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Removal of chlorinated phenol from aqueous media by guava seed (*Psidium guajava*) tailored activated carbon

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ABSTRACT

In this study, the activated carbons (ACs) were prepared from guava seeds via two stages activation. The dried guava seeds were semi-carbonized at 300 °C for 1 h, and then the carbonized samples were impregnated with zinc chloride ($ZnCl_2$). The $ZnCl_2$: sample impregnation ratios (w/w) were altered from 1:1 to 5:1. The ACs were characterized by the yield percentage, ash content, moisture content, pH value, adsorption quality of 2,4-dichlorophenol (2,4-DCP) and surface functional groups. The surface area of the best produced AC3 was found to be 919.40 $m^2 g^{-1}$. It was found that AC3 had highest 2,4-DCP adsorption capacity, which was 20.9 $mg g^{-1}$. The 2,4-DCP adsorption kinetic of prepared AC3 was pseudo-second order with correlation value of 0.995. In addition, the 2,4-DCP adsorption capacity of AC3 was fitted to the Langmuir model with correlation coefficient value of 0.977, indicating that chemisorption was a major contributor to the adsorption process.

1. Introduction

Extensive use of chlorophenols has brought many negative effects on human. For example, pentachlorophenol is one of the most common phenolic compounds found in human blood, plasma and fish [23]. Currently, the adsorption of chorophenol compounds from aqueous solutions with activated carbon (AC) has been reported as an effective method for water treatment [21]. AC is formed when the carbon particles are arranged in a quasi-graphitic manner. It is an amorphous carbon that consists of high degree of porosity and also good absorptivity [30,36].

From the past researches, there are many studies on preparation of AC from fruits stones, shells, seeds, and plant waste [33,42]. They contain high amount of lignocellulosic material, an example includes grape stalks [32], rice husk [44], Albizia lebbeck seed pods [2], coffee residues [27], oil palm shells [22], cattle-manure compost [34], oil palm empty fruit bunch [20], sour cherry stones [6], Crofton weed [50].

Guava is a berry like fruit of various mytaceous trees and often called as the apple of the tropics. The scientific name of guava fruit is known as *Psidium guajava* from Mytaceae family, and it is native from Mexico. Generally, the guava fruits are planted in the tropical or sub-tropical area of America, Asia and Africa [12]. In Malaysia, guava fruit is an important tropical fruit due to its high commercial and nutritional values, and there are various types of guava fruit, such as Gu4, Gu5, Gu7, Jambu Biji, Laknaw, Hongkong pink, Red Malaysian, Taiwan and Vietnamese [49]. All those species have a small size of 2.4–3.35 cm radius and have a thin mesocarp with 9–15 mm. In contrast, the Vietnamese guava fruit has a larger radius and mesocarp thickness of 5–5.5 cm and 19–25 mm respectively. The mesocarp colour of guava fruit can be either white or pink colour. The average vitamin C content of the fruits is around 40.1 $mg g^{-1}$ to 180.5 $mg 100 g^{-1}$ [49]. In the last decade, the importance of guava fruit was improved from neglected fruit to one grown largely for processing. The guava fruit can be either used to make canned food or processed to guava juices or used for producing jam and guava paste. Guava seeds are always considered as agriculture waste in food industries, seeds represent around 5% weight of guava fresh fruit. High amount of lignocellulosic materials can be found in the guava seeds, so it is suitable to be used to synthesize the AC [35]. Guava seed is considered as low cost agricultural waste and highly available in the factories of guava processing. The major components of the guava seeds are gluterlins, globulins, cellulose, hemicelluloses and lignin which are suitable for preparation of AC [14].

Therefore, in this study, guava seeds (*Psidium Guajava*) were used as the precursor for an alternative sorbent to determine its effect on the removal of 2,4-Dichlorophenol (2,4-DCP) aqueous solution, replacing the commercial AC in industrial fields. The AC was produced using two different methods. One of the methods is a two stage chemical activation. Zinc chloride ($ZnCl_2$) was used as the activating agent for the chemical activation with a fixed ratio of activating agent to precursor used. The ash, moisture content, pH, product yield, and

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2,4-DCP adsorption capacity was used to characterize the prepared AC.

2. Materials and methods

2.1. Sample preparation

In this study, the guava seeds were used as raw material to prepare AC. The samples were washed with distilled water and dried in an oven at 110 °C for 24 h. The dried guava seeds were used as precursor to synthesis AC [14].

2.2. Preparation of AC

Two stage self-generated atmosphere method was used to prepare AC from dried guava seeds. The precursor was semi-carbonized (first stage), and then it was subjected to activation process (second stage) with chemical activation agent which was $ZnCl_2$. Both semi-carbonization and activation were done in self-generated atmosphere. Self-generated atmosphere is the atmosphere that consists of volatile matter which is generated from pyrolysis process.

2.3. Semi carbonization process

Semi-carbonization by pyrolysis was carried out in muffle furnace. A known amount of guava seeds were placed on a pyrex petri dish and heated at 300 °C for 1 h in muffle furnace. After pyrolysis, the material was stored in a desiccator to minimize moisture contact [24].

2.4. Impregnation with $ZnCl_2$

Impregnation process was carried out before the activation process and $ZnCl_2$ was used as the dehydrating agent. The $ZnCl_2$: sample impregnation ratios (w/w) were altered from 1:1 to 5:1 (samples AC1-AC5). 20 g of AC was impregnated with 200 mL of aqueous solution of $ZnCl_2$ with the weight varying from 20 g to 100 g. After that, the mixture was heated at 85 °C until completely dried.

2.5. Chemical activation process

The impregnated samples were activated in a muffle furnace under self-generated atmosphere at the optimum temperature 500 °C for 2 h. Table 1 shows the data of activation process.

2.6. Washing process

The activated samples were refluxed with 0.01 M HCl at 85 °C for 30 min to remove excess $ZnCl_2$, tar, ash and metal ion. After that, the samples were washed with distilled water to remove all the acid until pH of wash water become neutral. The washing process was done in a water bath at 70 °C for 4 h each. The washed samples were then dried in an oven at 110 °C for 24 h [6].

2.7. Characterization of AC

2.7.1. Determination of percentage of yield

The percentage yield of activated carbon was calculated using Eq. (1). This analysis was performed to estimate the economics of scale for this process.

$$Percentage\ \ of\ \ yield = \frac{W_f}{W_i} x100 \tag{1}$$

where W_f is the final mass of the dry impregnated sample at the end of activation process and W_i is the initial mass of sample.

2.7.2. pH value determination

1.0 g of every activated sample was weighed and transferred into an Erlenmeyer flask. 100 mL of distilled water was added into the Erlenmeyer flask and boiled by using a reflux condenser to recycle water vapour. Then, the AC was filtered out from the solution, and the filtrate was cooled to 50 °C. Finally, the pH value of the filtrate was determined by using a pH meter [7].

2.7.3. Moisture content determination

1.0 g of the AC sample was placed into a dry, closed beaker and weighed. Then, the opened beaker with the lid was dried in an oven until a constant weight was achieved. The sample containing beaker was closed and took out from the oven, cooled to ambient temperature. The closed beaker was weighed again. The moisture content of the AC sample was calculated by using Eq. (2) [7,41]:

$$Percentage\ \ of\ \ moisture\ \ content = \frac{Loss\ \ of\ \ weight x100}{Weight\ \ of\ \ sample\ \ after\ \ drying} \tag{2}$$

2.7.4. Ash content determination

The AC sample from above was heated in a muffle furnace at 650 °C for several hours until a constant weight was achieved. The burned sample was cooled to ambient temperature in desiccators and weighed again. The ash content of sample was calculated by using Eq. (3) [7,41]:

$$Percentage\ \ of\ \ ash\ \ content = \frac{Weight\ \ of\ \ sample\ \ after\ \ ash\ \ process x100}{Weight\ \ of\ \ sample\ \ before\ \ ash\ \ process} \tag{3}$$

2.7.5. Scanning electron microscope (SEM) analysis

SEM is an instrument used to study morphological structure of the prepared AC. The sample was scanned with a focused beam of electrons with a spot smaller than 10 nm. The electrons interact with sample surface to a depth of approximately 1 mm. This interaction generates various signals that can be detected and used to produce an image [10]. Before SEM analysis, the samples were dried at 110 °C for one week. The granular form of AC sample was subjected to SEM and it was used to search for porous structure of sample.

Table 1
The temperature and time for activation process.

Sample	Ratio of impregnation (w/w) ($ZnCl_2$:AC)	Semi – carbonization		Activation	
		Temperature (°C)	Time (h)	Temperature (°C)	Time (h)
AC1	1:1	300	1	500	2
AC2	2:1	300	1	500	2
AC3	3:1	300	1	500	2
AC4	4:1	300	1	500	2
AC5	5:1	300	1	500	2

2.7.6. Fourier transform infrared spectroscopy (FTIR) analysis

The functional groups of activated carbon surface were analyzed by using FTIR. First, the prepared ACs were grinded and dried at 110 °C for 24 h. Then, small amount of grinded sample was putted into the FTIR spectrophotometer to obtain IR spectrum. The IR spectrum was obtained at a resolution of 1 cm^{-1} over the range 4000–400 cm^{-1}. Each peak in the spectrogram in specific wavelength represents the specific surface functional group present on the surface of AC sample.

2.8. Adsorption capacity

0.1 g of five AC samples with different impregnation ratios were placed into five 800 mL Erlenmeyer flasks containing 600 mL of 20 mg L^{-1} 2,4-DCP solution. The solution was stirred for 1 h. Then, the AC was filtered out from the solution and the filtrates were analyzed with UV–vis spectrophotometer. The pH and initial concentration of 2,4-DCP solution and adsorbent dosage of AC was used as the parameter to study the adsorption kinetic and adsorption isotherm for the sample that achieved highest adsorption capacity.

2.8.1. Effects of initial concentration 2,4-DCP

Batch adsorption was carried out in a set of 800 mL of beakers which contain 600 mL of 2,4-DCP solutions with different initial concentration (5, 10, 15, 20 mg L^{-1}). 0.5 g of prepared AC was added to each beaker and stirred for 1 h to reach equilibrium. The original pH of the solution was maintained without any pH adjustment. After the equilibrium was achieved, the ACs were filtered out form the solution to reduce interference of the prepared carbon with analysis. UV–vis spectrophotometer was used to test the adsorption of 2,4-DCP by the AC [9]. The total quantity of adsorbed 2,4-DCP was calculated by Eq. (4):

$$q_e=(C_0-C_e)V/W \tag{4}$$

where C_0 is the initial concentration of 2,4-DCP in liquid phase (mgL L^{-1}); C_e is the equilibrium concentration of 2,4-DCP in liquid phase (mg L^{-1}); V is the volume of the solution (L); W is the mass of the dry adsorbent used (g).

2.8.2. Effects of solution pH

Adsorption of 2,4-DCP by prepared AC in different pH solution was analyzed. Before the 0.5 g of the prepared AC was added to the 600 mL with 20 mg L^{-1} of 2,4-DCP, 0.01 M HCl and 0.01 M of NaOH were used to adjust the pH of each solution to an appropriate value (pH, 3–9). The mixture was stirred for 1 h in without heating. After that, the solution was filtered and analyzed by using UV–vis spectrophotometer [47].

2.8.3. Effects of adsorbent dosage

Different amounts (0.1–0.5) of prepared AC were added to 4 different conical flasks with 50 mg L^{-1} of 2,4-DCP. The solution was stirred for 1 h without heating. After the equilibrium was achieved, the solution was filtered and analyzed using UV–vis spectrophotometer, to determine the optimum amount of adsorbent required for maximum adsorption [45,46].

3. Results and discussion

3.1. Physical characterization

The yield, moisture and ash content percentage along with pH of AC1-AC5 are shown in Table 2.

Table 2
ACs with their relative yield, moisture, ash and pH.

Sample	Yield (%)	Moisture content (%)	Ash content (%)	pH
AC1	20.05	3.58	4.59	6.07
AC2	20.89	2.61	5.41	5.57
AC3	24.02	2.13	6.79	5.30
AC4	22.77	1.80	7.82	5.10
AC5	20.03	1.60	8.16	5.03

The yield of the AC initially increased by $ZnCl_2$ ratio, and then decreased. $ZnCl_2$ impregnation ratio gave a significant effect on the yield of prepared carbon. Table 2 shows an increasing trend for AC1 with 20.05% to AC3 with 24.02%, and followed by a decreasing trend for AC4 with 22.77% and AC5 20.03%. For AC1, AC2, and AC3, the increment of $ZnCl_2$ impregnation ratio increases the AC yield. The $ZnCl_2$ rearrange the carbon structure to form a rigid matrix with numerous of cross-links, so more product can be produced [18]. Cross linking reaction occurred in a low impregnation ratio, so the production of volatile components were reduced, leading a high AC yield [43]. The $ZnCl_2$ selectively remove H and O from the samples H_2 and H_2 rather than hydrocarbon. In addition, the AC yield was increased due to polymerization which was promoted by the $ZnCl_2$. Larger polycyclic aromatic molecules were produced from these reactions, and this resulted in an increased AC yield [1]. However, further increase in the impregnation ratio of $ZnCl_2$ gave a dehydrating effect during activation. So it can inhibit the formation of tars and other liquid matter that could block the pores on the surface of the samples. Therefore, the released volatiles from the pores during activation and yield are decreased [18]. During the activation process, the lignocellulosic materials were transformed into carbon, involved releasing of O and H atoms as water, carbon monoxide, carbon dioxide, methane, aldehydes or distillation of tar [47]. Since impregnation ratio of AC4 is much lower than AC5, so the yield of AC4 is higher than AC5.

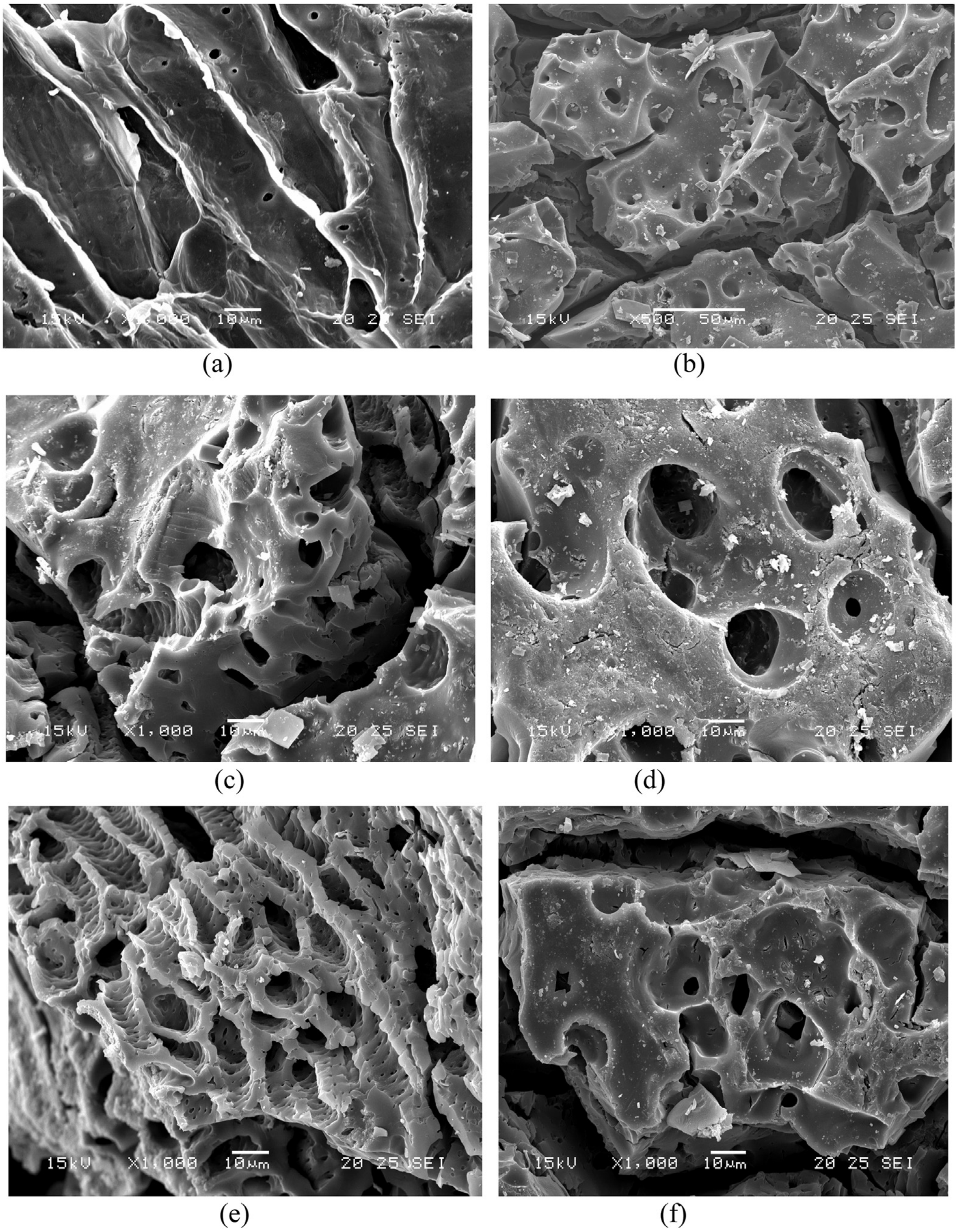
From the Table 2, the moisture content of the samples shows a decreasing trend for AC1 with 3.58%, AC2 with 2.61, AC3 with 2.13%, AC4 with 1.80%, and AC5 with 1.60%. Overall, the moisture content of the samples is reduced by increasing $ZnCl_2$ impregnation ratio and this is because of the excellent dehydration characteristic of $ZnCl_2$ as well as some of the $ZnCl_2$ were not washed out from the samples [20]. Although $ZnCl_2$ is an excellent activating agent in AC preparation, but it is seldom used in food and pharmaceutical industries due to contamination problem [17].

High moisture content can reduce the adsorption of 2,4-DCP by AC, so the sample must be dried in an oven at 110 °C for 24 h. Furthermore, pre-drying the samples before running the adsorption experiment can avoid high moisture content, dilutes the carbon and necessitates the use of additional weight carbon during the experiment [8]. The difference of moisture content between AC4 and AC5 is insignificant, because further increase in $ZnCl_2$ impregnation ratio has little or no effect on the moisture content of the AC.

The ash content is the non-carbon or mineral impurities, which does not chemically bond with carbon surface. The ash is made up from different unwanted mineral substance; it becomes more concentrate after pyrolysis. Normally, the type of raw material has a major effect on the ash content of activated carbon. AC with high ash content is not ideal, because it reduces the adsorption capacity and mechanical strength [13].

The effects of $ZnCl_2$ impregnation ratio on the ash content of the samples are shown in the Table 2. Overall, the ash content of each sample is less than 10%. Table 2 shows an increasing trend for AC1 with 4.59%, AC2 with 5.41%, AC3 with 6.79%, AC4 with 7.82% and AC5 with 8.16%. Obviously, the ash content of the samples was contributed by the $ZnCl_2$ salt, so higher ash content was obtained. Apart from this, the formation of insoluble inorganic product increased when the impregnation ratio became higher [31].

The pH of the samples was determined by ASTM (1999) method and the pH depends on the surface functional group [7]. For example, the acidic functional group such as phenolic and carboxyl group may cause an acidic pH value. Overall, the pH of all the samples are 5 and



(a) (b) (c) (d) (e) (f)

Fig. 1. SEM micrographs (×1000 magnification) (a) guava seed (b) AC1 (c) AC2 (d) AC3 (e) AC4 (f) AC5.

above. Table 2 shows a decreasing trend for AC1 with pH 6.07, AC2 with pH 5.57, AC3 with pH 5.30, AC4 with pH 5.10 and AC5 with pH 5.03. From the observation, the samples become more acidic when the impregnation ratio increased, because the $ZnCl_2$ salts were hydrolyzed in the presence of natural alkalinity. Therefore, the metal hydroxide was formed and the alkalinity of the samples was reduced [20].

In addition, the adsorptions of inorganic ions depend on the surface charge of adsorbent, which in turn is affected by its pH value [38]. On the other hand, the adsorption of organic substances is favored at lower pH value [29]. Based on these assumptions, the prepared AC is deduced to be able to adsorb high amount of organic substances.

3.2. Morphological study of AC

SEM was used to study the morphological structure of the prepared AC (Fig. 1).

From the observation, chemical impregnation with $ZnCl_2$ of AC results in formation of mesopores and micropores on the carbon surface. In this experiment, the porosity of the AC depends on the impregnation ratio. The AC with 1:1 impregnation ratio characterized by the least pores amount and cracks. Based on the observation, the amount of pores and cracks increase from AC1 to AC5 as shown in Fig. 1(a)–(f). As shown in the Fig. 1, the pore size of the samples increased from AC1 to AC3, but the pore size of AC4 and AC5 were less than AC3 pore size. The pore size of AC3 is around 10 µm and largest among all the samples, and this is because the excess $ZnCl_2$ brought shrinkage effect on the porous structure of AC4 and AC5 [11]. From the adsorption capacity data, these become more obvious for a impregnation ratio of 3:1 which is an optimal ratio for AC preparation. From the Fig. 1(d) numerous clear and well defined pores can be observed. AC4 and AC5 showed lower 2,4-DCP adsorption capacity than the AC3 and their pores are not deeper and larger than AC3 as shown in Fig. 1(e) and (f). When the impregnation ratio is larger than 3:1, destructive effect may occur on the micropore structure of AC [1].

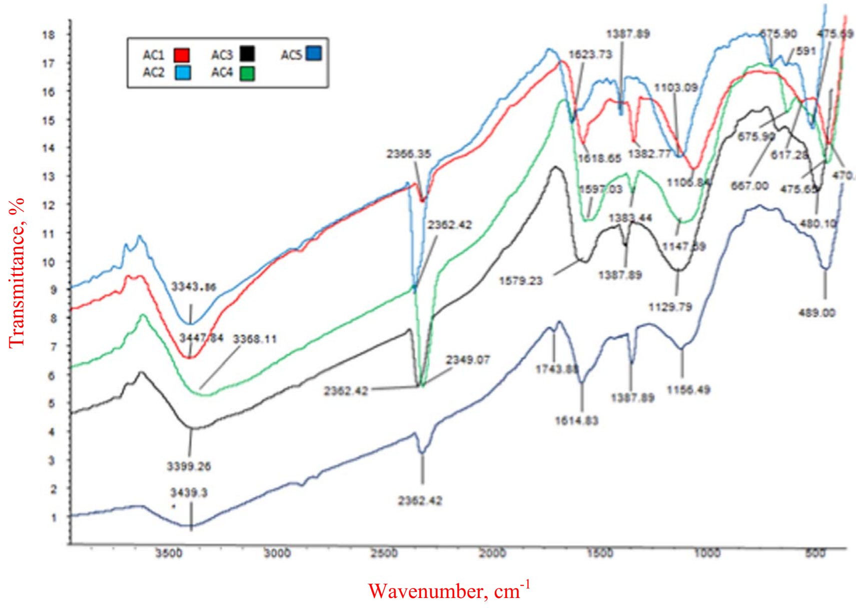


Fig. 2. Combined FTIR spectras of the AC1 to AC5 samples.

3.3. Surface functional groups of prepared AC

From the FTIR spectra as shown in Fig. 2, all the samples have the similar functional groups, because all the samples were prepared from the same type of guava seed with procedure. The small difference between the spectrums is caused by the difference in impregnation ratio. All of the FTIR spectrum show a broad band between 3300 cm^{-1} and 3500 cm^{-1}, and this this broad peak indicates the N–H bond stretching alkyl or aryl amine which can be found in the amino acid of guava seed protein. Besides that, two significant bands were identified in the range between the 2932 cm^{-1} and 2951 cm^{-1}, this is caused by the presence of asymmetric C–H bonds and symmetric C–H bonds respectively. In addition, a sharp band observed in the range between 2349 cm^{-1} and 2462 cm^{-1} are assigned to C≡C stretching present in the alkynes group. On the other hand, the aromatic C═C bond may present in the activated sample due to the presence of broad band at around 1600 cm^{-1}. A strong band at around 1383 cm^{-1} may be contributed by the C-H bending present in the alkyl group. A broad band was obtained in the region between 1300 and 1000 cm^{-1}, this may be attributed to C-O stretching present in alcohol and ether. However, the presence of a weak sharp band around 660 cm^{-1} may be deduced to C-Cl. The samples were washed by HCl, then acidic functional group may present on the surface of the samples. In the region of 500–1000 cm^{-1}, a lot of overlapping and complex bands were collected from the analysis. This is due to the different types of motion of the various types of functional groups. Overall, the $ZnCl_2$ impregnation ratio did not give an obvious influence on the surface functional groups of the samples.

3.4. Specific surface area and pore-distribution

AC3 was selected for surface area and pore distribution analysis. The maximum Brunauer, Emmett and Teller (BET) surface area of 919.40 m^2 g^{-1} and the average pore diameter of 23.68 Å obtained are comparable with the findings of other researchers [3–5,19,20,25,26]. Table 3 represents the porous and surface characteristics of AC3.

The BET isotherm shown in Fig. 3, exhibited a Type I isotherm without any adsorption hysteresis loop. This is a typical of a microporous solid with chemisorption properties, which is corroborated by the compliance to the pseudo-second-order model. As shown in Fig. 3, during the initial stage, the adsorbed volume significantly increased in the low relative pressure region (P/Po < 0.1). This result provides a strong indication that the prepared carbon is primarily microporous in nature.

Table 3
Surface area, pore volume and pore size of AC3.

Surface area	
BET surface area, m^2/g	9.194×10^{2}
BJH method cumulative adsorption surface area, m^2/g	7.800×10^{2}
BJH method cumulative desorption surface area, m^2/g	8.028×10^{2}
Pore volume	
BJH method cumulative adsorption pore volume, m^3/g	0.2726×10^{-3}
BJH method cumulative desorption pore volume, m^3/g	0.2763×10^{-3}
Pore size	
Average pore diameter, Å	23.68
BJH method adsorption pore diameter (mode), Å	8.845
BJH method desorption pore diameter (mode), Å	9.152
DH method adsorption pore diameter (Mode), Å	8.870
DH method desorption pore diameter (Mode), Å	9.164
DR method micropore width, Å	1.802

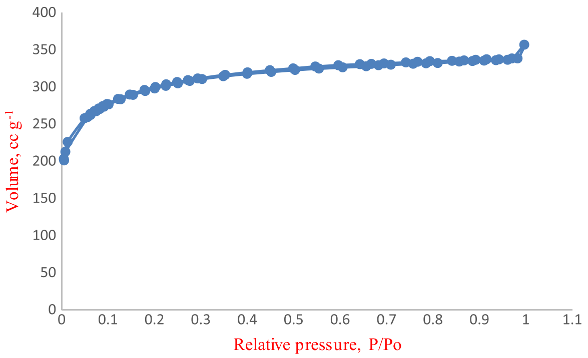


Fig. 3. Nitrogen adsorption-desorption isotherm for AC3 sample.

3.5. Adsorption capacity of AC

The 2,4-DCP adsorption indicates the adsorption capacity of an AC for molecules having similar molecular size to 2,4-DCP. 0.5 g of AC was added and stirred with 600 mL of 20 ppm of 2,4-DCP for 3 h to achieve

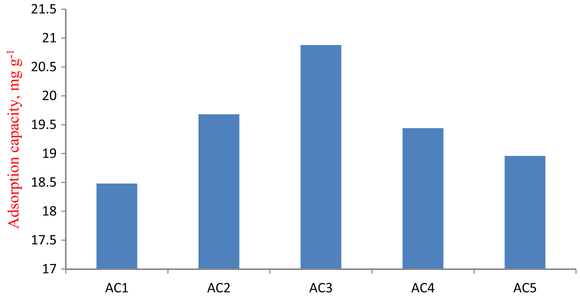


Fig. 4. The 2,4-DCP adsorption capacity of the prepared guava seed based AC samples.

the adsorption equilibrium at 28 °C. After that, the 2,4-DCP adsorption capacity by AC was analyzed using UV–vis spectrometer. Fig. 4 shows that the adsorption capacity of the samples increases as the $ZnCl_2$ impregnation ratio increase up to 3:1. As the impregnation ratio above 3:1, the 2,4 DCP adsorption capacity by AC decreases.

From the result it was found that, the impregnation ratio gives a significant effect on the quality of prepared AC. AC3 achieved the highest adsorption capacity among other samples, and its adsorption capacity is 20.88 mg g^{-1}. The quantity and size of the pores increased as the impregnation ratio increased. However, 3:1 impregnation ratio is the optimum ratio required for the AC preparation. When the impregnation ratio is larger than 3:1, destructive effect may occur on the porous structure of activated carbon [48]. From SEM image, AC3 consists large and widely distributed pores compared to other samples with different impregnation ratio, so it can provide more free surface area for adsorption to occur. Since the AC3 possess highest adsorption capacity, the batch adsorption and further adsorption studies were done with sample AC3, for adsorption isotherm and kinetic of 2,4 DCP adsorption.

3.6. Batch adsorption of 2,4-DCP by prepared AC

3.6.1. Effect of 2,4 DCP solution pH on adsorption capacity

The adsorption of 2,4-DCP onto the prepared AC, AC3 at pH 3, 7, and 9 were investigated. As shown in Table 4, the value of equilibrium adsorption capacity, q_e at pH 3 was higher than those at pH 7 and 9. These results indicate that lower pH value is favourable for the better adsorption of 2,4-DCP onto the prepared AC, AC3 in aqueous medium. Since 2,4-DCP is a hydrophobic organic compound, it can form protonated and deprotonated species in aqueous medium. The percentage of both species present in solution is dependent on the pH of the solution. 2,4-DCP molecules are protonated in acidic condition, while the dichlorophenate anion is formed when the pH value larger than 7. The decrease in the adsorption capacity of 2,4-DCP on the prepared AC at higher pH was due to the electrostatic repulsion between the dichlorophenate anion and AC. Then, the relatively strong electrostatic repulsion forces reduce van der Waals forces between adsorbent surface and the adsorbates molecules. Therefore, the adsorbates could not adsorb tightly on the adsorbent surface [45]. On the other hand, most of the 2,4-DCP molecules are maintained in the nonionized form at pH 7, so no electrostatic repulsion force between the adsorbent surface and adsorbates. Thus, the adsorption capacity of activated carbon at pH 7 slightly higher compared to pH 9 [39].

Table 4
Effect of 2,4-DCP solution pH by prepared AC3.

pH of 2,4-DCP solution	Initial concentration, C_0 (mg L^{-1})	Equilibrium concentration, C_e (mg L^{-1})	Volume of 2,4-DCP solution, V (L)	Weight of activated carbon, W (g)	Adsorption capacity, q_e (mg g^{-1})
3	20	2.70	0.60	0.50	20.76
7	20	4.20	0.60	0.50	18.96
9	20	4.60	0.60	0.50	18.48

Table 5
Effect of AC3 dosage on the 2,4-DCP adsorption.

AC dosage (g)	Initial concentration of 2,4-DCP, C_0 (mg L^{-1})	Concentration of 2,4-DCP after adsorption, C_e (mg L^{-1})	Concentration of 2,4-DCP adsorbed (mg L^{-1})	Removal efficiency (%)
0.1	20	13.10	6.90	34.50
0.3	20	7.50	12.50	52.50
0.5	20	2.60	17.40	87.00

3.6.2. Effect of AC dosage on adsorption of 2,4-DCP

Adsorbent dose is a parameter that is used to determine the capacity and removal efficiency of the adsorbent for a given initial concentration of 2,4-DCP. Table 5 shows the effect of AC, AC3 dosage on the 2,4-DCP adsorption. The trend of 2,4-DCP removal efficiency increases with AC dosage. The percentage removal of 2,4-DCP increased from 34.50–87% along the increase of AC dose from 0.1g to 0.5 g. When the dose of AC is increased, the free surface area and adsorption sites also increase. Therefore, more 2,4-DCP molecules can be adsorbed on the AC surface.

3.6.3. Effect of initial concentration of 2,4-DCP solution on adsorption capacity

Table 6 shows the adsorption capacity versus the different initial concentrations of 2,4-DCP. From the result, the initial concentration of 2,4-DCP gave a significant effect on the adsorption of 2,4-DCP on AC. The concentration of 2,4-DCP adsorbed on the surface AC increased when initial concentration of 2,4-DCP increased. This change reflectsW an increase in the driving force of concentration gradient when the initial concentration of 2,4-DCP is getting higher [40].

3.7. Adsorption isotherm

Linear form of Langmuir and Freundlich equation were applied to study the 2,4 DCP adsorption isotherm of the AC. In the present study the 2,4 DCP adsorption was analyzed by Langmuir and Freundlich isotherm model in order to describe the sorption equilibrium by Eqs. (5) and (6) respectively.

Langmuir equation

$$C_e/q_e = \frac{1}{(q_{max}K_L) + \frac{C_e}{q_{max}}} \tag{5}$$

where C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}); q_e is the equilibrium adsorbate concentration in the adsorbent (mg g^{-1}); q_{max} is the monolayer capacity of the adsorbent (mol g^{-1}); K_L is the Langmuir adsorption constant (L mg^{-1}).

Freundlich equation

$$In(q_e) = In(K_F)+\frac{1}{n}In(C_e) \tag{6}$$

Table 6
Effect of initial concentration of 2,4-DCP on the 2,4-DCP adsorption by prepared AC3.

Initial concentration of 2,4-DCP, C_0, (mg L^{-1})	Equilibrium concentration, C_e (mg L^{-1})	Volume of 2,4-DCP solution, V (L)	Weight of activated carbon, W (g)	Adsorption capacity, q_e (mg g^{-1})
5	0.10	0.60	0.50	5.88
10	0.60	0.60	0.50	11.28
15	0.90	0.60	0.50	16.92
20	2.60	0.60	0.50	20.88

Table 7
Adsorption isotherm data of 2,4-DCP onto AC3.

Adsorption capacity, q_e, (mg g^{-1})	C_e/q_e	$In(C_e)$	$In(q_e)$
5.88	0.0170	−2.3026	1.7716
11.28	0.0531	−0.5108	2.4230
16.92	0.0532	−0.1054	2.8285
20.88	0.1245	0.9555	3.0388

where C_e is the equilibrium concentration in the solution (mg/dm^3); q_e is the equilibrium adsorption capacity (mg/g); $K_{F,}$ and n the Freunlich model constant [30].

Adsorption isotherm data of 2,4-DCP onto AC3 presented in Table 7. According to the fitting results, Langmuir isotherm model was more suitable than the Freundlich isotherm model since the correlation coefficients of Langmuir model (R^2=0.977) was higher than Freundlich model (R^2=0.961). These results indicate the Langmuir equation is more applicable than Freundlich equation. The validity of Langmuir equation indicates monolayer adsorption of 2,4 DCP on the specific homogeneous sites of AC [45].

3.8. Adsorption kinetics studies

The kinetics and dynamics of 2,4 DCP adsorption onto AC, AC3 can be studied by employing the Langergren first order and pseudo-second order rate equations. Both equations are very suitable used to study the adsorption of an adsorbate from an aqueous solution, which are expressed by the equations as bellows:

$$\text{In}\,(q_e - q_t)=\text{In}q_e - \frac{k_{ad}}{2.\,303}t \tag{7}$$

where q_e is the amount adsorbed (mg/g) at equilibrium; q_t is the amount adsorbed (mg/g) at time; t is the time (min); k_{ad} is the rate constant (min^{-1}).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e is the amount adsorbed (mg/g) at equilibrium; q_t is the amount adsorbed (mg/g) at time; t is the time (min).

Fig. 5(a) and (b) shows the Langergren first order and pseudo-second order plots, respectively. It can be seen in the Fig. 6 that the Langergren's first – order plot does not fit with the experimental kinetic data very well. While the correlation coefficient, R^2 of pseudo second – order plot is equal to 0.995, these indicate that the applicability of the pseudo-second order equation is better than Langergren's first – order plots. The results indicate chemisorption occurs between the adsorbent and adsorbate, so the rate of the adsorption depends on the amount of adsorption sites on the adsorbent surface rather than the adsorbate concentration in bulk solution [15,16,28,37]. In order to understand the mechanism of 2,4 DCP adsorption onto the AC, intra-diffusion model was used to determine rate limiting step and the involved mechanism. Fig. 6 shows a plot of q_t versus $t^{1/2}$. Since the plot gave a multi-linear nature, so the adsorption process involves more than one mechanism [42]. 3 parts can be divided from the plot, which is phase 1, phase 2, and phase 3. The phase 1 represents surface diffusion. The phase 2 indicates adsorption process between 2,4 DCP and AC3 and it is the rate-limiting step. On contrary, the phase 3 indicates where equilibrium had been achieved. The adsorption process was controlled by 3 steps, but only one step can predominates at any particular time phase.

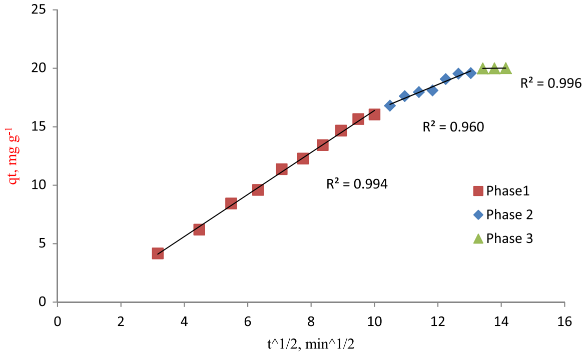


Fig. 6. Intraparticle diffusion kinetic plot for the adsorption of 2,4-DCP at 28 °C exhibiting multi linearity in the regions phase1, phase2 and phase3.

4. Conclusion

The AC was produced with semi – carbonization followed by chemical activation in a self – generated atmosphere. Overall, the maximum yield of activated guava seed was produced with 1:3 (w/w) ratio of sample: ZnCl$_2$. The prepared AC was slightly acidic with a pH value in between 5 and 6. The average moisture content of prepared AC was in the range of 1.5–3.5%, the moisture content of prepared AC showed a decreasing trend with higher impregnation ratio. The ash

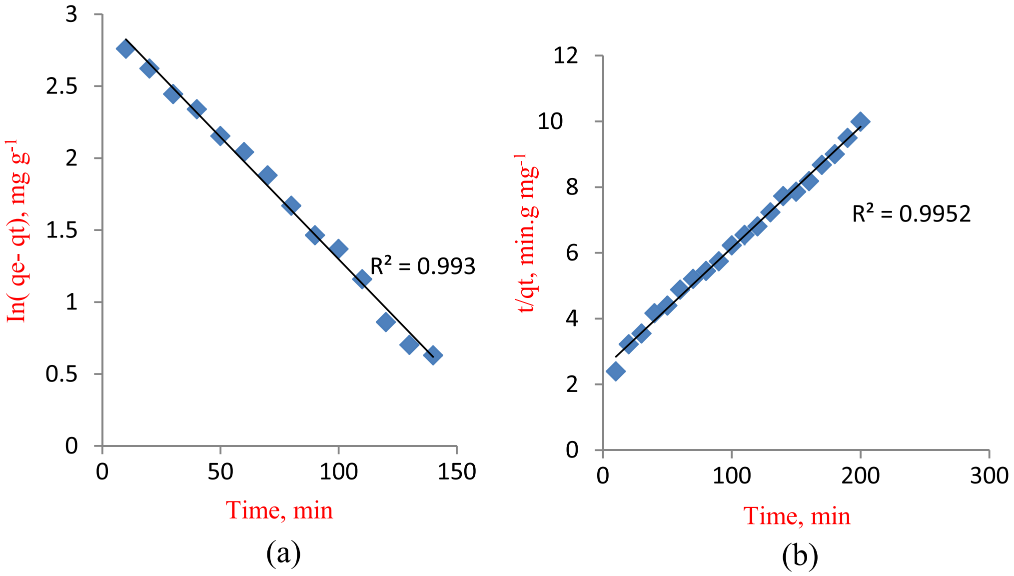


Fig. 5. (a) Langergren first-order rate plot and (b) pseudo second-order rate plot of 2,4-DCP adsorption by AC3.

content increased as the $ZnCl_2$ impregnation ratio increased. The 2,4-DCP adsorption kinetic of prepared AC3 was pseudo-second order with correlation value of 0.995. In addition, the 2,4-DCP adsorption of prepared AC3 fitted to the Langmuir model with correlation coefficient of 0.977, so chemisorption occurred between specific homogeneous site of AC3 and 2,4-DCP. From the FTIR spectra, the main functional groups present on the surface prepared AC3 include amine, carbonyl, symmetric and asymmetric alkyl group and chloride group. It was found that AC3 with 1:3 of impregnation ratio consists of micropores and mesopores widely distributed on the surface of prepared AC by the observation from the SEM image taken from all samples. From the results of batch adsorption of 2,4-DCP by AC3, 0.5 g of AC3 provided better removal efficiency of 5 ppm of 2,4-DCP solution at pH 3. The AC3, which is prepared from the guava seed found to be an efficient adsorbent for removal of 2,4-DCP from aqueous medium.

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