Characterization of bio char derived from tapioca skin

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Abstract. Pyrolysis of tapioca skin was conducted to produce bio chars in the range between 500°C–800°C. Surface modification treatment were performed on bio chars by using chemicals within 24 hours at 30°C and hot water within 1 hour to enhance the bio char’s adsorption properties according to surface area, pore volume, pore size, crystallinity structure and functional groups. The samples were characterized by using BET, XRD, FTIR and Methylene Blue adsorption. Based on BET result, it showed the surface area increased as the pyrolysis temperature increased followed by pore volume and pore size for S0. The optimum temperature for SNaOH, SHW and SMethanol was at 600°C, 700°C and 800°C with the surface area of 75.9874, 274.5066 and 351.5531 m²/g respectively compared to S0 while SP3HO4 has the worst result since it felt on macroporous structure. The percentage of MB adsorption was followed the size of bio chars surface area. Based on FTIR result, at temperature 500°C to 700°C, the bio chars still have functional groups while at 800°C, many functional groups were diminished due to high temperature struck on them. XRD result showed all the bio chars were amorphous. In conclusion, the best surface modification treatment was by Methanol followed by hot water and Sodium Hydroxide at temperature of 700°C and 800°C while Ortho-Phosphoric acid was the worst one and was not suitable for bio char’s surface modification for adsorption purpose.

1. Introduction
In the era of globalization now, world-wide carbon dioxide CO₂ emissions from energy uses are increasing, and estimated at 2020, the world will produce 33.8 billion metric tons of CO₂ [1]. Regarding this issue, it can be seen the world strive for high and infinite development from developed countries which uses fossil fuel to generate energy for their development. Therefore, this action causes the CO₂ gas release to surrounding become increase from year to year. The increases of CO₂ emission have contributed to the research in alternative energy, which is from biomass [2]. Biomass energy is abundant, cheap and clean since it trapped solar energy through photosynthesis process to produce sugar and oxygen.

The agriculture waste also known as biomass, which can be converting into value-added products. Waste of agricultural product such as apricot kernel shell, hornbeam sawdust, rice straw, rice bran and rice husk has been widely used in research in order to produce bio char. According to [3], organic biomass which undergoes pyrolysis process has high carbon content is called bio char. As stated by [4], bio char also known as activated carbon. Bio char was widely used as a tool for waste management, sequestration and mitigation of climate change, treatment of waste water, building...
sector, cosmetics industries, metallurgy, food industry, energy production, and last but not least as a support for catalyst development. This can be show bio char has various purposes in human life.

On the other hand, a developed country has improper solid and agricultural waste management including in Malaysia. Since many Small and Medium Industries (SMI) present [5], many agriculture wastes such as tapioca skins were produced which contribute to the increasing of waste and affect the usage area of disposal site.

Other than that, water pollution was one of the problems faced by many countries and need more attention to treated in a safe way with lowest cost. Therefore, tapioca skin can be converting into bio chars due to its ability in treating wastewater. The properties of bio-char depend on types of biomass used and the production condition like temperature, pressure and moisture content. The method of producing bio char by using pyrolysis may remove the carbon dioxide from the air, increase the crops growth and keep the carbon on the soil from returning to the atmosphere.

In a view by [7], bio char is the most effective and widely used method for removal of organic compound such as chlorine, pesticides, volatile compounds, certain metal and many more since it has high content of activated carbon. In wastewater treatment scope, bio char can help in treating water by adsorption process that is by carbon filtering. This can proved that active bio-char filters are most effective in removing of odour, sediments, volatile organic compounds (VOCs), chlorine and taste. According to [8] due to the presence of anions like hydroxyl and carboxyl groups, bio-char acts as cation exchanger. In addition to that, classical graphite structure of carbon in bio-char enables the carbon to connect with neighbouring atoms or atoms from foreign molecules, which increases adsorption capacity. This has been proven by [6], potato peel waste has the ability in removing cobalt ions from synthetic wastewaters (composed of various Co(II) concentrations in distilled water which adjusted previously at different pH values) without any co-existing ions.

Bio char can be used as a material to treat wastewater due to its large surface area and high porosity if it produced by pyrolysis at certain condition. Large surface area of bio-char helps in increasing water holding capacity by combining the impurities with its active sites, cation exchange capacity (CEC) and microbial activity. Therefore, tapioca skin waste produced from SMI can be converted into bio chars in treating wastewater besides can decrease the emission of CO₂ in the air. Many other studies have done to produce bio char for treatment of wastewater. However, the search for process to produce bio-char with better yield for absorption properties still face a major challenge in this field.

The main objectives of this study is to prepare bio char from tapioca skin by using pyrolysis at difference temperature (500°C, 600°C, 700°C and 800°C) and to enhance bio char properties for adsorption purpose by using surface modification treatment that is hot water treatment and chemical treatment that is alkali, acid and solvent.

2. Methodology

2.1. Sample Preparation

Dried tapioca skins were cut into small pieces and were compressed into 4 different crucibles to be pyrolyzed in Carbolite Furnace at 500°C, 600°C, 700°C and 800°C within 30 minutes respectively. The samples were collected and were kept in sealed plastic after it was cooled to room temperature.

2.2. Surface modification Treatment

Three samples of 1.0 g of bio chars at temperature 500°C were weighted and were put into 100 ml solution of NaOH.H₂O, H₃PO₄ and Methanol respectively. All the three samples were stirred within 24 h at 30°C. Next, the samples were filtered and were dried at 80°C for 24 h. The steps were repeated for bio chars at 600°C, 700°C and 800°C. Similarly, for hot water treatment, 1.0 g of bio char was weighted and was put into 100 ml of hot water at temperature 90°C for 30 minutes. Next, the sample was filtered and dried in oven at 80°C for 24 h. All the samples were kept in desiccator for further used. S0 was stand for untreated bio chars while SMeOH, SNaOH, SHW and SH₃PO₄ were stand for
biochars treated with Methanol, Sodium Hydroxide, hot water and Ortho-Phosphoric acid respectively. All the methods were adopted from [9].

2.3. Characterization

The samples were characterized by using BET, Methylene blue adsorption, XRD and FTIR. BET characterization was performed at 250°C digest temperature within 30 minutes. Based on MB adsorption, 5 different concentrations of MB at 2, 4, 6, 8 and 10 ppm were prepared to create calibration curve. Then, 0.2 g of biochar samples were put into 20 ml of 10 ppm MB solution and were left for 1 h for absorption process. Lastly, the filtrates were filtered before analyzed by using UV-Vis at 645 nm. Other than that, for XRD characterization process, the initial and end angle used was 100 and 700 respectively with 10°/min speed. The Voltage used was 20 Watt and the amplitude was 20 mA.

3. Result And Discussion

3.1. BET Result Regarding Surface Area, Pore Volume and Pore Size

Based on Figure 1, surface area of biochar samples was increase as the pyrolysis temperature increased. This can be shown surface area for S0 at 500°C, 600°C, 700°C and 800°C was 1.7007, 6.0385, 134.4512 and 206.3966 m²/g respectively. The highest S0 surface area was at 800°C. Other than that, for SMeOH, the surface area at 500°C to 800°C was 3.2426, 10.3776, 237.2951 and 351.5531 m²/g respectively, compared to S0. SMeOH at 800°C has the highest surface area that was 351.5531 m²/g. This can be concluded Methanol solvent has the ability in widen the pores wall from micro-pores to meso-pores. According to [10], the presence of Methanol or other alcohols contributed to mesoporous materials with fibrous, high surface area, large pore volume and open web-like structures. In a view [11], the presence of hydrophilic and the strongly polarity compound with the polarity index of 6.6 of sugar in Methanol solvent has proved its ability to increase the pore size and surface area. Based on Graph 1, SMeOH showed the largest surface area compared to others biochars.

Similarly, surface area of SHW at 500°C, 600°C, 700°C and 800°C was 2.4024, 2.9233, 274.0566 and 188.2421 m²/g respectively. It showed at 700°C, the surface area produced was the highest compared to S0 at 700°C. This can be shown hot water increased the surface area from temperature of 500°C to 700°C compared to S0, while at 800°C, the surface area decreased from 206.3966 to 188.2421 m²/g. This proven that hot water has the ability to remove any minerals deposited on the pore’s wall. In accordance to [12], biochars were heterogeneous materials contain high carbon and minerals. Related to the statement, [12] proved hot water vapor penetrated biochar layers during water quenching process. This seen that hot water has an activating effect and expulse minerals out from biochars in his analysis. In conclusion, hot water has the ability in increasing the surface area, pore volume and pore size of biochars pyrolyzed at 500°C to 700°C. Briefly, the optimum temperature for SHW was at 700°C since it has the highest surface area compared to biochars at 800°C.

Other than that, for SNaOH, the surface area at 500°C, 700°C and 800°C was decreased a little compared to the original ones except at temperature 600°C. This clearly seen in Graph 1, the surface area was 2.3235, 75.9874, 88.3366 and 121.7390 m²/g respectively. From the observation and comparison between the SNaOH against S0, it can be concluded NaOH was not suitable to modify biochars compared to the Methanol. In conclusion, the optimum SNaOH was at temperature 600°C compared to the original biochars.

Lastly, surface areas of SH3PO4 were 1.5183, 1.9945, 7.1621 and 1.2931 m²/g for temperature of 500°C to 800°C respectively. Ortho-phosphoric acids were used in treating biochars since it was a triprotic acid. Triprotic acid was an acid that has highest proton and readily to donate it to reagents, with the three protons. Based on the surface treatment, compared to the S0, SH3PO4 has the lowest surface area and the worst result. The acid was too strong until diminish the surface wall. Hence, it indicated SH3PO4 at temperature 500°C-800°C best as solid fuel as the porosity produced was not in the range for adsorption purposes.
In conclusion, the higher the pyrolysis temperature, the higher the surface area of the bio chars. Besides that, it’s can be concluded SMeOH has the highest surface area followed by SHW, S0, SNaOH and SH3PO4.

![Figure 1. Bio chars versus Surface Area.](image1)

Referring to Figure 2, the pore volume also increased according to the pyrolysis temperature that was 0.000572, 0.002743, 0.043207 and 0.062053 cm³/g respectively for S0 at temperature 500°C to 800°C. Other than that, pore volume for SMeOH also increased according to the pyrolysis temperature that was 0.001135, 0.003444, 0.071476 and 0.175246 cm³/g at 500°C to 800°C respectively. Next, the pore volume for SHW also increased according to the pyrolysis temperature that was 0.000566, 0.000890, 0.082317 cm³/g for temperature of 500°C to 700°C compared to the S0 but decrease at 800°C with 0.055122 cm³/g. This is due to bio char has reached its resistance temperature at 700°C.

Meanwhile, for the pore volume of SNaOH, the result also showed decreasing in value that was 0.000618, 0.024615, 0.027207 and 0.033994 cm³/g respectively. Last but not least, for SH3PO4, no reading showed since BET only cover the micro-porous and meso-porous structure only. In conclusion based on pore volume size, this can be concluded pore volume was related to the surface area.

![Figure 2. Bio chars versus Micropore Volume.](image2)

Based on table 1, pore size of S0 at temperature 500°C to 800°C decreased. At temperature of 500°C and 600°C the pore size was 105.1759 and 35.8640 Å respectively which fell on mesoporous line while for temperature of 700°C and 800°C lied in microporous category with the pore size of 18.4649 and 18.6010 Å respectively. Other than that, for SMeOH, at 500°C, 600°C and 700°C the pore was in mesopores category which has pore size of 104.6779, 31.6062 and 20.2156 Å. Meanwhile
at temperature of 800°C lied in micropores type with the pore size of 19.9396 Å. Hence, the small pore diameters showed that narrow and deep pores of bio char was formed.

Other than that, pore type for SHW at temperature of 500°C to 600°C were in mesopores category with the pore size of 118.4134 and 76.7675 Å. Meanwhile, at temperature of 700°C and 800°C, SHW were in micropores category with the pore size of 18.7016 and 19.7218 Å. In addition to that, SNaOH, lied on mesopores category that was 150.4447, 24.6137, 23.2339 and 22.4776 Å for temperature of 500 to 800°C. Based on observation and comparison between SNaOH against the S0, it can be concluded NaOH was not really suitable in modifying bio chars compared to Methanol and hot water.

Lastly, pore size for SP3HO4 were lied on macropores line. This can be concluded, SP3HO4 was not suitable to be used in adsorption purposes in treating waste water but can be used as fuel solid that was charcoal.

| Sample | Pore Size (4V/A by BET) (Å) |
|--------|-----------------------------|
| S0: 500 | 105.1759                    |
| 600    | 35.8640                     |
| 700    | 18.4649                     |
| 800    | 18.6010                     |
| SMeOH: 500 | 104.6779                 |
| 600    | 31.6062                     |
| 700    | 20.1258                     |
| 800    | 19.9396                     |
| SHW: 500 | 118.4134                   |
| 600    | 76.7665                     |
| 700    | 18.7016                     |
| 800    | 19.1278                     |
| SNaOH: 500 | 150.4447                 |
| 600    | 24.6137                     |
| 700    | 23.2339                     |
| 800    | 22.4776                     |
| SP3HO4: 500 | 28.7092                   |
| 600    | 12.7470                     |
| 700    | 2.7643                      |
| 800    | 18.6344                     |

3.2. Methylene Blue Analysis

Based on figure 3, the percentage of MB adsorption for S0 was 87.43, 87.48, 95.97 and 99.45% for temperature 500°C to 800°C respectively. Other than that, for SMeOH, the percentage of MB adsorption was 86.86%, 91.66%, 98.27% and 99.50%. Compared to S0, SMeOH has the higher absorption at
temperature from 600°C to 800°C and the maximum absorption was at temperature 800°C with 99.50%. Therefore, based on the percentage of the MB absorption by $S_{\text{MeOH}}$, this data related and was supported the surface area data obtained from BET result.

The percentage of MB absorption by $S_{\text{HW}}$ was 87.71%, 91.82%, 95.11% and 95.59%. Other studies indicated bio chars treated with hot water possess higher adsorption capacities. However, opposite results were observed in this experiment. At temperature of 500°C to 800°C the percentage of MB absorption showed a little decrement compared to the $S_0$ even though the surface area of the treated one was larger. This can be concluded $S_{\text{HW}}$ followed the rule in which the highest surface area that can be yield by $S_{\text{HW}}$ was 700°C, since it was the maximum temperature resistance.

Other than that, for percentage of MB absorption by $S_{\text{NaOH}}$, the value was 84.14%, 92.26%, 94.93% and 97.53%. The percentage of the MB absorption was tele with the surface area as shown in Figure 1 that was 2.3235, 75.9874, 88.3366 and 121.3790 m²/g at temperature of 500°C to 800°C. In addition to that, the percentage of MB absorption by $S_{\text{P3HPO4}}$ was 57.11%, 50.79%, 58.42% and 64.12%. The percentage of the MB absorption was also tele with the surface area as shown in Figure 1 that was 1.5183, 1.9945, 7.1621 and 1.2931 m²/g.

In conclusion, the bio chars surface area gave a very important impact on the percentage of MB absorption. The result showed every temperature gave different surface area for adsorption purposes. The larger the surface area of bio chars yield the larger percentage of MB absorption. From the analyzed data in Figure 3, the best bio char performance in MB absorption was $S_{\text{MeOH}}$ followed by $S_{\text{NaOH}}$ and $S_{\text{HW}}$. This can be concluded the optimum temperature for $S_{\text{NaOH}}$ was at temperature 600°C, while for $S_{\text{HW}}$ and $S_{\text{MeOH}}$ was at temperature 700°C and 800°C. The worse bio char in MB absorption was bio char treated by Ortho-Phosphoric acid since it produced smallest surface area resulted too strong acid which destroyed the samples wall. Therefore, the optimum temperature of bio chars in MB absorption was 700°C and 800°C.

![Figure 3](image)

**Figure 3.** Chart of Bio-Chars at Different Temperature Versus Percentage of MB Absorption.

### 3.3. XRD analysis

Based on the results at Figure 4, it showed all bio chars has the amorphous structure since at 500°C, all the crystalline structures were diminished due to high temperature penetrate on bio chars surface.
3.4. FTIR analysis

FTIR was conducted to determine the functional group presented on bio chars surface.

Based on Figure 5, the band at 3348 cm\(^{-1}\) represented the stretching vibrations of the OH groups, which could be attributed to the adsorbed water on the bio char. It showed the intensity and shaped was strong. Other than that, the band at 1569.92 cm\(^{-1}\) represented the stretching variations C=C aromatic. The double bonds appeared as medium to strong absorptions. Based on the C=C bond, it indicated the presence of adjacent carbon in the bio chars. At band 1043.58 cm\(^{-1}\), it represented the stretching variations of the C-OH. It showed strong intensity of hydroxyl group.
Regarding Figure 6, the band at 1391.76 cm\(^{-1}\) represented the stretching vibrations of NO\(_2\) (aliphatic). It belonged to nitro group. It showed the intensity was strong. Other than that, at band 873.39 cm\(^{-1}\) represented C-H bend (meta) aromatics.

![Figure 6 Bio Chars at 700°C.](image)

Based on figure 7, the band at 1420.22 cm\(^{-1}\) represented the vibrations of C-H in-plane bend. At band 1028.72 cm\(^{-1}\) represented C-O stretch. This can be concluded alcohol presented on the bio char after treated with Methanol. At band 877.72 cm\(^{-1}\) represented the vibrations of C-H bend (para). This can be concluded many aromatics present in the bio chars.

![Figure 8 bio chars at 800°C.](image)

Referring to figure 8, the band at 879.12 cm\(^{-1}\) represented the vibrations of C-H bend (para). It showed it belonged to aromatic group. At band 647.09 cm\(^{-1}\) and 618.94 cm\(^{-1}\) represented acetylenic C-H bend. This showed alkynes group present in the bio chars. At the end of the data, it showed the graph was interrupted due to high temperature during pyrolysis until diminish all the functional groups.

4. Conclusion
Optimum temperature for S\(_0\) was at 800°C, while for S\(_{MeOH}\), S\(_{HW}\) and S\(_{NaOH}\) was at 800°C, 700 and 600°C respectively. The best surface modification treatment for adsorption purpose was by Methanol solvent, followed by hot water and Sodium Hydroxide. The largest surface area and pore volume size was achieved by S\(_{MeOH}\) and S\(_0\) at 800°C that was 351.5531 m\(^2\)/g and 206.3966 m\(^2\)/g respectively. Meanwhile, surface area for S\(_{HW}\) at 700°C and S\(_{NaOH}\) at 600°C was 274.5066 m\(^2\)/g and 75.9874 m\(^2\)/g compared to S\(_0\). The sample’s pore volume also related to the surface area and majority of samples were in microporous and mesoporous line which indicated the bio chars suitable for adsorption purposes.
Based on MB adsorption, percentage of MB adsorption by $S_{\text{MeOH}}$ was the highest followed by $S_0$, $S_{\text{NaOH}}$ and $S_{\text{HW}}$ at 800°C that was 99.50, 99.45, 97.53 and 95.59 %.

Lastly, $S_{\text{P3HO4}}$ has the smallest surface area and pore volume compared to $S_0$. The pore size also decreased and lied on macroporous line. Therefore, Ortho-Phosphoric acid was not suitable in modifying bio chars, since it was too strong until break the micropores and mesopores wall. Hence, it indicated the modified bio chars with Ortho-Phosphoric acid at temperature 500°C-800°C best as solid fuel as the porosity produced was not in the range for adsorption purposes.

XRD result showed bio chars have amorphous structure since all the crystallinity has been diminished due to high temperature started at 500°C. FTIR result showed some functional group presents on bio chars surface at 500°C to 700°C. However, it became diminished at temperature 800°C due too strong temperature resistance. In a nutshell, all the bio chars have the ability in adsorption purposes except for $S_{\text{P3HO4}}$.

Acknowledgment
Thank you to Fakulti Kejiriteraan Kimia, Universiti Teknologi MARA to facilitate the facility in accomplishment of these research activity

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