Synthesis and Characterization of Natural, Pectin and Activated Carbon as Low Cost Potential Adsorbents from Kepok Banana Peels (Musa paradisiaca L.)

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Abstract. The objective of this research was to synthesize of natural, pectin, and activated carbon from Kepok banana peels (Musa paradisiaca L). The use of raw banana peels as precursor for synthesis of adsorbent have significant advantages. Kepok banana peels were modified into three types of compounds with different physical and physicochemical treatments. Type 1 is natural, which is made by only thermal and physical treatment. Type 2 is pectin which was made by esterification reaction. Type 3 is activated carbon which was made by chemical activation using NaOH reagent for activation and carbonized at 400 °C. The yields of type 1, type 2 and type 3 are 11, 52 and 26%, respectively. FTIR characterization showed that type 1 and type 2 have the hydroxyl and carboxyl groups, while in type 3 has only carboxyl groups. Chemical treatment of dehydrated banana peels with acid (HCl) and alkali (NaOH) agents modified the surface morphological and fundamental physical properties of pectin and activated carbon. Types 1 – 3 are low cost potential adsorbent and these functional groups play major roles in adsorption.

1. Introduction

Adsorbents from biomaterials have recently attracted attention for wastewater treatments. Biosorbents which have been utilized for the separation of lanthanides are mainly marine algae [1], novel hybrid adsorbent [2], novel chelating polysaccharide [3], spirulina biomass [4]. The biosorbents from the peels and shells of the fruits are of interest due to their low cost, abundancy, and utilization of wastes [1-5]. As an important example of fruit peels as an adsorbent is banana peels, which have been utilized to remove Ni, Zn, Cu, Pb, Co metal ions [6-8], Mn²⁺ [9], Sr²⁺ [10], Cr⁶⁺ [11], cationic dye [12], and palm oil mill effluent [13].

Banana peels are easily and cheaply found from the market. On the other hand, this waste can be generated and can be used for many treatments in wastewater. Considering such the potential of banana peels as adsorbents for metal separation, we focus on Kepok banana (Musa paradisiaca L.) as starting material for preparation of low cost potential adsorbents. With the vast production of banana, as it is
one of the main fruit commodities all over the world [9-11], the banana peels is abundant. Kepok banana is the main ingredient of banana-based commodities in food industry in Indonesia, and the banana peels can potentially become environmental problem. In Indonesia the banana production in 2016 was about seven million tons.

The aim of this study is to synthesize of natural, pectin, and activated carbon from Kepok banana peels (Musa paradisiaca L.) with thermal, physical and physicochemical methods. Banana peels containing carboxylic acid, phosphate and hydroxyl groups [9]. These functional groups acted as the active site for the adsorption of metal ions from aqueous medium [9-11]. Thus, utilization of biosorbent from the banana peels could overcome the environmental problem. This biosorbent can be produced in massive industrial scale. It is also noteworthy that banana peels generally consists of organic carbons, such as pectin (10 - 21%), lignin (6–12 %), cellulose (7.6–9.6 %) and hemicellulose (6.4–9.4 %) in w/w dry basis [14].

2. Experimental
2.1. Preparation of natural, pectin and activated carbon

Mature Kepok banana with yellow peels were collected as solid agricultural waste from Pondok Cina, Depok (Indonesia). They were cut into small pieces (1 - 2 cm) and washed once with tap water followed by distilled water to remove dust and particulates. To obtain the dehydrated banana peels, wetted banana peels (642.5 g) were dried in an oven at 110°C for 24 h. After that, the dehydrated banana peels was grinded with pulverize mill – blender and homogenized to 60 mesh with sieve shaker. For convenience, the dehydrated banana peels is abbreviated as natural (Type 1). The average yield of type 1 that made with four times drying was obtained of 11%.

For pectin obtained from the dehydrated banana peels (type 1) was prepared according to the method that reported by Mohammed & Chong [13]. Generally, 9 grams of type 1 was contacted with 633 mL of methanol (99.9%) and 5.4 ml HCl (37%). The solution was stirred for 16 h at 60°C. Then, it was washed using distilled water (20°C) until it reached the pH of 7. The solid material was separated and dried in oven at 110°C for 8 h. The esterified pectin was extracted from dehydrated banana peels in three times. The average yield of the pectin was obtained of 52%. The esterified pectin based type 1 is abbreviated type 2 hereafter.

The dehydrated banana peels (type 1) was carbonized at 400°C for 1 h in furnace. The char was cooled at room temperature. Then, it was activated with the alkaline (NaOH) 45% solution for 16 h at the room temperature. The solution was filtered and dried in oven at 110°C for 24 h. The char was heated in furnace at 500°C for 1 h. The solid materials were then washed and filtered using cold distilled water until pH reach neutral. The wetted materials were dried at 110°C for 8 h. The yield of activated carbon was obtained of 26%, with the initial weight of type 1 is 19.91 g to 5.22 g of activated carbon. The activated carbon based type 1 is abbreviated type 3.

2.2. Characterization

All three types of natural, pectin and activated carbon (Type 1–3) were characterized using FTIR and SEM-EDX. All samples were further identified by Fourier-transform infrared (FTIR; Bruker). FTIR was used to identify the chemical bonding and/or the functional groups of the samples. The surface morphology was determined by scanning electron microscopy and energy dispersive x-ray (SEMEDX) analysis.

3. Results and discussion
3.1. Preparation of natural, pectin and activated carbon
3.1.1. Type 1

Schematic representation for preparing of types 1–3 is shown in Figure 1. Table 1 shows the conversion from wet banana peels to be dehydrated banana peels (type 1) with average yields of 11%. In this study, mature Kepok banana peels were dried in oven at 110°C for 24 h until it reached a constant weight (see
Figure 2). The time is shorter than time need for drying banana peels (48 h) to produce natural that reported by Mohammed & Chong [13].

Dried banana peels is grounded with pulverize mill and blender, then it was sieved to obtain the mesh size 60 and screened by sieve shaker with size of 250 µm. Blender is used to smooth again pulverize mill results that have not reached the size of 60 mesh. The advantage of using pulverize mill is that it can bear the weight of banana peels and takes a short time (± 1 minute). While the blender only accommodates a little and takes a long time (± 15 minutes). The dehydrated banana peels is crushed to a mesh size 60 aiming to obtain a larger surface area. Natural material included as granular forms (Fig. 3A). For granular materials have a mesh size ≥ 80 µm, it can be used for both liquid and gas applications [12]. The purpose of smoothing is to get a larger surface area.

3.1.2. Type 2
Type 2 would be hydrolysed in aqueous solutions, thus it resulted to carboxyl (COO⁻) groups. The esterified pectin was washed using distilled water at 20°C to neutralize the acid. This neutralization is aimed to facilitate for further application, such as as adsorbent for lanthanide adsorption performance by pH initial solution variation. The distilled water (20°C) was used to minimize the loss of carboxylic acid of pectin because the solubility of carboxylic acids in 20°C water is small. In addition, we used distillate water (20°C) for washing is to stop the esterification reaction [10]. The pH of pectin refers to distilled water pH is 5.5. In this study, pectin was dried at 110°C in oven to remove water content. Fig. 3B shows the solid of pectin from Kepok banana peels.

Figure 1. Schematic process for preparation of natural, pectin and activated carbon from Kepok banana peels (Musa paradisiaca L.)

Table 1. Conversion from Kepok banana peels as natural material

| Number | Initial weight (g) | Dried weight (g) | Yield (%) |
|--------|--------------------|------------------|-----------|
| 0.5    | 1750               | 218.0            | 12        |
| 1      | 3500               | 380.73           | 11        |
| 2      | 7000               | 803.19           | 11        |
| 3      | 10500              | 1144.23          | 11        |
3.1.3. Type 3
Natural material was activated chemically and thermally to obtain the activated carbon. Natural as starting material was burned in a furnace with minimum oxygen at 400°C for 1 hour, as pyrolytic temperature for precursor decomposition. Burning temperature setting was considered successfully if no ash was formed or minimized. This process is called carbonization [15]. Reaction of carbonization which is given as

\[
2\text{C}_6\text{H}_{10}\text{O}_5 (s) + \text{O}_2 (g) \rightarrow 10\text{C} (s) + 2\text{CO} (g) + 10\text{H}_2\text{O} (g)
\]

Furthermore, the char was chemically activated by NaOH impregnation. This chemical activation is appropriate to degrade materials containing cellulose. Activation reaction using NaOH which is given as

\[
6 \text{NaOH} + 2 \text{C} \leftrightarrow 2 \text{Na} + 3 \text{H}_2 + 2 \text{Na}_2 \text{CO}_3
\]

After NaOH impregnation, the char was heated at temperature of 500°C to purify the char from oxygen and hydrogen. This purification includes activation with heat treatment. Activation of carbon thermally is char treatment placed in oxidizing atmosphere in the presence of gases such as water vapour, air, and carbon dioxide or its combination in the temperature range 500–1000°C [15]. The presence of water vapour and carbon monoxide will react further into carbon dioxide. This allows carbon to be further activated by CO or \(\text{H}_2\text{O}\) gases. All the reactions of thermally activation is shown in below.

\[
\text{C} (s) + \text{H}_2\text{O} (g) \rightarrow \text{CO} (g) + \text{H}_2 (g)
\]
\[
\text{C} (s) + 2\text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2 (g)
\]
\[
\text{C}(s) + \text{CO}_2 (g) \rightarrow 2 \text{CO} (g)
\]

The results from this process produced the activated carbon. Activation of NaOH and heat produce more porous structure for activated carbon [15], which contributes to enlarge the surface area of activated carbon. Activated carbon was washed with 0.1 M HCl to remove the ash. Then, it was neutralized with distilled water pH of 5.5. After being washed, activated carbon was dried in the oven to reduce water content. Fig. 3C shows the activated carbon from Kepok banana peels.
Figure 3. Type 1 natural (A), Type 2 pectin (B) and Type 3 activated carbon (C) from left to right sides

3.2. SEM-EDX Characterization

SEM characterization is used to find out the surface morphology and fundamental physical properties of materials, while EDX characterization is used to determine the element composition on materials. The content of elements obtained from the characterization of EDX is a qualitative result because the data acquisition is based on the shooting of a single data. However, this result can be used as a reference to represent the surface and existing morphology.

Figure 4(A-C) showed adsorbents Types 1–3, namely natural, pectin and activated carbon that origin from banana peels. Natural material has morphology surface of steep roads with small hills – cliff, irregular and surface exhibits a micro rough texture (see Fig. 4A). SEM image of type 1 is similar observed with the banana peel powder that reported by Mahindrakar & Rathod [10]. Pectin compound has a morphological surface of a cloud that congregates or winding road surrounded such circles (see Fig. 4B). The activated carbon has a hollow and pore morphology structure (see Fig. 4C). The activated carbon from Kepok banana peels activated by NaOH seems broken, lost its original structure of natural, and changed to be pore and more sponge. The NaOH is a strong alkaline reagent, thus it be able to interact with carbon atoms, so it support and catalyse the dehydrogenation and oxidation processes, thus increasing the pore size and porosity of activated carbon. Morphology of activated carbon in this study is different with activated carbon banana peels that produced by Mohammed & Chong [13]. This is due to the lower temperatures for carbonized and activated as well as the alkaline reagent used.

Figure 4. SEM images of natural (A), pectin (B) and activated carbon (C)

The EDX composition is shown in Table 2. In pectin compound, the oxygen percentage of mass increased, this indicated that the formation of COO⁻ was successfully performed. In the activated carbon, the carbon content increased, indicating the activation process of natural material was successful. Both sodium and chlorine were observed in activated carbon. These elements were detected as residual from NaOH activation and HCl washing.
Table 2. EDX composition of natural, pectin and activated carbon

| Element | Type 1 (%w) | Type 2 (%w) | Type 3 (%w) |
|---------|-------------|-------------|-------------|
| C       | 74.02       | 70.92       | 90.84       |
| O       | 20.79       | 22.92       | 5.59        |
| Na      | -           | -           | 1.05        |
| Cl      | -           | -           | 0.82        |

3.3. FTIR studies
To identify the functional groups on the surface of types 1 – 3, FTIR analysis was carried out. The FTIR spectra depicted in Figure 5. The identified functional groups (CO, COO⁻, CH₂ and OH) were observed in types 1 and 2. The presence of OH and CO groups confirmed the existence of acidic oxygen containing functional groups that as active center for heavy metal adsorption. It can be seen that carboxyl (C=O) group at around 1100 cm⁻¹ indicated the vibrations in carboxylic acid or ester. The broader and stronger peaks at 3300 cm⁻¹ were assigned to hydroxyl groups have been detected for types 1 and 2. In type 3, the band assigned to hydroxyl group does not found because the carbonization process [16]. The CH₂ group at around 3000 cm⁻¹ indicate the possibility of the presence of methyl as a branch. In activated carbon (type 3), the CH₂ and OH groups are not observed. This is due to thermally carbon activation released the oxygen and hydrogen in gas form. The reaction can be seen in the subset of preparation of activated carbon. The identified carboxyl group is a source of carboxylic compounds, not carbon monoxide. The identified COO groups showed that banana peels have not been converted to carbon completely. The surface of materials containing functional groups such as hydroxyl and carboxyl play significant roles for adsorption [17].

Figure 5. FTIR spectra of natural (A), pectin (B) and activated carbon (C) from Kepok banana peels

4. Conclusion
In this paper, we discussed the synthesis and characterization of natural, pectin and activated carbon from Kepok banana peels (*Musa paradisiaca L.*). The use of banana peels waste as precursor for synthesis of bioadsorbent have significant advantages. Type 1 (natural) was prepared by thermal and physical methods, while for the type 2 (pectin) and type 3 (activated carbon) were synthesised by chemical treatments. Chemical treatment of dehydrated banana peels with acid (HCl) and alkali (NaOH) agents modified the surface morphological and fundamental physical properties of pectin and activated...
carbon. The alkaline reagent (NaOH) raised its pore size and porosity in type 3. The type 3 is a low cost potential adsorbent for future biosorbent applications in aqueous medium.

5. References
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