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Synthesis of Activated Carbons from Durian Peel and Their Adsorption Performance for Lead Ions in Aqueous Solutions

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Abstract

In this research, activated carbons were synthesized from durian peel based on the physical activation method using carbon dioxide as the activating agent. In the carbonization process, nitrogen atmospheric or vacuum pyrolysis was carried out and the properties of activated carbons synthesized from the pyrolysis process were compared. The synthesized activated carbons were used for the removal of lead (II) ions from water. The characterization of the synthesized activated carbons included the yield (determined by weighing), specific surface area, pore volume and average pore diameter (determined by nitrogen adsorption), iodine number (based on ASTM D4607-94), methylene blue adsorption capacity (based on JIS K1474-1991) and the surface functional groups (determined by Fourier Transform Infrared (FTIR) spectroscopy). The results showed that the durian peel-derived activated carbon synthesized under vacuum pyrolysis had better performance than that synthesized under nitrogen atmospheric pyrolysis for the removal of lead ions. Although the durian peel-derived activated carbon synthesized under vacuum pyrolysis had a greater specific surface area than a commercial activated carbon derived from coconut shells, its adsorption capacity for lead ions was lower. There are other factors apart from the specific surface area that can significantly affect the adsorption capacity.

Keywords: Activated carbon, Carbon dioxide activation, Durian peel, Lead adsorption, Vacuum pyrolysis

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Introduction

The growing industries have caused the increasing release of wastewater containing heavy metals which are harmful to human life and that create a major environmental problem. Lead is one of the toxic heavy metals obtained from the effluents of wastewater from battery manufacturing, steel and alloys manufacturing, electronic, plating, paint, pigment, pulp and paper industries. The accumulation of lead in the human body can destroy the nervous system, organs and tissues such as heart, bones, intestines and kidneys [1]. Chronic toxicity is reported to take place at blood levels of 40–60 μg/dL [2] and if not treated it can ultimately lead to a coma and even death [3]. Unlike most organic pollutants, heavy metals are usually refractory and are not easily degraded [4]. Therefore, it is necessary to find an efficient method to reduce lead ions from wastewater to acceptable levels before disposal into the environment.

There are several techniques to remove lead from aqueous solutions such as ion-exchange, chemical precipitation of Pb^{2+} as the hydroxide and sulphide, membrane filtration, ultrafiltration and reverse osmosis, and adsorption. These methods have some disadvantages such as high operational cost, low performance, difficult implementation and the production of a chemical residual as a byproduct that requires further treatment [3]. Among these, adsorption is considered as an inexpensive and high efficient method to remove trace amount of heavy metals [5-6]. Adsorption is also a simple, time-saving and feasible method which requires low consumption of energy. The fact that the adsorbent can be regenerated and reused has attracted a lot of attentions from researchers to develop efficient adsorbing materials from local agricultural wastes.

In the adsorption process, activated carbon is an interesting candidate since it can efficiently adsorb various substances from water and wastewater. Its adsorption capacity can be further modified by changing its surface chemistry and porous characteristics. However, commercial activated carbon is quite expensive. Therefore, the production of activated carbon from agricultural wastes is promising since these wastes can be acquired with no cost and they are environmentally friendly.

Durian peel is an agricultural and zero-cost waste that can be easily found in our country. It has been used as a raw material to produce activated carbon [7-9]. Chandra et al. [7] synthesized activated carbon from durian peel using KOH as an activating agent. The durian peel-derived activated carbon was studied in the adsorption of methylene blue from aqueous solution. Tham et al. [8] used H_3PO_4 as the activating agent for the production of activated carbon. The synthesized activated carbon was applied to the removal of toluene in the vapor phase. In our previous study, durian peel-based activated carbon was synthesized and used for the removal of a Basic Green 4 dye [9]. Kurniawan et al. [10] studied the capability of durian shell waste biomass for the removal of Cr(VI) from synthetic wastewater in batch mode at different temperatures and pH. In this research, the adsorption performance of durian peel-derived activated carbon for lead ions (Pb^{2+}) in aqueous solutions was carried out. The

activated carbons were produced based on the physical method using CO_2 as the activating agent. Prior to the activation process, durian peel was carbonized under either nitrogen atmospheric or vacuum pyrolysis in order to compare the properties of the synthesized activated carbons. The performance of the durian peel-derived activated carbons was also compared with a commercial activated carbon.

Experimental

Preparation of Activated Carbons

Activated carbons were synthesized according to the method described in the previous study [9]. The locally acquired durian peel was washed with water, cut into approximately 1 x 1 cm^2 and dried at 80 ^oC for 24 h. Carbonization of 100 g of dried durian peel was performed in a furnace (Model N7 Naber) under either nitrogen atmospheric (150 mL/min) or vacuum (56 kPa) pyrolysis. The set up equipment is shown in Scheme 1. The dried durian peel precursor was heated from room temperature to 900 ^oC with a heating rate of 5 ^oC/min. Activation with CO_2 (300 mL/min) was immediately performed and maintained for 1 h. Then, the product was cooled under a nitrogen flow, put into an aqueous solution of HCl (2 M) for 24 h to remove ash, washed with deionized water, dried at 110 ^oC for 3 h and grounded to a required particle size of less than 0.18 mm. In this study, activated carbons synthesized under nitrogen atmospheric and vacuum pyrolysis were denoted as ACN and ACV, respectively. The pictures of dried durian peel and the synthesized activated carbon are presented in Figure 1.

Scheme 1. *The Equipment Used for the Production of Activated Carbons*

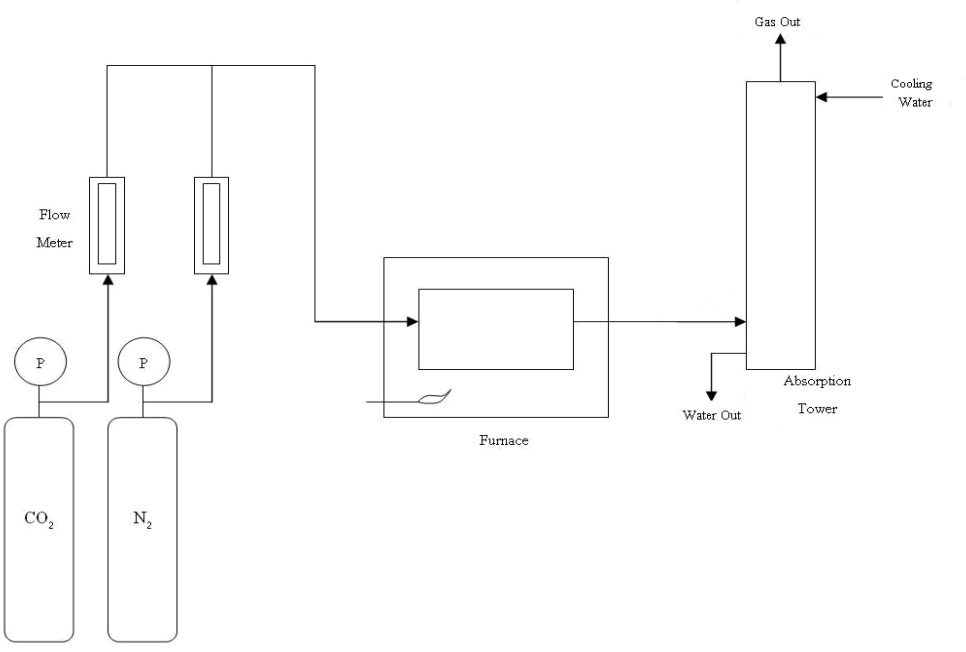
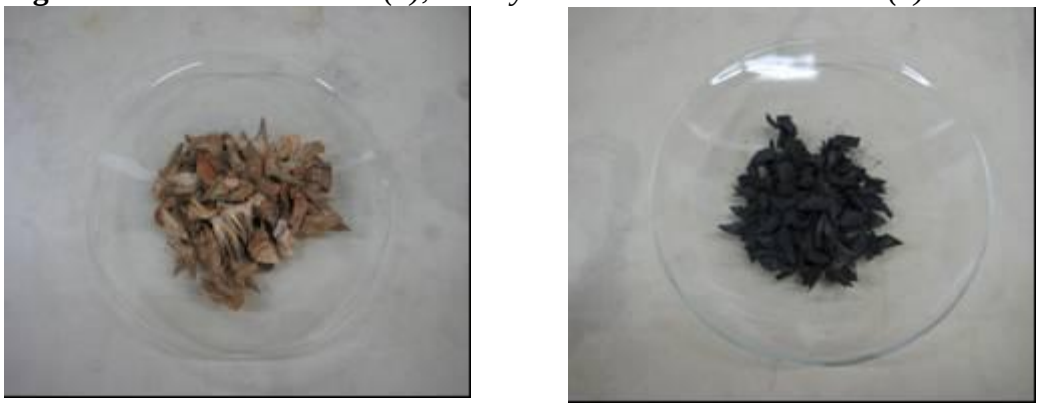


Figure 1. *Dried Durian Peel (a); The Synthesized Activated Carbon (b)*



(a) (b)

Characterization of Durian Peel and Durian Peel-derived Activated Carbons

The proximate and ultimate analysis of durian peels was performed with a thermogravimetric analyzer (TGA, ASTM D 5142-90) and a CHNO analyzer (ASTM D 5373-93), respectively. The synthesized activated carbons were characterized in terms of yield (determined by the weight of the synthesized activated carbon compared to that of the dried bamboo precursor), the BET specific surface area, pore volume and average pore diameter (determined by nitrogen adsorption at -196 ^{o}C with Autosorb I, Quantachrome Corporation), iodine numbers (determined based on ASTM D4607-94) and methylene blue adsorption capacities (determined based on JIS K1474-1991). The surface functional groups of the synthesized activated carbons were determined with Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer Spectrum 2000).

Adsorption Performance for Lead Ions in Aqueous Solutions

The adsorption capacities of ACN and ACV for lead ions (Pb^{2+}) were studied in a batch operation. The preparation of the aqueous solutions (25 mL) of lead ions were carried out using lead nitrate [$Pb(NO_3)_2$] as the source of Pb^{2+}. The concentration of Pb^{2+} was 10 mg/L. The aqueous solutions of Pb^{2+} were mixed with the required amounts of ACN or ACV (0.02-0.10 g). The mixtures were placed in a thermostatic shaker bath and stirred for the required contact time. The adsorption temperature used in this study was at 30 ^{o}C. After the required contact time of adsorption, the activated carbons were rapidly separated from the mixtures using the centrifugal method. The concentrations of lead ions in the clarified supernatant solutions were analysed based on the dithizone colorimetric method [11-12]. After forming lead-dithizone complexes, the colour solutions were measured photometrically with a double beam UV/vis spectrophotometer (UV500 model, UNICAM). The wavelength used in the measurement was 540 nm. The concentrations of Pb^{2+} were determined from a prepared linear calibration curve. The adsorption performance of the activated carbons was measured in terms of q_e (mg/g) and q_t (mg/g) which represented amounts of lead ions adsorbed onto activated

carbons per unit mass of activated carbons at equilibrium and any time *t*. The concentrations of lead ions in aqueous solutions at the equilibrium were assigned as C_e (mg/L).

Results and Discussion

Properties of Durian Peel and the Synthesized Activated Carbons

The properties of the dried durian peel used in the production of activated carbon are summarized in Table 1. The proximate analysis revealed that durian peel has high content of volatile matter. However, the fixed carbon content, which is an important property of raw materials that produce activated carbon, is similar to the coconut shell [13]. The coconut shell is extensively used as raw material to produce commercial activated carbons.

Table 1. *Properties of Durian Peel*

Properties	**Durian peel**	**Coconut shell [13]**
Proximate Analysis (%)		
Moisture content	4.54	9.35
Volatile matter	69.82	68.28
Ash	4.22	1.21
Fixed carbon	21.42[†]	21.16
Ultimate Analysis (%)		
Carbon	42.86	26.68
Hydrogen	5.71	16.26
Nitrogen	0.18	1.14
Oxygen, sulfur and others	51.25	55.92

Note: [†] by difference

The activated carbons synthesized from the durian peel under vacuum and nitrogen atmospheric pyrolysis had properties as shown in Table 2. The higher yield of ACN over ACV indicates the greater degree of reactions between CO_2 and the char obtained from vacuum pyrolysis. The higher degree of reaction lead to the greater BET specific surface area, the pore volume and average pore size of the activated carbon synthesized under vacuum pyrolysis was compared to that synthesized under nitrogen atmospheric pyrolysis. Volatilization takes place under vacuum pyrolysis more than under nitrogen atmospheric pyrolysis; as a result, the surface of the char obtained from vacuum pyrolysis has a smaller amount of deposits. When this char is brought to contact with CO_2 in the activation process, the reactions take place to a greater extent. Therefore, a greater BET surface area, pore volume and average pore size are obtained. The greater BET specific surface area and pore volume of ACV lead to higher adsorption capacities for iodine and methylene blue than ACN.

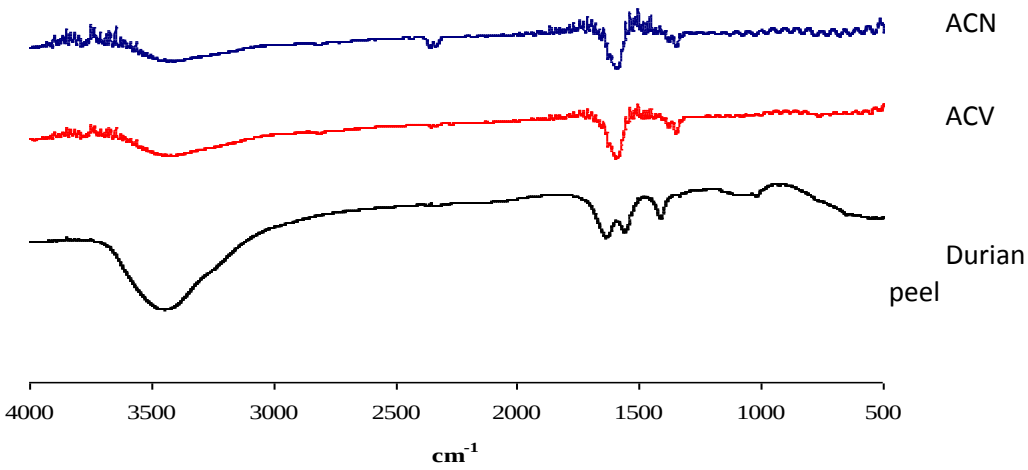
Table 2. *Properties of ACN, ACV and Commercial Activated Carbon (C. Gigantic Carbon)*

Properties	**ACN**	**ACV**	**C. Gigantic carbon**
Yield (wt%)	21.32	18.74	-
BET specific surface area (m^2/g)	748	1015	805
Pore volume (cm^3/g)	0.46	0.66	0.45
Average pore diameter (nm)	2.488	2.602	
Iodine number (mg/g)	580	739	861
Adsorption capacity for methylene blue (mg/g)	176	253	-

The properties of a commercial activated carbon (C. Gigantic carbon) which is a coconut shell-based activated carbon are also reported in Table 1. As can be seen from Table 1, our synthesized activated carbon under vacuum pyrolysis had a greater specific surface area and pore volume than the commercial activated carbon. This verifies that our conditions for the synthesis of activated carbon can be applied to a larger scale to produce activated carbon that is compatible to a commercial grade. However, our synthesis condition might produce activated carbon with larger pore size as the iodine numbers of ACN and ACV were lower than that of the C. Gigantic carbon. It is generally known that the iodine number represents the microporous structure of materials. The greater the iodine number, the greater the number of micropores.

The FTIR spectra of durian peel, ACN and ACV are presented in Figure 2. The spectrum of the durian peel displayed peaks at ~3450 cm^{-1} (-OH in alcohols, phenols and water), ~1640 and ~1560 cm^{-1} (C=O stretching), ~1420 cm^{-1} (C=C) and ~1020 cm^{-1} ($-OCH_3$). The surface chemistry of the durian peel was significantly changed when it was converted to the activated carbons. The OCH_3 groups were diminished. The C=C stretching vibrations and C=O stretching and C–OH bending vibrations became more important for both ACN and ACV. The O–H stretching vibrations in alcohols, phenols and chemisorbed water generated the broad peaks at ~3400 cm^{-1} of ACN and ACV. However, the peak intensities of the hydroxyl groups of ACN and ACV were lower than the peak intensity of the durian peel. The hydroxyl groups can have cation exchange capacity for lead ions [14].

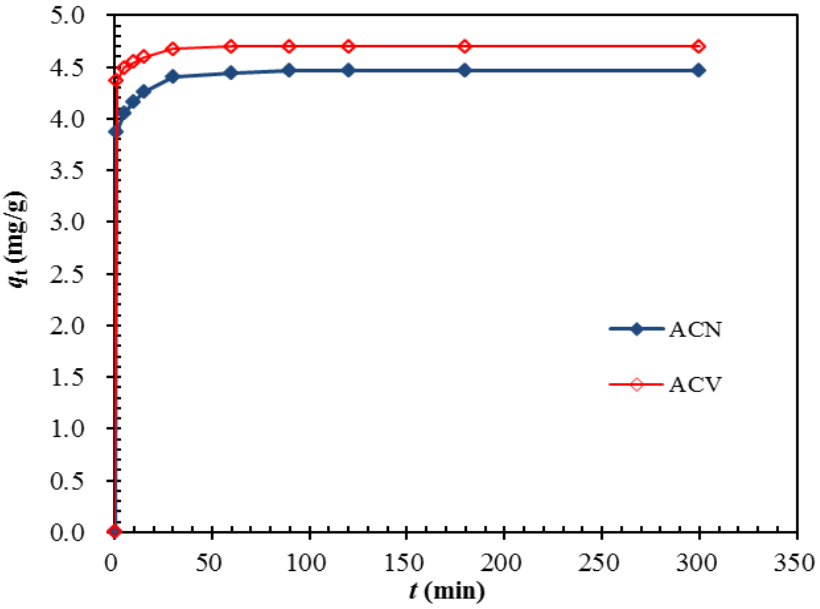
Figure 2. *FTIR Spectra of Durian Peel, ACN and ACV*



Lead Adsorption of the Synthesized Activated Carbons

The adsorption capacities of ACN and ACV for lead ions (Pb^{2+}) when the amounts of the activated carbons were 0.05 g are shown in Figure 3.

Figure 3. *Lead Adsorption Capacities of ACN and ACV*



Lead ions rapidly adsorbed the activated carbons during the first one minute. This is likely due to a great number of sites available for the sorption operation at the beginning. The adsorption process then occurred slowly and the adsorption equilibrium was achieved at 120 min of contact time. This clearly shows that activated carbon synthesized from vacuum pyrolysis had higher adsorption capacities for lead ions than that synthesized from nitrogen

atmospheric pyrolysis. This is because the former has a greater specific surface area than the latter. As previously shown in Table 2, ACV had a higher BET surface area than ACN.

When the amounts of activated carbons were varied between 0.02-0.10 g, the equilibrium adsorption capacities of ACN and ACV at 5 h of contact time are summarized in Table 3. The greater the amount of activated carbon is, the lower the equilibrium adsorption capacity for the lead ions is. The activated carbon synthesized from vacuum pyrolysis had a greater adsorption capacity than that synthesized from nitrogen atmospheric pyrolysis because the former had a greater specific surface area as shown in Table 2. However, ACV had a lower equilibrium adsorption capacity than the commercial activated carbon at the same amounts of the activated carbons. Although ACV had a greater specific surface area than C, the adsorption capacity of the gigantic carbon (see Table 2) was lower. This implies that there are other factors apart from specific surface areas that affect the lead adsorption capacity. These factors include the presence of micropores and the surface functional group. As shown in Table 2, the iodine adsorption of C. Gigantic carbon was higher than ACV. This indicates the presence of more micropores in the structure of C. Gigantic carbon. The iodine number is reported to be related to the surface area available for micropores: adsorbents with high iodine numbers typically have a high surface area and are suitable for adsorbing small compounds [15]. It is very likely that a microporous structure is preferential for the adsorption of lead ions which are a small compound. Another factor that can explain the result is the surface functional group. The adsorption of lead ions might come from the chemical forces between the positive charges of lead ions and the negative charges of the surface of the activated carbon rather than the physical forces, i.e. van der Waals force. Functional groups and chemical compositions are reported to be important factors affecting the adsorption mechanism and capacity [16].

Table 3. *Equilibrium Concentration of Lead Ions (C_e) and Equilibrium Adsorption Capacity (q_e)*

Amount of activated carbon (g)	**ACN**		**ACV**		**C. Gigantic carbon**	
	C_e (mg/L)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)
0.02	4.33	7.08	3.66	7.92	2.79	9.01
0.04	1.70	5.18	1.39	5.38	0.83	5.73
0.05	1.07	4.47	0.60	4.70	0.51	4.74
0.06	0.78	3.84	0.39	4.00	0.30	4.04
0.08	0.45	2.98	0.21	3.06	0.05	3.11
0.10	0.11	2.47	0.03	2.49	0.01	2.50

Conclusions

Activated carbon synthesized under vacuum pyrolysis had a better adsorption performance for lead ions in aqueous solutions than that synthesized under nitrogen atmospheric pyrolysis due to its greater specific surface area and total pore volume. Moreover, the activated carbon synthesized under vacuum pyrolysis had a greater specific surface area than a commercial activated carbon derived from coconut shell. However, the lead adsorption capacity of durian peel-derived activated carbon was lower than the commercial activated carbon, suggesting some factors such as microporous structure and surface functional group play an important role on the adsorption mechanism and capacity for lead ions.

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