Surface modification of rubber seed shell activated carbon with malic acid for high CO\textsubscript{2} adsorption

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Abstract. Carbon dioxide (CO\textsubscript{2}) has been stated as one of major contributor to climate change and affects marine ecosystems. Among other CO\textsubscript{2} capturing technology, adsorption is widely used due to its numerous advantages. Rubber seed shell (RSS), an agriculture waste from rubber plantation was used as precursor for preparing activated carbon (AC) by chemical activation using Malic acid as activating agent for CO\textsubscript{2} adsorption. In this research, the AC was characterized and analysed by SEM, Micrometric ASAP 2020, TGA and FTIR instruments. The optimum condition was found at activation temperature of 600 °C, sample A. Results from specific surface and porosity analyzer shows the AC total pore volume, specific surface area and diameter were 0.2635 cm\textsuperscript{3}/g, 480.5692 m\textsuperscript{2}/g and 2.1937 nm, respectively. The CO\textsubscript{2} adsorption studies showed the CO\textsubscript{2} uptake for the AC was 2.26 mmol/g which is better most agricultural wastes' and commercial AC. It was found that malic acid helps to prolong the thermal stability of AC. The presence of a new FTIR peak in samples indicated N-H stretching and C=N stretching might due to remaining malic acid on the surface which increased the CO\textsubscript{2} affinity and was an attractive source for CO\textsubscript{2} adsorption applications.

1. Introduction

Higher accumulation of CO\textsubscript{2} content in the atmosphere from the burning of fossil fuels is the main reason of the climate change [1]. Additionally, noticeably acidifying surface waters and affecting marine ecosystems once the atmospheric CO\textsubscript{2} is diffusing into ocean. The concentration of CO\textsubscript{2} in the atmosphere has rises from 280 ppm to almost 400 ppm nowadays [2]. Dockrill [3] reported that the atmospheric CO\textsubscript{2} has exceeded 415 ppm for the first time in human history.

Several methods of CO\textsubscript{2} capturing and storage, such as adsorption [4], membrane separation [5], cryogenic separation [6] and amine scrubbing [7] had been proposed to reduce the emission of CO\textsubscript{2}. Among all the methods, CO\textsubscript{2} adsorption with AC is more encouraging due to its low energy required, maintenance and cost effective [2,4,8,9]. Besides that, AC has large surface area per unit volume and submicroscopic pores, in which adsorption occurs [2,4,8,9]. AC is also reported to is stable under acidic and basic conditions [10].

Considering in term of cost reduction in AC production, researchers have developed different precursors from agricultural waste, such as rubber seed shell, palm shells, sea mango, rice husks, peanut hulls, oat hulls, coconut shell etc. [11]. The shell of rubber seed from rubber tree (Hevea
*brasiliensis*), was used in this project as raw precursor to produce AC for CO$_2$ removal since rubber industry is one of the main incomes for Malaysia. Although it has vast areas of application including food sources, animal feedstock and alternative fuel resources for diesel engine, the disposal of large amount of RSS could lead to serious local environmental problems as emphasized by Kang [12].

Chemical activation to produce AC has shown great performance in CO$_2$ uptake, besides it is more controlled and proven to influence in the formation of the surface area of the AC [13]. The general solvent used for impregnation such as amine type, ionic liquid and KOH to assist in CO$_2$ capturing but such chemicals are difficult to prepare because they are highly toxic and expensive [14,15]. Thus, organic acid is introduced as an activating agent for chemical activation process in this study. Malic acid which is extracted from fruits is chosen as it has lower pKa value, low environment impact and relatively cheap as compared with other organic acids such as acetic acid, citric acid etc. The study on impregnation process using this organic acid is yet to be reported. Therefore, this study has been focusing on the preparing of the rubber seed shell activated carbon (RSSAC) by using green activating reagent, which is malic acid in the chemical activation method.

2. Materials and Methods

2.1. Equipment and Materials

The equipment used were porcelain mortar and pestle, grinder, siever, oven, tube furnace, glassware, pH meter, glass veil and desiccator. The raw material, RSS was obtained from a local rubber plantation in Perak was used as a precursor for this research. The RSS was cleaned to remove dirt and organic matter, dried, crushed, sieved to 500 µm and dried in oven at 110 °C overnight. The RSS was then kept in container for further step.

2.2. Preparation of Activated Carbon

About 10 g of RSS was impregnated in 100 mL of 10 g malic acid solution for 24 h. The impregnation was carried out for full day to let the malic acid fully adsorbed into the raw material. The RSS was carbonized in the tube furnace unit under a flow of nitrogen gas for 90 minutes. The tube furnace temperature was set to 600 °C, 700 °C and 800 °C with holding time of 1.5 h. The produced AC was cooled to room temperature before it washed with distilled water to remove impurities. Then the AC was dried in an oven at 80 °C overnight. All the produced AC was kept in air tight container and stored in desiccator for further use.

2.3. Characterization

SEM: All samples were observed by Zeiss EVO-50 Scanning Electron Microscope (SEM) at magnification of 10-100000 times. The Zeiss EVO-50 SEM was used to observe the structural of the RSS. In SEM, secondary electrons and backscattered electrons are produced by electron-sample interaction when the incident electrons are decelerated in the solid sample. Secondary electrons showing morphology and topography on samples and backscattered electrons for illustrating contrasts in composition. Samples were degassed, and the adhesive surface was pressed into the sample, placed into the SEM, and imaged.

Specific surface and porosity analyzer: The specific surface and porosity of the RSS after carbonized was analyzed by nitrogen adsorption-desorption isotherms. The Micrometric ASAP 2020 equipment was used and the adsorption of N$_2$ was performed at 77 K. Before that, all the sample was degassed under N$_2$ flow at 350 °C for 2 hours in vacuum at 27 Pa [12]. Then, the specific area was observer by BET method using adsorption isotherm data [12]. The micropore volume was calculated by subtracting the amount adsorbed at relative pressure of 0.1 from relative pressure of 0.95 [16]. The pore size distribution was calculated by using Barret-Joyner-Halenda (BJS) (Rouquerol et al.,1999).
FTIR: Fourier-transform infrared spectroscopy (FTIR) is an equipment used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. In this research, FTIR was used to determine structure of bond and present of C-H bond of the RSS before and after carbonization.

TGA: The pyrolysis behavior of the RSSAC was observed by using Thermo-gravimetric analyzer, TGA (Netzsch STA 409). The experiment was carried out at temperature range of 30-900 °C at heating rate of 10 °C min⁻¹ under flowing of nitrogen gas flow and held at 900 °C for 10 minutes [12].

2.4. Adsorption Studies

HPVA II analyzer was used to determine the AC capability for CO₂ adsorption at temperature of 25 °C and 100 °C. The HPVA II adsorption analyzer uses the static volumetric method to obtain high-pressure adsorption and desorption isotherm utilizing gases such as hydrogen, methane, and CO₂. Its pressure ranged from ultra-high vacuum to 200 bars. The volumetric technique consisted of dosing a known amount of gas (adsorptive) into the chamber containing the sample to be analyzed. When the sample reached equilibrium with the adsorbate gas, the final equilibrium pressure was recorded. These data were then used to calculate the quantity of gas adsorbed by the sample. This process was repeated at given pressure intervals until the maximum preselected pressure is reached.

3. Results and Discussions

3.1. Surface Analysis and Yield

Table 1 shows the preparation conditions and results of RSS AC of raw, sample A, B and C at different activation temperature. The results showed that sample A which was prepared at activation temperature of 600 °C and activation time of 90 minutes yield the highest values of total pore volume, \( V_T \) (0.263561 cm³ g⁻¹), \( S_{BET} \) (480.5692 m²g⁻¹), pore diameter, \( D \) (2.19374 nm) and yield (22.25%).

| Sample | Act. Time (h) | Act. Temp. (°C) | Specific surface area, \( S_{BET} \) (m²g⁻¹) | Total pore volume, \( V_T \) (cm³ g⁻¹) | Average pore diameter, \( D \) (nm) | Weight before carbonized (g) | Weight after carbonized (g) | Yield (%) |
|--------|--------------|----------------|---------------------------------------------|-------------------------------------|-----------------------------------|-------------------------------|--------------------------|-----------|
| raw    | -            | -              | 18.6776                                     | 0.0021                              | 0.3889                            | -                            | -                        | -         |
| A      | 1.5          | 600            | 480.5692                                    | 0.2635                              | 2.1937                            | 4.00                         | 0.89                     | 22.25     |
| B      | 1.5          | 700            | 169.0529                                    | 0.0923                              | 2.1844                            | 3.50                         | 0.75                     | 21.43     |
| C      | 1.5          | 800            | 121.0292                                    | 0.0364                              | 2.1134                            | 3.30                         | 0.62                     | 18.79     |

According to Azry et al., [16], activation temperature at 500 °C and above enhances the removal of molecular weight volatile compound and creates new pores on AC materials. This arrange of activation temperature is optimum for developing high porosity of AC. From the results obtained, the surface area increased at the beginning of carbonization and stopped at 600 °C whereby it was a turning point, then decreased as the activation temperature was increased to 800 °C. If the activation temperature is too high, the excessive heat energy will knock and break the porous wall of the AC [16], resulting in low \( S_{BET} \). Kang et al., [12] also stated that increase in activation temperature will affect the pore size distribution inside the AC.
The results showed that the yield decreased as the temperature increased. This was due to the combustion of the RSS in the tube furnace during the carbonization process [18], stated that the weight of the RSS shows a progressive decrease as the temperature increases is due to combustion of the residual and volatile matter in the shells.

3.2. Ultimate Analysis of Activated Carbon

Table 2 shows the ultimate analysis between the raw RSS and Sample A. The ultimate analysis shows the component found at the surface of RSS between before and after activation and carbonization process.

Table 2. Ultimate analysis of raw RSS and sample C

| Sample  | C   | O   | Al | Si  | Ca  | K  |
|---------|-----|-----|----|-----|-----|----|
| Raw RSS | 59.4| 38.7| 0.3| 0.4 | 0.4 | 0.3|
| Sample A| 73.8| 24.4| 0.8| 0.6 | 0.2 | 0.2|

Raw RSS sample showed high percentage of carbon content presence followed by the oxygen with percentage of 59.4% and 38.7%, respectively. Other component had a low percentage from 0.3% to 0.4%. Sample A showed similar component presence with the raw RSS, but the sample A has higher percentage of carbon which was 73.8% compared to raw RSS. While, the percentage of oxygen in sample A was lower than the RSS, 24.4%. Other component still had low percentage from 0.2% to 0.6%. The percentage of carbon content was increased from 59.4% to 73.8% due to the activation and carbonization process. In addition, the percentage of carbon was increased after activation and carbonization process was due to the released of volatile matter that content in the RSS [17].

3.3. FTIR Result

Figure 1 shows the FTIR results for raw RSS, sample A, B and C. As shown in the figure, similar organic functional group presence detected in all samples including the C-H, C=C and C-O bond. These show that the organic functional group was still present in the RSSAC although after been carbonized. Furthermore, with the increasing of activation temperature from 600 °C to 800 °C, the organic functional group was still present during the carbonization processes. The additional bond (C=N stretching and N-H bending) presence in the sample A, B and C shows there were some new bond attached to the surface of RSS AC. Additionally, Chiang [19] and Pevida [20] reported that nitrogen enrichment effectively helped in introducing basic functionalities that enhanced the specific adsorbent-adsorbate interaction for CO₂, hence increased affinity towards CO₂. There was also remaining malic acid whereby could enhance the CO₂ affinity. Furthermore, the difference organic functional group presence before and after carbonization is due to some reorganization of the surface oxides on subjection to activation at the high temperature occurred, [21].
3.4. Surface Morphology

The morphological structure of the raw RSS and the three selected AC prepared at different temperature are shown in Figure 2 (a - d). As can be seen in the micrograph of raw RSS, there are very few presences of pores at the structure of raw material but displays the passage construction in RSS sample, which is a good texture for preparing AC. As the activation temperature was increased to 600 °C, there were a lot of well-developed pores presences at the structure of RSS AC. Many new large pores were clearly observed on the surface of the AC. Figure 2 (c) and (d) show the effect of implying excessive heat during carbonization, which was at 700 °C and 800 °C for 90 minutes, resulting in the knocking and breaking of the porous formation in the sample. Sample A in Figure 2(b) shows the most well-developed porous structure among the three AC. This justified that sample A has the highest $S_{BET}$, $V_T$ and D compared to other samples.

Figure 2. Surface morphology for (a) Raw rubber-seed shell, (b) Sample A, (c) Sample B, (d) Sample C
3.5. TGA Analysis

The TGA profile clearly gives an approximation about the weight loss with respect to temperature due to the release of surface bounded water, volatile matter, hemicellulose, cellulose and lignin present in the precursors. It also gives an insight of the carbonization temperature range required for production of AC. Figure 3 shows the weight loss in thermograms of the thermal decomposition of the 4 samples. From the TGA of raw RSS, the initial step shows weight loss of about 12% in the temperature range of 110 °C to 300 °C, which might have resulted from the release of moisture content and surface bounded water. The second step shows steep weight loss of about 65% at the temperature range from 280 °C to 380 °C. The weight loss may be associated mainly to the decomposition of hemicellulose and other low molecular weight compounds to condensable (i.e. methanol, wood tar, acetic acid) and non-condensable gas (i.e. H₂O, CO, CH₄, CO₂, H₂) [22]. The third step involved a gradual loss in weight at temperature above 380 °C, which may be attributed to decomposition of cellulose and continued up to 900 °C due to the decomposition of lignin with weight loss of about 23%.

![Figure 3. Comparison TGA graph of sample Raw, sample A, sample B and sample C](image_url)

The TGA for samples A to C showed final weights loss of less than 50% compared than the raw RSS. Due to this, it can be said that raw RSS was the least thermally stable compared than the one activated with malic acid. All samples showed that thermal degradation that took place after 470 °C, and the samples had distinct decomposition regions. Sample C had only one decomposition region or curve where starting to decompose temperature was at about 480 °C. This indicated that samples consist of less volatile components and impurities and less be removed from the biomass during pyrolysis. However, the weight % of samples A and B dropped drastically after 470 °C. On the other hand, samples A and B have three distinct decomposition regions due to presence of more volatile components, impurities and moisture. It can be concluded that, sample C (480 °C) had the highest thermal stability compared to B (475 °C), A (474 °C) and raw RSS (236 °C), respectively. These shows, the malic acid have prolonged the temperature of the rubber seed shell from 374 °C to 470 °C.
and above. Rashidi [4] emphasizes that, the higher impregnation ratio (IR), the lower the weight percentage loss.

3.6. Carbon dioxide Adsorption Studies

Figure 4 shows the CO₂ adsorption capacity for sample A at 25 °C and 100 °C. As can be seen in the figure, both lines show similar trend of adsorption isotherm which is Type I isotherm. According to Azry et al., [16], the Type I isotherm is a good precursor for preparing excellent and effective AC. The CO₂ quantity adsorbed was increased as the pressure increased. The maximum CO₂ adsorption capacity for sample A was 46.45 cm³/g at temperature of 25 °C and pressure of 1.2523 bar and was 16.28 cm³/g at 100 °C and pressure of 1.2525 bar, respectively. AC adsorption capacity was decreased as the temperature increased. This is due to the reaction of the CO₂ at different temperature. According to Azry et al., [16], the adsorption of CO₂ is ideal at lower temperature due to the exothermic process. Due to the heat released from the exothermic process, AC adsorption capacity is decreases. Furthermore, the adsorption CO₂ is more significant at lower temperature due to the physical adsorption process in the AC.

![Figure 4. Adsorption capacity of CO₂ at 25 °C and 100 °C for sample A](image)

Table 3 shows the comparison of CO₂ uptake (mmol/g) on various types of AC from agricultural ranging from rapeseed, chestnut tannin, sewage sludge and commercial AC [23,24].

| Sample               | CO₂ Uptake, mmol/g | Precursor                      |
|----------------------|--------------------|--------------------------------|
| This research        | 2.26               | Rubber Seed Shell              |
| David and Kopac [23] | 1.55               | Rapeseed                       |
| González et al. [22] | 2.27               | Chestnut tannin                |
| Rashidi et al. [2]   | 1.88               | Norit® SX2 (peat) (commercial AC) |
| Andres et al. [24]   | 1.27               | Sewage Sludge                 |
From this comparative study, it shows that the RSS AC of sample A has a higher adsorption capacity compared to Norit SX2 commercial AC, sewage sludge and rapeseed. Only chestnut tannin AC fared slightly better at 2.27 mmol/g, followed by RSS AC sample A at 2.26 mmol/g, Norit SX2 commercial AC at 1.88 mmol/g, rapeseed at 1.55 mmol/g and lastly sewage sludge AC at 1.27 mmol/g. This proven the RSSAC with malic acid as activating agent is capable to be used for CO₂ removal.

4. Conclusions

In conclusion, this study showed the potential of RSS and malic acid as a precursor and activating agent for CO₂ capturing. The resulting AC yield a high surface area, pore volume and average diameter at activation temperature of 600 °C and activation time of 90 minutes. New peaks discovered during FTIR analysis helped to improve the thermal stability of the precursor when activated with malic acid. The AC with a high surface area was also verified to have higher CO₂ adsorption capacity using static volumetric instrument. Moreover, the adsorption capacity test proved that adsorption using RSS based AC has high prospective in reducing CO₂ and at par with some already existed conventional biomass AC.

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References

1. National Research Council. 2015. Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration. Washington, DC: The National Academies Press. https://doi.org/10.17226/18805.
2. Rashidi, N. A., Yusup, S., & Borhan, A. (2016). Isotherm and Thermodynamic Analysis of Carbon Dioxide on Activated Carbon. *Procedia Engineering*, 148, 630-637. doi:10.1016/j.proeng.2016.06.527
3. Dockrill, P. (2019, May 13). It's Official: Atmospheric CO2 Just Exceeded 415 ppm For The First Time in Human History. Retrieved from sciencealert: https://www.sciencealert.com/it-s-official-atmospheric-co2-just-exceeded-415-ppm-for-first-time-in-human-history
4. Rashidi, N. A., Yusup, S., Borhan, A., & Loong, L. H. (2014). Experimental and modelling studies of carbon dioxide adsorption by porous biomass derived activated carbon. *Clean Technologies and Environmental Policy*, 16(7), 1353-1361. doi:10.1007/s10098-014-0788-6
5. Liu, S., Liu, G., Wei, W., Xiangli, F., & Jin, W. (2013). Ceramic Supported PDMS and PEGDA Composite Membranes for CO₂ Separation. *Chinese Journal of Chemical Engineering*, 21(4), 348-356. Retrieved 6 21, 2019, from https://sciedirect.com/science/article/abs/pii/S1004954113604784
6. Annaland, S., Tuinier, M. J., & Gallucci, F. (2015). Cryogenic CO₂ capture. Retrieved 6 21, 2019, from https://onlinelibrary.wiley.com/doi/10.1002/9781118449394.ch2.
7. Rochelle, G. (2016). 3 – Conventional amine scrubbing for CO₂ capture. Retrieved 6 21, 2019, from https://sciedirect.com/science/article/pii/b978008100514900032
8. Keith, D. W., Holmes, G., St. Angelo, D., & Heidel, K. (2018). A Process for Capturing CO₂ from the Atmosphere. *Joule*, 2(8), 1573-1594. doi:https://doi.org/10.1016/j.joule.2018.05.006
9. Thanchanok Pagketanang, P. W., Mallika Thabuot (August 2015). Characteristics of Activated Carbon Produced from Rubber Seed Shell by Using Different Methods of Chemical Activation with KOH. *Applied Mechanics and Materials*, 781, 659-662. doi:10.4028/www.scientific.net/AMM.781.659
10. Zulkurnai, N. Z., Md. Ali, U. F., Ibrahim, N., & Abdul Manan, N. S. (2017). Carbon Dioxide (CO₂) Adsorption by Activated Carbon Functionalized with Deep Eutectic Solvent (DES). *IOP
11. Ioannidou, O., & Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production—A review. Renewable and Sustainable Energy Reviews, 11(9), 1966-2005. doi:10.1016/j.rser.2006.03.013
12. Sun, K., & Jiang, J. (2010). Preparation and characterization of activated carbon from rubber-seed shell by physical activation with steam. Biomass and Bioenergy, 34(4), 539–544. https://doi.org/10.1016/j.biombioe.2009.12.020
13. Pagketanang, T., Artmaseaw, A., Wongwicha, P., & Thabuot, M. (2015). Microporous activated carbon from KOH-activation of rubber seed-shells for application in capacitor electrode. Energy Procedia, 79, 651-656.
14. García, G., Aparicio, S., Ullah, R., & Atilhan, M. (2015). Deep Eutectic Solvents: Physicochemical Properties and Gas Separation Applications. Energy & Fuels, 29(4), 2616-2644. doi:10.1021/ef5028873
15. Yu, C.-H., Huang, C.-H., & Tan, C.-S. (2012). A Review of CO2 Capture by Absorption and Adsorption. Aerosol and Air Quality Research, 12(5), 745-769. doi:10.4209/aaqr.2012.05.0132
16. Borhan, A., Thangamuthu, S., Taha, M. F., & Ramdan, A. N. (2015). Development of activated carbon derived from banana peel for CO2 removal. AIP Conference Proceedings, 1674(August 2015). https://doi.org/10.1063/1.4928819
17. Anis, D., Ishak, M. A. M., Zaidi, A. G., Khudzir, I., Iqbaldin, M. N., Osman, U. M., & Nawawi, W. I. (2014). Production of Rubber Seed Pericarp Based Activated Carbon Using Microwave-Induced Different Chemical Activating Agent.
18. Ekebafe, L. O. (2017). Effect of carbonization on the processing characteristics of rubber seed shell. Arabian Journal of Chemistry, 10, S174–S178. https://doi.org/10.1016/j.arabjc.2012.07.018
19. Chiang, Y. C., Hsu, W. L., Lin, S.-Y., & Juang, R.-S. (2017). Enhancement of CO2 adsorption on activated carbon fibers grafted with nitrogen-doped carbon nanotubes (Vol. 10).
20. Pevida, C., Drage, T. C., & Snape, C. E. (2008). Silica-templated melamine–formaldehyde resin derived adsorbents for CO2 capture. Carbon, 46(11), 1464-1474. doi:https://doi.org/10.1016/j.carbon.2008.06.026
21. Onn, M., Mohamad, N. F., Hidayu, N., Rani, A., Zulkifly, Z. A., & Shamsuddin, F. (2017). Green carbonized rubber seed shell filler, 3, 361–368.
22. M. Shoaib and S. M. Al-Swaidan,"Oprimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation," Biomass and bioenergy 73, pp. 124-134,
23. David, E & Kopac, Janez. (2014). Activated carbons derived from residual biomass pyrolysis and their CO2 adsorption capacity. Journal of Analytical and Applied Pyrolysis. 110. 10.1016/j.jaap.2014.09.021.
24. de Andrés, Orjales L, Narros A, and E Rodriguez. (2013). Carbon dioxide adsorption in chemically activated carbon from sewage sludge. J Air Waste Manag Assoc.;63(5):557-64.