increase. These can be assumed as following reasons. At lower pH, the isoelectric point indicates an excess H^+ ions or positive charges that initiate the reaction of phenol with the maximum adsorption at pH 3. However at higher pH, the amount of positive charges decrease but the negative charge increases. In fact, the adsorption phenol decreases from solution pH from 3-7 and then the phenol increase after Ph-7.

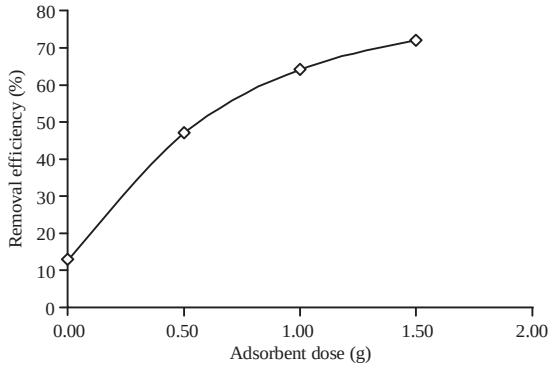


Fig. 7: Effect of adsorbent dose on the removal of phenol

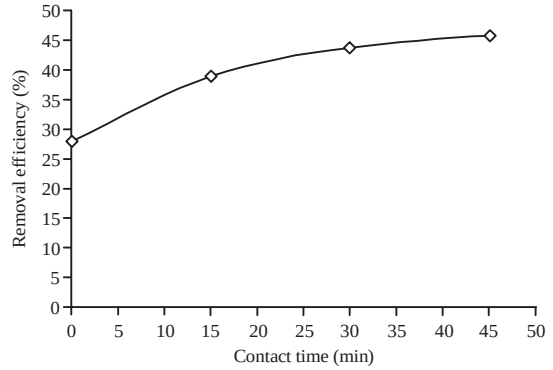


Fig. 8: Effect of contact time on the removal of phenol

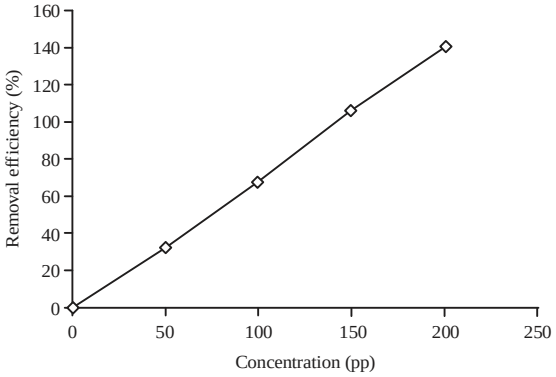


Fig. 9: Effect of initial concentration on the removal phenol

The effects of activated carbon dose on the equilibrium adsorption of phenol removal were investigated over range 0.5-2.0 g. The equilibrium adsorption of phenol removal was shown in Fig. 7. The investigation showed that isotherm phenol removal sharply increases as the activated carbon dose increases. Furthermore, once the activated carbon dosages increase, the number of vacant surface sites and large surface area for adsorption also increase. On the other hand, adsorptive capacities of phenol removal increase as long as activated carbon dose increase.

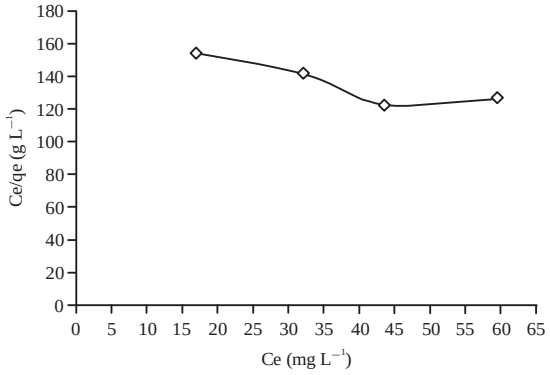


Fig. 10: Plot of Langmuir Adsorption isotherm

The effects of contact time on equilibrium adsorption of the phenol removal over range 15-45 min were shown in Fig. 8. The efficiency of phenol removal rapidly increases with the increasing of contact times starting from 0-30 min and relative plateau to higher contact time to 45 min. The sorption rate of phenol was nearly reaching equilibrium after reaching contact time 30 min. The higher sorption rate might be occurred due to an increased contact time between phenol and active site of activated carbon during adsorption process. The effects of concentration of equilibrium adsorption of phenol removal were shown Fig. 9. The sorption rate of phenol sharply increases with the increasing of initial concentration and tends to low uptake at the higher concentration. The maximum uptake of phenol was obtained at 200 ppm. This result indicated that the activated carbons are effective for phenol removal. On the other hand, the more pores and surface areas were available on the adsorbent, the higher sorption rate of phenol in the solution.

Adsorption isotherms of phenol: Determination of the equilibrium adsorption isotherm revealed the relationship adsorption process between the amount of phenol removal and carbon active. Equilibrium absorption of phenol was evaluated using the Langmuir and Freundlich isotherm models. In this study, both isotherm models were conducted for study the equilibrium adsorption to describe the behavior isotherms. The plot of Langmuir adsorption isotherm which was calculated from plot C_e/q_e (mg L^{-1}) Vs. Ce (mg L^{-1}) was shown in Fig. 10. While, the plot of Freundlich adsorption isotherm could be assumed as an essential multisite adsorption isotherm for heterogeneous surface as shown in Fig. 11.

Comparison study of the Langmuir and Freundlich isotherm models of the activated carbons was shown in Table 2. Freundlich isotherm model results a goodness-of-fit adsorption data with correlation coefficient, R^2 values 0.9958.

Table 2: Langmuir and Freundlich isotherms for phenol removal

	Langmuir isotherm model			Freundlich isotherm model		
Adsorbent	Langmuir constant Q (mg g^{-1})	Maximum adsorption K_L (L mg^{-1})	Correlation coefficient (R^2)	Freundlich constant, K_f (mg g^{-1}) (L mg^{-1})	n	Correlation coefficient (R^2)
Activated carbon	-0.02388	-22.4874	0.79064	1.1970	1.0257	0.9958

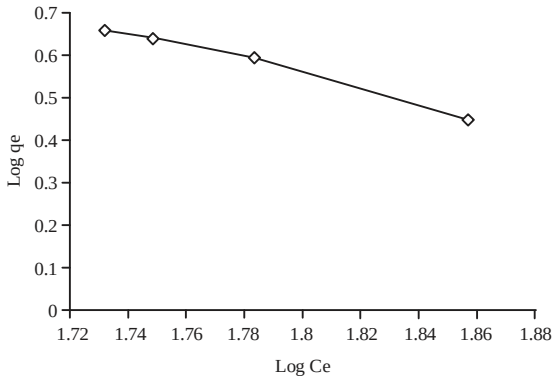


Fig. 11: Plot of Freundlich isotherm adsorption

While the Langmuir isotherm has correlation coefficient, R^2 values 0.79064. It can be assumed that the Freundlich isotherm was more favorable than those in the Langmuir isotherm. The adsorption process might occur in a heterogeneous surface with multi-site pores[18]. This result was relevant with the pore site distribution data by which the activated carbon from banana empty fruit bunch might have predominantly mesopores structures. Based on the data, activated carbon prepared from the banana empty fruit bunch showed mesopores with heterogeneous surface. It was efficiently used for removal of phenol in solution.

This study is very valuable work to enrich of source of raw material for activated carbon production. The achievement of high quality of activated carbon can be obtained by exploring the method whether by physical or chemical activation. In the future, preparation of activated carbon from banana empty fruit bunch can be explored by variety of methods by carbonization (high temperature) or hydrothermal carbonization (low temperature). Obviously, high quality of physical and chemical properties of activated carbon can be used for separation and purification process.

CONCLUSION

Banana empty fruit bunch was successfully converted to activated carbon for removal of phenol. Preparation of activated carbon was carried out using zinc chloride activation in which zinc chloride was able to initiate the formation of pores. The evaluations proved that activated carbon has the mesoporous structure, enough oxygen-functional group and irregular surface. Equilibrium adsorption of phenol was investigated from the Freundlich and Langmuir isotherms. The Freundlich isotherm has a best-fit linear with correlation coefficient, $R^2 = 0.9958$ than the Langmuir with correlation coefficient, $R^2 = 0.79064$. The results clearly showed that the activated carbon prepared from banana empty fruit bunch could be promising to be used as alternative precursor of activated carbon and used as adsorbent for phenol removal.

SIGNIFICANCE STATEMENT

This study discovers the banana empty fruit bunch as alternative precursor using chemical activation under hydrothermal carbonization that can be beneficial for activated carbon production. This study will help researchers to reveal the critical areas of raw materials that many researchers were not able to explore. There are many agriculture waste can be considered as new source of raw materials due to low-cost raw material and available in large quantity. Exploration of activated carbon from biomass waste encouraged a growing research interest to find alternative resources. Thus, a new method on the preparation such as hydrothermal carbonization using low energy composition may be arrived it. Resulted activated carbon may be used for multiplications in separation and purification methods.

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