Adsorption of carbon dioxide (CO$_2$) by activated carbon derived from waste coffee grounds

H K Lim$^{1}$, U F Md Ali$^{1,2}$, R Ahmad$^{3}$ and M K Aroua$^{4}$

$^1$Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
$^2$Centre of Excellence Biomass Utilization (CoEBU), University Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
$^3$Faculty of Civil Engineering Technology, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
$^4$Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Science and Technology, Sunway University, Selangor, Malaysia

E-mail: umifazara@unimap.edu.my

Abstract. Currently, three are several agricultural bio-based materials have been successfully utilized as gas adsorbents. In this study, waste coffee grounds (WCGs) have been selected as a potential precursor of Carbon Dioxide (CO$_2$) adsorbents. The preparation parameters for activated carbon derived from WCGs were optimized using Response Surface Methodology (RSM). The optimized preparation parameters were found to be 1:3.67 impregnation ratio of acid, 533°C of carbonization temperature and 1.13 hours of activation time, which resulted in 23.6 wt% of yield. The physical and chemical characteristics of WCGAC in terms of surface morphology, carbon content, ash content and yield were also investigated. The CO$_2$ breakthrough time using WCGAC were carried out at the temperatures of 30, 40, and 60°C. It was found that WCGAC shows a longer CO$_2$ breakthrough times (5 mins) and a higher adsorption capacity (4.33 mg CO$_2$/g adsorbent) at 30°C.

1. Introduction
Generally, over the past century there has been a dramatic increase in global warming. This is due to the fact that emissions of greenhouse gases (GHG) e.g. CO$_2$ into the atmosphere keep on increasing and has resulted the greenhouse effect. CO$_2$ constitutes more than 60% of greenhouse gases that contribute to global warming [1].

There are several kinds of technologies which have been applied for CO$_2$ capture such as membrane separation, cryogenic separation, chemical separation and adsorption method [2]. Among these technologies for CO$_2$ capture, adsorption has been determined as superior technology due to its simplicity of design, low capital and operating cost, low energy requirement and less secondary wastes generated. In the present study, WCGs will be used as the precursory material. Since it is abundantly available in Malaysia and commonly discarded by cafes, hotels and restaurants as organic waste, therefore the cost of AC preparation can be significantly reduced. The exhausted coffee residues, or called waste coffee grounds (WCG), are inevitably generated from soluble coffee production during the extraction process. WCG is characterized by high organic content, in the form of insoluble polysaccharides and minerals.
In this study, Box–Behnken design (BBD) which is one of the Response Surface Methodology (RSM) methods with an independent quadratic design has been adopted to define the output parameters or so-called responses that are decided by the input process parameters. RSM is a well-known set of advanced design of experiments (DOE) techniques. In this design, the treatment combinations are locate at the midpoints of edges of the process space and locate at the center [3].

2. Methodology

In order to obtain a high yield percentage of AC, Box–Behnken Design (BBD) of RSM was applied to optimize the preparation parameters for WCGAC in terms of impregnation ratio, carbonization temperature and activation time. The impregnation ratio of precursor-to-activant was set as 1:1, 1:2.5 and 1:4, the carbonization temperature range from 400-550°C, and the activation time was 1-2 hr. The modified waste coffee grounds activated carbon is designated as optimized WCGAC. Following this, the WCGAC were characterized in terms of iodine number, carbon content, surface morphology, ash content and yield percentage. On completion of WCGAC preparation, it was utilized for CO₂ adsorption experiment. The performance assessment was conducted in terms of breakthrough time and adsorption capacity.

2.1. Waste coffee grounds activated carbon preparation

The raw waste coffee grounds (WCG) was turned into waste coffee grounds activated carbon (WCGAC) using physicochemical activation process.

2.1.1. Materials and methods. WCGs were sponsored by McDonalds in Kangar, Perlis. In the process of activating the carbon, H₃PO₄ was used as the chemical activating agent while CO₂ as the physical activating gases.

2.1.2. Pre-treatment of the waste coffee grounds. The WCGs was first washed with distilled water to remove the impurities present on the surface before it undergoes further treatment. The coffee wastes were then dried inside the oven for 24 hours at 105°C to remove the moisture content so that the growth of fungal, which will affect the efficiency of the AC produced. After drying, the dried WCGs were sieved and stored in a cool and dry container.

2.1.3. Carbonization process. Tube furnace was used to perform the carbonization and activation process for the production of AC. 10g of the dried coffee waste was measured using the electronic balance and placed in the ceramic tubing. The sample was positioned in the centre of the constant temperature zone of the ceramic tubing in the horizontal tube furnace. The ceramic tubing is flowed with continuous nitrogen (N₂) gas with a constant flow rate of 2 L/min for 1 hour in order to remove the oxygen content inside the tubing. After 1 hour, the sample was heated to the desired temperature, which is 750°C. The sample was allowed to cool to 100°C after the completion of heating process before it is removed from the furnace. The sample was then undergoing impregnation process.

2.1.4. Physicochemical activation process. Char was subsequently impregnated with different precursor-to-activant ratio of H₃PO₄ (1:1, 1:2 and 1:4) for 1 hr, and then dehydrated in the oven at 105 °C until dryness. The char was weighed and placed in the tube furnace with carbon dioxide (CO₂) for activation. The furnace was heated until the desired temperature of 400, 475 and 550°C was reached. Activation process was conducted for 1, 1.5 and 2 hr. The samples are left to cool to room temperature (25°C) and washed with hot distilled water few times in order to remove excess H₃PO₄. The AC was then filtered and dried in the oven. Consequently, the yield percentage of each sample was measured.
2.2. Waste coffee grounds activated carbon characterization

2.2.1. Iodine number. The adsorption capacity of WCGAC was determined using ASTM standard D4607-1, which namely “Standard Test Method for Determination of Iodine Number of Activated Carbon”.

2.2.2. Surface morphology and carbon content. Surface morphology and element composition of materials was performed using Hitachi TM3000 Scanning Electron Microscope equipped with Energy Dispersive X-Ray (SEM-EDX).

2.2.3. Ash content and yield percentage. Ash content was performed using the ASTM D2866-94 method while the yield percentage was calculated based on the equation (1):

\[
Yield, (\%) = \frac{\text{Weight of activated carbon (g)}}{\text{Weight of raw material (g)}} \times 100\%
\] (1)

2.3. Packed bed CO₂ adsorption column

2.3.1. Breakthrough time. Two types of gases; N₂ and CO₂ were introduced in this experiment. The N₂ and CO₂ flow rates were regulated accurately by using two digital mass flow controllers (Aalborg GFC17). In order to achieve the desired inlet composition of the feed gas (15% CO₂/N₂, v/v), the CO₂ and N₂ gas flow rates were adjusted by mass flow controllers before entering the column to attain constant total flows of 90 and 910 mL/min of the feed gas. The AC sample (100 g) was then weighted and inserted into the packed bed column from the top for breakthrough study. Then, the adsorbent bed was pre-treated by purging process with a 300 mL/min flow of N₂ at room temperature and atmospheric pressure for 5-10 minutes. Subsequently, the bed was heated to desired adsorption temperature. Once reached the desired adsorption temperature, the adsorption breakthrough experiments were carried out at the temperatures of 30, 40, and 60°C. A CO₂ analyzer (Alpha Omega series 9610) with measuring 15% CO₂ was used to measure the concentration of CO₂ exiting the adsorption packed bed. The CO₂ analyzer displayed a value when the adsorption column was saturated with CO₂ and thus causes the gas to breakthrough out of the column. The breakthrough time was recorded for every sample. When the experiments ended, the results were recorded in the data logger, which installed on the packed bed CO₂ adsorption system (Figure 1).

Figure 1. Packed bed CO₂ adsorption column.
2.3.2. Adsorption capacity. The CO$_2$ adsorption capacities for the modified WCGACs at different temperature were calculated through the equation (2):

$$\text{CO}_2 \text{ adsorption capacity (\%) = } \frac{[v (\text{mL/min}) \times \rho (\text{mg/mL}) \times c(\%) \times t_b (\text{min})]}{w (\text{g})}$$

where, $v =$ inlet gas flow rate (mL/min); $\rho =$ CO$_2$ density (mg/mL); $c =$ concentration of inlet CO$_2$ (%); $t_b =$ breakthrough time (min); $w =$ weight of activated carbon (g).

3. Results and Discussion

3.1. RSM optimization of WCGAC preparation

The WCGACs were prepared according to the 17 experimental runs designed by BBM. The percentages of yield obtained from this research range were from 20.12-23.61%. After running 17 trials designed by BBM in terms of H$_3$PO$_4$ impregnation ratio, carbonization temperature and activation time, the sequential model sum of squares had shown that this research fulfilled two-factor interactions (2FI) model. In advance, analysis of variance (ANOVA) evaluated the reliability of the developed 2FI model for the yield percentage was shown in Table 1. The modelled p-value which was smaller than 0.0002 implies that 2FI model was significant. This explains that there was only a 0.02% of chance that this model will not fit to the experiment data set due to noise. Indeed, it could be conclude that the overall main effects (A, B, C) and one of the interaction terms (AB) were significant model terms to the response based on the p-values of the 2FI regression model. Therefore, this can conclude that the model factors (A, B, C, and AB) positively contribute to the model equation. Moreover, based on the F-value of the preparation parameters, which were in a decreasing sequence: A (22.19) > C (19.01) > B (9.65). This sequence illustrates that the H$_3$PO$_4$ impregnation ratio effect was the largest, pursued by the activation time while the carbonizing temperature has the slightest significant effect. In terms of lack of fit, the model p-value of 0.6363 indicates that it was non-significant and there was no significant relative to pure error.

| Source           | Sum of Squares | df | Mean Square | F-value | P-value Prob > F |
|------------------|----------------|----|-------------|---------|-----------------|
| Model            | 13.19          | 6  | 2.2         | 14.83   | 0.0002 significant |
| A-Impregnation ratio | 3.29        | 1  | 3.29        | 22.19   | 0.0008 significant |
| B-Carbonizing temperature | 1.43       | 1  | 1.43        | 9.65    | 0.0111 significant |
| C-Activation time   | 2.82          | 1  | 2.82        | 19.01   | 0.0014 significant |
| AB                | 4.26          | 1  | 4.26        | 28.73   | 0.0003 significant |
| AC                | 0.14          | 1  | 0.14        | 0.94    | 0.3548           |
| BC                | 0.63          | 1  | 0.63        | 4.23    | 0.0667           |
| Residual          | 1.48          | 10 | 0.15        |         |                 |
| Lack of Fit       | 0.79          | 6  | 0.13        | 0.76    | 0.6363 not significant |
| Pure Error        | 0.69          | 4  | 0.17        |         |                 |
| Total             | 14.68         | 16 |             |         |                 |
In RSM optimization, the 3-dimensional response surface plots (Figure 2 - 4) of the interaction effects were constructed. Manga and his research team [4] mentioned that a remarkable degradation of the microstructure would result from the thermal treatment performed at the same temperature under an inert atmosphere followed by impregnation with H$_3$PO$_4$. The high activation temperature showed adverse effect on the carbon yield. This was expected because more volatiles were released, resulting in a lower percentage of yield at a higher temperature [5]. The response surface showed a nearly curvature indicating that the interaction effect between carbonizing temperature and impregnation ratio on the yield is pronounced. The result obtained was in agreement with the work done by [6]. From Figure 2, it is obvious that the yield of activated carbon decreased as the impregnation ratio of H$_3$PO$_4$ increased. On the other hand, to optimize the preparation parameters, the response (yield percentage) was set to maximum range while kept the three variables (H$_3$PO$_4$ impregnation ratio, carbonization temperature and activation time) within the studied range. It was found that the optimum preparation parameters were 1:3.67 impregnation ratio of H$_3$PO$_4$, 533.08°C of carbonization temperature and 1.13 hrs of activation time, which resulted in obtaining a WCGAC with a predicted yield percentage of 23.79%.

![Figure 2. 3D-plot of yield percentage with the interact effect of impregnation ratio of H$_3$PO$_4$ and carbonizing temperature. (Actual factor: Activation Time, C = 1.50 hrs)](image-url)
Figure 3. 3D-plot of yield percentage with the interact effect of impregnation ratio of H$_3$PO$_4$ and activation time. (Actual factor: Carbonizing Temperature, B = 475°C)

Figure 4. 3D-plot of yield percentage with the interact effect of carbonizing temperature and activation time. (Actual factor: Impregnation Ratio of H$_3$PO$_4$, A = 2.50)

3.2. WCGAC characterization

3.2.1. Iodine number. The iodine number obtained was 825.04 mg/g (Figure 5). Saka [7] demonstrated that a high iodine number indicates a high microporosity and approximates the surface area with good precision.
3.2.2. Surface morphology and carbon content. SEM analysis was performed to observe the textural morphology and porosity development of raw precursor and WCGAC at different magnification level of 200 and 1000 times. Figure 6(a) revealed a porous structure with an appearance in the form of a ‘sponge-puff’ and had irregular pores found on the raw precursor. Marian et al. [8] claimed that irregular pores are found on the coffee grounds adsorbents that have not yet been activated and the cavity on the pores was still loose and rough as shown in Figure 6(b). The pores indicated a widening in the diameter as the structure developed into rough porous networks in the form of a honeycomb [9]. This may due to the removal of volatile matter after physicochemical activation at 533.08°C. Besides, H₃PO₄ carbon reaction which includes the cleavage of aryl bond and hydrolysis of glycosidic linkage in cellulose and hemicellulose also promotes the pore development [10]. As compared to its precursor, WCGAC has a well-developed pore on its surface due to the aid of H₃PO₄. Previous studies have revealed similar observations in their research in preparing AC derived from corn cub residue [11].

Figure 5. Log plot (X/M) versus C.

Figure 6. SEM micrograph of raw precursor (a) 200x, (b) 1000x; and WCGAC (c) 200x, (d) 1000x.
3.2.3. Ash content and yield percentage. WCGAC that produced with physicochemical activation under optimum preparation conditions was characterized by low ash content with 1.92%. The formation of ash content in AC was caused by the burn-off of non-carbon and inorganic substance which were not chemically bind with carbon surface during activation process [12].

3.3. CO₂ breakthrough time and adsorption capacity

Figure 7 compares the breakthrough curves of the WCGACs by varying different temperature at 1000 mL/min flow and 100g adsorbent. The curves reveal the ratio of outlet and inlet concentration (C/C₀) against the contact time at atmospheric pressure (1 atm) and different temperature (30, 40 and 60°C). All of the breakthrough curves show a rapid CO₂ uptake in the initial, and then increase gradually over contact time thereafter and finally reached constant which is 1. This is because initially all of the adsorption sites on both ACs are available, after a certain time the number of available adsorption sites decrease and finally all of the adsorption sites are occupied with CO₂ molecular, so called saturation.

![Breakthrough curves of CO₂ adsorption](image)

**Figure 7.** Effect of temperature on the breakthrough curves of CO₂ adsorption

For WCGAC, which adsorb CO₂ at 30°C, the adsorption breakthrough occurred at 5 min. While for WCGAC at 40°C and 60°C, the adsorption breakthrough both occurred at 3 and 2 min respectively. The CO₂ breakthrough times significantly decreased with increasing adsorption temperature due to the exothermic nature of the adsorption process [13]. Moreover, based on Table 2, a lower adsorption temperature leads to a longer saturation time. The breakthrough profile became steeper as the temperature increased. Interestingly, this view is supported by Dantas et al. [14].

**Table 2.** Breakthrough time and saturation time of the adsorbent at different temperature.

| Adsorbent | Temperature, (°C) | Breakthrough time, tₜ (min) | Saturation time, tₛ (min) |
|-----------|-------------------|-----------------------------|--------------------------|
| Raw       | -                 | -                           | -                        |
| WCGAC     | 30                | 5                           | 18                       |
|           | 40                | 3                           | 16                       |
|           | 60                | 2                           | 13                       |

The adsorption capacity of WCGAC at breakthrough time (5 min) and saturation time (18 min) were 1.20 mg CO₂/g adsorbent and 4.33 mg CO₂/g adsorbent respectively (Table 3). While for the WCGAC at
breakthrough time (3 min) and saturation time (16 min), the adsorption capacity were 0.70 mg CO₂/g adsorbent and 3.72 mg CO₂/g adsorbent, respectively. Due to higher adsorption temperature (60°C), the CO₂ adsorption capacity of WCGAC at breakthrough time (2 min) and saturation time (13 min) were 0.44 mg CO₂/g adsorbent and 2.84 mg CO₂/g adsorbent, respectively. These findings were supported by Hauchhum & Mahanta [15] who claimed that there is a decrease in CO₂ adsorption capacity when increasing the bed temperature due to the exothermic nature of adsorption process.

Table 3. Adsorption capacities of WCGAC at different temperature.

| Adsorbent | Temperature (°C) | Breakthrough adsorption capacity (mg CO₂/g adsorbent) | Maximum adsorption capacity (mg CO₂/g adsorbent) |
|-----------|------------------|------------------------------------------------------|--------------------------------------------------|
| WCGAC     | 30               | 1.20                                                 | 4.33                                             |
| WCGAC     | 40               | 0.70                                                 | 3.72                                             |
| WCGAC     | 60               | 0.44                                                 | 2.84                                             |

4. Conclusion

In conclusion, activated carbon made from carbonaceous material such as waste coffee ground (WCGAC) was successfully prepared and may be used for replacement of commercial AC for CO₂ adsorption. The CO₂ adsorption capacity was found to decrease with the increasing of adsorption temperature with the optimized WGAC prepared. Furthermore, regeneration ability is important parameter in performance evaluation for CO₂ adsorbent. Thus, in future work, heat energy required to remove CO₂ from the adsorbent during regeneration process will be investigated.

Acknowledgement

The authors are grateful for the financial support provided the Royal Society-Newton Mobility Grant (Grant No.: 9008-00011), which made this research possible.

References

[1] Krishnaiah D, Bono A, Anisuzzama S M, Joseph C and Khee T B 2014 *Journal of Applied Sciences* **14** 3142-48
[2] Lee C S, Ong Y L, Aroua M K and Daud W M A W 2013 *Chemical Engineering Journal* **219** 558-564
[3] Ferreira S L C, Bruns R E, Ferreira H S, Matos G D, David J M, Brandão G C and dos Santos W N L 2007 *Analytica Chimica Acta* **597** 179-86
[4] Manga H N, Mbadcam J K, Kouotou D, Baçaoui A and Yaacoubi A 2012 *Journal of Chemistry* **2013** 1-10
[5] Ould-Idriss A, Sitou M, Cuerda-Correa E M, Fernandez-Gonzalez C, Macias-Garcia A, Alexandre-Franco M F and Gomez-Serrano V 2011 *Fuel Processing Technology* **92** 261–65
[6] Ahmad A A, Hameed B H and Ahmad L A 2009 *Journal of Hazardous Materials* **170** 612-619
[7] Saka C 2012 *Journal of Analytical and Applied Pyrolysis* **95** 21-24
[8] Mariana, Marwan M, Mulana F, Yunardi Y, Ismail T A and Hafidiansyah M F 2018 *IOP Conference Series: Materials Science and Engineering* **334** 7-15
[9] Yeung P T, Chung P Y, Tsang H C, Cheuk-On T J, Yin-Ming C G, Gambari R and Lam K H
2014 *RSC Advances* **4** 38839–47

[10] Shamsuddin M S, Yusoff N R N and Sulaiman M A 2016 *Procedia Chemistry* **19** 558–65

[11] Chen J, Zhang L, Yang G, Wang Q, Li R and Lucia L A 2017 *Bioresources* **12** 5928–5941

[12] Abdullah A H, Kassim A, Zainal Z, Hussien M Z, Kuang D, Ahmad F and Wooi O S 2001 *Malaysian Journal of Analytical Sciences* **7** 65–8

[13] Shafeeyan M S, Daud W M A W, Shamiri A and Aghamohammadi N 2015 *Energy and Fuels* **29** 6565–77

[14] Hauchhum L and Mahanta P 2014 *International Journal of Advanced Mechanical Engineering* **4** 27–32

[15] Dantas T L P, Luna F M T, Silva I J, Torres A E B, De Azevedo D C S, Rodrigues A E and Moreira R F P M 2011 *Brazilian Journal of Chemical Engineering* **28** 533–44