

## Adsorption Isotherm and Surface Analysis for the Carbonate Formation on Nano Coral-Shaped Iron(III) Oxide

(Isoterma Penjerapan dan Analisis Permukaan bagi Pembentukan Karbonat di atas Ferum(III) Oksida Berbentuk Karang Nano)

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*Received: 22 March 2022/Accepted: 25 June 2022*

### ABSTRACT

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized using the hydrolysis method to obtain the nano coral-shaped morphology. The adsorption isotherm and surface analysis upon CO<sub>2</sub> adsorption were identified. The adsorption capacity for nano coral-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was measured at 8.66 cm<sup>3</sup>/g (17.00 mg/g). Experimental data from CO<sub>2</sub> adsorption isotherm at 25 °C best fits with the Freundlich isotherm model which implies the adsorption process is favorable and the multilayer adsorption on the heterogeneous surface. A decrease in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystallite peaks in the X-ray diffractogram after the CO<sub>2</sub> adsorption was associated with the carbonate complexes species formation. IR spectra indicate higher intensities over the CO<sub>2</sub> exposure time of 4, 12 and 24 h, especially at absorption bands 1041 and 1627 cm<sup>-1</sup> that corresponded to C-O and asymmetry O-C-O stretches, respectively, for carbonate. The morphology of the carbonate formation on nano coral-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> over the CO<sub>2</sub> exposure time was analyzed using FESEM-EDX. Although the carbonate formation was not distinct, the increment in the C element also confirmed the capability of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in adsorbing CO<sub>2</sub> for a long adsorption time of 24 h.

Keywords: Adsorption isotherm; carbonate formation; CO<sub>2</sub> capture; hydrolysis method; iron(III) oxide

### ABSTRAK

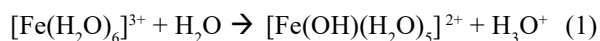
$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> telah disintesis menggunakan kaedah hidrolisis untuk mendapatkan morfologi berbentuk nano karang. Isoterma penjerapan dan analisis permukaan terhadap penjerapan CO<sub>2</sub> telah dikenal pasti. Keupayaan penjerapan bagi  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> berbentuk nano karang telah diperoleh sebanyak 8.66 cm<sup>3</sup>/g (17.00 mg/g). Isoterma penjerapan CO<sub>2</sub> pada 25 °C daripada data uji kaji paling sesuai dengan model isoterma Freundlich menunjukkan proses penjerapan adalah berlaku dengan mudah dan penjerapan lapisan berganda pada permukaan yang heterogen. Penurunan puncak kekisi  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dalam difraktogram sinar X selepas penjerapan CO<sub>2</sub> adalah dikaitkan dengan pembentukan spesies karbonat kompleks. Spektrum IR menunjukkan keamatan yang lebih tinggi terhadap masa pendedahan CO<sub>2</sub> pada 4, 12 dan 24 jam, terutamanya pada jalur-jalur serapan bagi 1041 dan 1627 cm<sup>-1</sup> yang masing-masing sepadan dengan regangan C-O dan O-C-O tak simetri bagi karbonat. Morfologi bagi pembentukan karbonat di atas  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> berbentuk nano karang terhadap masa pendedahan CO<sub>2</sub> dianalisis menggunakan FESEM-EDX. Walaupun pembentukan karbonat adalah tidak jelas, peningkatan unsur C juga telah mengesahkan keupayaan  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dalam menjerap CO<sub>2</sub> dalam masa penjerapan yang panjang pada 24 jam.

Kata kunci: Ferum(III) oksida; isoterma penjerapan; kaedah hidrolisis; pembentukan karbonat; penjerapan CO<sub>2</sub>

## INTRODUCTION

Numerous iron oxide synthesis methods were reported to obtain nanoparticles and controlled shape. Besides physical and biological methods, chemical methods such as thermal decomposition, hydrothermal, co-precipitation, sol-gel, hydrolysis, electrochemical and microemulsion were commonly reported for iron oxide synthesis (Andrade, Veloso & Castanheira 2020). Whereas metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{NiO}$ ) deposited on other metal oxide or support materials applying the impregnation method (Hakim et al. 2015a, 2015b; Lahuri et al. 2022a, 2020a, 2020b). Generally, the hydrolysis method is the initial pathway for hydrothermal, sol-gel and co-precipitate methods (Zhong et al. 2012). This method would be the simplest, economically safe and less using hazardous chemicals.

In the hydrolysis method, the metal ions form aqua coordination complexes  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  in which the hydrolysis reaction takes place in water or aqueous solutions as shown in Equation (1). A selected non-aqueous solvent such as ethanol is applied as a stabilizer (Hakim et al. 2016c). This method does not form a gel structure due to no addition of shaping agents such as a polymer (polyethylene glycol, polyethyleneimine) and surfactant (oleyamine, octadecylamine) (Andrade, Veloso & Castanheira 2020). Usually, the shaping agent forms a hydrogen bond as a linkage that influences the shape, morphology and particle growth. However, a simpler ethanol molecule also could form a linkage of hydrogen bond between hydrate of the salt. The final process of calcination is the thermal treatment is significant to the geometrical and crystal structure of the particle.



The particle shape can be controlled kinetically or thermodynamically. In the thermodynamic process, the chemical reaction potential is associated with controllable parameters such as supersaturation of the solution and temperature. Whereas the kinetic process involves stable nucleation sites in supersaturated regions in which reduce the reaction energy barrier (Wu, Yang & Wu 2016). During the particle growth by thermodynamically driven, the reaction favors reducing the particle's surface free energy (Lisjak & Mertejeli 2018). It involves two significant mechanisms that influence the rate of deposition of atoms in the nuclei's surface. The two mechanisms are reaction-limited and diffusion-limited which correspond to low and high

solution concentrations, respectively. At low solution concentration, the reaction-limited take place as the particle growth toward its final shapes are depending on the surface reaction limit. At high concentrations, the diffusion-limited is due to the monomers being precipitated on the particle surfaces which favor the monodisperse nanoparticles. Thus, the final shape is affected by synthesis parameters such as solvent, temperature, precursor concentration and pH (Shaba et al. 2021).

The particle shape also exhibits different activity toward  $\text{CO}_2$  adsorption capacity. The mesoporous silica in rod-shaped exhibited higher surface area and  $\text{CO}_2$  adsorption capacity compared to spherical-shaped (Khary et al. 2018). The ethylene glycol was added as a shaping agent to obtain rod-shaped mesoporous silica, while spherical-shaped was synthesized without ethylene glycol. A nanowire morphology of lithium silicate was synthesized using plasma oxidation exhibiting ultrafast  $\text{CO}_2$  adsorption in 3 minutes with an adsorption capacity of 25 wt. % (Nambo 2019). A chemical precipitation method was applied to obtain the spherical shape of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles at 21 nm by using 0.05 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as a precursor (Lassoued et al. 2017). Meanwhile, an ultrasonic-assisted hydrolysis technique using ammonium bicarbonate as the precipitation agent and phosphoric acid as pH controller also resulted in uniform spherical shape  $\alpha\text{-Fe}_2\text{O}_3$  with an average particle size of 50 nm (Chen, Chen & Liu 2016). Nonetheless, the synthesis method for  $\alpha\text{-Fe}_2\text{O}_3$  toward  $\text{CO}_2$  capture activity is not widely explored.

Therefore, this work attempt to study the  $\text{CO}_2$  adsorption activity through the carbonate formation onto  $\alpha\text{-Fe}_2\text{O}_3$  which is synthesized by the hydrolysis method. This extended work from Hakim et al. (2016b) emphasizes the long period of  $\text{CO}_2$  exposure onto the particle shape generated by the hydrolysis method. The adsorption mechanism will be analyzed by applying the experimental  $\text{CO}_2$  adsorption isotherm at 25 °C to the adsorption isotherm models. The carbonate formation on  $\alpha\text{-Fe}_2\text{O}_3$  will be observed using Fourier transform infrared (FTIR) spectroscopy and field emission scanning electron microscope equipped with energy dispersive X-ray (FESEM-EDX).

## MATERIALS AND METHODS

The synthesis method was adapted from Hakim et al. (2016b). The ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.7%) was obtained from System, Malaysia, while iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%) from Sigma-Aldrich,

USA. The bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was purchased from BDH, United Kingdom. Pre-treatment was performed by calcining the bulk  $\alpha$ -Fe<sub>2</sub>O in a nitrogen atmosphere at 150 °C for 1 hour. Briefly, the precursor of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was dissolved in distilled water to have a concentration of 2 M solution. The ethanol was added to the solution with a volume percentage of 25% from the distilled water used. The mixture was stirred for 1 hour at room temperature and followed by sonicating for 20 minutes. The mixture was dried by stirring at the temperature of 80 - 100 °C. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was ground using a mortar and continued to dry in an oven for 24 hours at 110 °C. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was calcined under ambient air at the temperature of 450 °C. The precursor concentration and calcination temperature were chosen from the most efficient in CO<sub>2</sub> adsorption capacity from Hakim et al. (2016c).

CO<sub>2</sub> adsorption isotherm at 25 °C was measured using a static volumetric technique from a gas sorption analyzer, Micromeritics ASAP 2020. Approximately 500 mg sample was outgassed for 6 hours at 200 °C. The CO<sub>2</sub> adsorption was conducted in a circulating water bath to control the adsorption temperature of 25 °C. The CO<sub>2</sub> adsorption isotherm data will be analyzed using the linearized form of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models.

The composition of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was characterized using surface analysis of X-ray Diffraction (XRD) with Bruker AXS D8 Advance type. The diffraction angle was recorded from 20° to 90°. The composition was identified by matching with standard diffraction data (JCPDS). The carbonate formation on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was analyzed by XRD to compare the crystalline phase composition. Meanwhile, the carbonate formation was conducted using temperature programmed desorption CO<sub>2</sub> (CO<sub>2</sub>-TPD) from a chemisorption analyzer model Micromeritics 2920 Chemisorb. Approximately 50 mg of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has treated heat exposure in an inert atmosphere of He flow at 150 °C for 30 minutes to eliminate traces of moisture and humidity gases. When the furnace temperature was cooled to 30 °C, the gas feed was switched to a mixture of 5 % (V/V) CO<sub>2</sub> in He to perform the CO<sub>2</sub> adsorption by saturating flow for 1 hour. The mixture gas was switched to He for 30 minutes with a flow rate of at 50 °C to remove the weak adsorbed CO<sub>2</sub>. It was followed by the desorption process at elevated temperatures from 30 to 650 °C. The method was performed separately until the adsorption process and desorption process. After the reaction, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample was collected to analyze using XRD.

The surface chemistry of the carbonate formation on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was studied by using FTIR spectroscopy and FESEM-EDX. The reaction was conducted using a fluidized bed reactor. Approximately 4 g of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was placed in the column. The fresh sample was cleaned by flowing N<sub>2</sub> at 150 °C for 30 minutes prior to CO<sub>2</sub> exposure for 4, 12 and 24 hours separately, at 30 °C. The bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, fresh  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and after being exposed to CO<sub>2</sub> were analyzed using FTIR spectroscopy and FESEM-EDX. The trend of the carbonate formation on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> could be observed over time through the presence of functional groups using FTIR spectroscopy from a Perkin Elmer model GX. The sample is prepared by KBr pellet techniques mixing the sample with KBr. The wavenumbers of the spectra obtained from the FTIR method are between the range of 450 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Whereas, the morphology and elemental analyses of the fresh  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and carbonate formation were evaluated using FESEM-EDX (ZEISS Supram<sup>TM</sup> 55).

## RESULTS AND DISCUSSION

The CO<sub>2</sub> adsorption isotherm at 25 °C is shown in Figure 1. A significant difference in the adsorption capacity between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits the adsorption capacity of 8.66 cm<sup>3</sup>/g (17.00 mg/g) compared to bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 1.53 cm<sup>3</sup>/g (3.00 mg/g). Although this value is slightly lower than amine-functionalized solid sorbent (Abu Tahari et al. 2020, 2017), amine-based materials face several drawbacks such as causing equipment corrosion and removal of amine compound during the desorption process that reduces the sorption capacity. The hydrolysis method generates a higher surface area and trimodal pore size distribution for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> compared to the bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hakim et al. 2016c). This would be the reason for an abrupt increase in the adsorption capacity, which more space to occupy the CO<sub>2</sub>. Hence, a further analysis was studied to provide an insightful understanding of the adsorption mechanism.

The adsorption mechanism was evaluated by analyzing the experimental data for CO<sub>2</sub> adsorption isotherm at 25 °C with adsorption isotherm models such as Langmuir, Freundlich, Temkin and D-R. The linearized form of the adsorption isotherm models are shown in Figure 2 and their parameters are tabulated in Table 1. The Langmuir isotherm model best describes gas-solid phase adsorption, the dynamic equilibrium of the surface adsorption and comparing the approximate adsorption capacity (Lahuri et al. 2022c). The experimental data

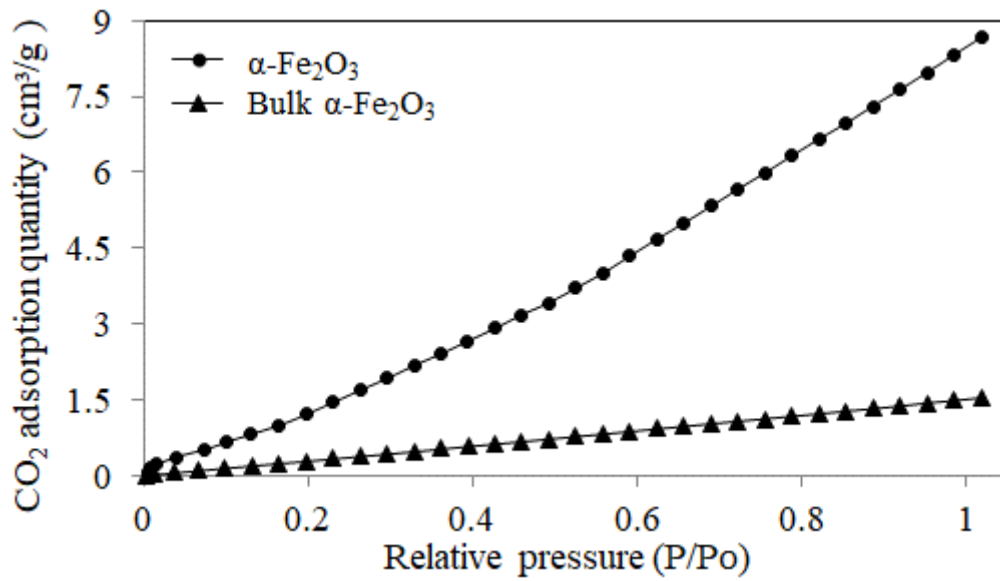


FIGURE 1. CO<sub>2</sub> adsorption isotherm at 25 °C

fit well with the Langmuir isotherm with  $R^2 = 0.4243$ . The theoretical adsorption quantity ( $Q_o = 3.497 \text{ cm}^3/\text{g}$ ) and adsorption energy ( $K_L = 0.8252$ ) were calculated from the slope and intercept respectively. It explains the maximum adsorption that refers to a saturated monolayer

of CO<sub>2</sub> molecules on the adsorbent surfaces without transmission of adsorbate in the plane of the adsorbate surface. Based on the results,  $Q_o$  deviates from the experimental value but the CO<sub>2</sub> adsorption is favorable due to the dimensionless separation factor ( $R_L = 2.885 \times 10^{-6}$ ) within the range of 0-1 (Lahuri et al. 2020c).

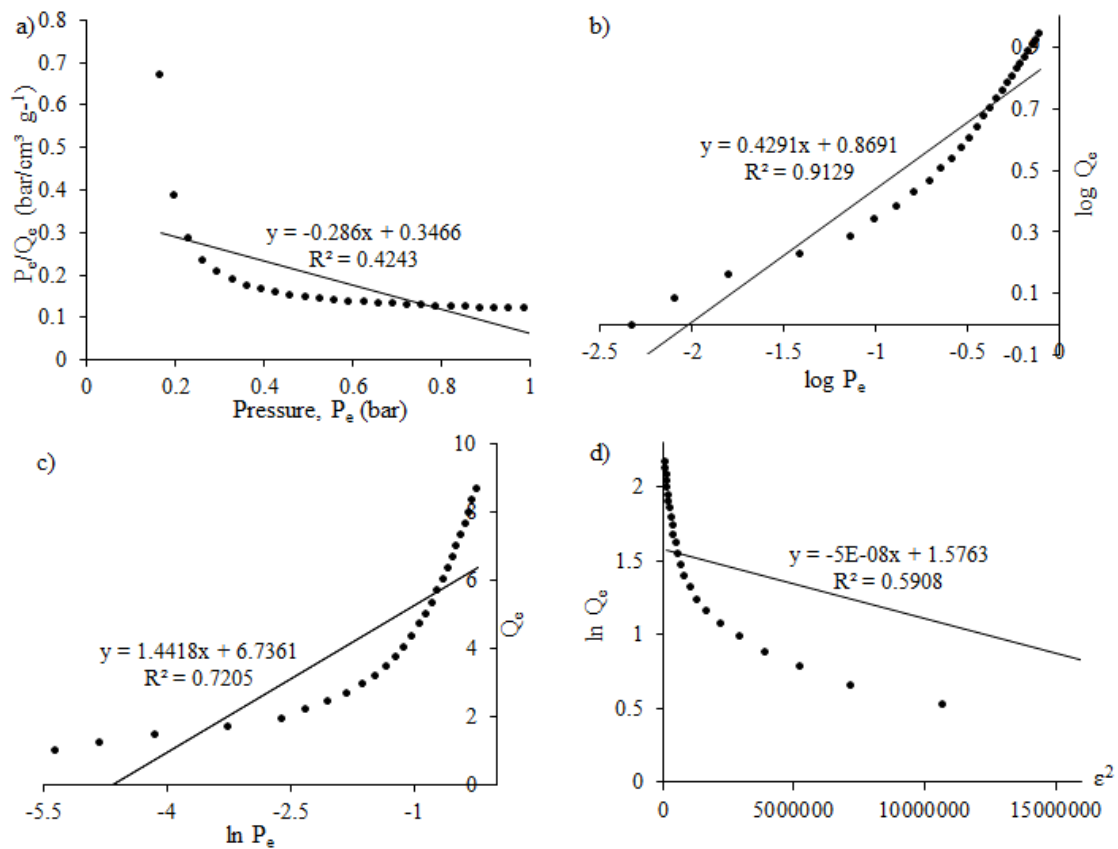


FIGURE 2. Adsorption isotherms by a) Langmuir, b) Freundlich, c) Temkin and d) D-R models in linearized form using CO<sub>2</sub> adsorption isotherm at 25 °C for  $\alpha\text{-Fe}_2\text{O}_3$

The Freundlich isotherm exhibits the best fit with the experimental data with  $R^2 = 0.9129$  and the theoretical adsorption quantity ( $K_F = 7.398 \text{ cm}^3/\text{g}\cdot\text{bar}^{1/n}$ ) closest to the experimental adsorption quantity. When the number of molecules bound to the adsorption site increases, smaller chances of molecule binding at the same sites due to higher energy is required to allow another molecule to bind at the same adsorption sites (Lahuri et al. 2022c; Rashidi & Yusup 2017). Therefore, this model assumes multilayer adsorption onto a heterogeneous surface that is ascribed to the physicochemical properties of active sites and adsorbed molecules (Ammendola, Raganati & Chirone 2017). The adsorption does not comply with driving force or cooperative adsorption attributed to the  $1/n$  value of 0.429, which is  $1/n < 1$  suggests greater heterogeneity when the smaller the value (Ammendola, Raganati & Chiro 2017; Lahuri et al. 2022c). This model also suggests a favorable adsorption process with the Freundlich constant of  $n = 2.330$  which is  $n > 1$ .

For the Temkin isotherm model, it derives the surface coverage linearly proportional with the heat of

adsorption for all molecules in the layer (Lahuri et al. 2022c). The parameters of the model are bond constant ( $A_T = 106.91 \text{ L/g}$ ) corresponds to the maximum binding energy and heat of adsorption ( $b_T = 1718.39 \text{ J/mol}$ ). Meanwhile, the D-R isotherm constant ( $K_{ad} = 5.0 \times 10^{-8} \text{ mol}^2/\text{J}^2$ ) is associated with the mean energy of sorption as it is transferred from the adsorbate to the surface of the adsorbent. This model could obtain the mean free energy ( $E = 3162.28.14$ ) which both  $b_T$  and  $E$  from Temkin and D-R model, respectively, are below  $8 \text{ kJ/mol}$ , suggesting the adsorption is physical in nature (Djomgoue et al. 2012). Although the correlation coefficient of  $R^2$  for Temkin and D-R isotherm are fitted well, the theoretical isotherm saturation capacity ( $Q_s = 4.837 \text{ cm}^3/\text{g}$ ) deviates from the experimental value.

Based on the  $R^2$  values, the Freundlich isotherm model is fit better with the experimental  $\text{CO}_2$  adsorption data and best describes the adsorption process. Thus, the  $\text{CO}_2$  adsorption process implies multilayer adsorption on the heterogeneous surfaces of  $\alpha\text{-Fe}_2\text{O}_3$ .

TABLE 1. The adsorption isotherm parameters for Langmuir, Freundlich, Temkin and D-R models using  $\text{CO}_2$  adsorption isotherm at  $25 \text{ }^\circ\text{C}$  for  $\alpha\text{-Fe}_2\text{O}_3$

| Isotherm                                   | Plot                          | Parameters  | Values                 |
|--|-------------------------------|---|------------------------|
| Langmuir                                   |                               |   |                        |
| Non-linear equation                        |                               | $Q_{o \text{ cal.}}$ ( $\text{cm}^3/\text{g}$ )       | 3.497                  |
|  |                               | $K_L$   | 0.8252                 |
| Linear equation                            |                               | $R_L$   | $2.885 \times 10^{-6}$ |
| $P_e/Q_e = 1/Q_s K_L + P_e/Q_s$            | $P_e/Q_e$ against $P_e$       | $R^2$   | 0.4243                 |
| Freundlich                                 |                               |   |                        |
| Non-linear equation                        |                               | $K_F$ ( $\text{cm}^3/\text{g}\cdot\text{bar}^{1/n}$ ) | 7.398                  |
|  |                               | $1/n, (n)$  | 0.429, (2.330)         |
| Linear equation                            |                               | $R^2$   | 0.9129                 |
| $\log Q_e = 1/n \log P_e + \log K_F$       | $\log Q_e$ vs. $\log P_e$     |   |                        |
| Temkin                                     |                               |   |                        |
| Non-linear equation                        |                               | $A_T$ (L/g)   | 106.91                 |
|  |                               | $b_T$ (J/mol)   | 1718.39                |
| Linear equation                            |                               | $B$   | 1.4418                 |
| $Q_e = B \ln A_T + B \ln P_e$              | $Q_e$ vs. $\ln P_e$           | $R^2$   | 0.7205                 |
| Dubinin-Radushkevich                       |                               |   |                        |
| Non-linear equation                        |                               | $Q_s$ ( $\text{cm}^3/\text{g}$ )                      | 4.837                  |
|  |                               | $K_{ad}$ ( $\text{mol}^2/\text{J}^2$ )                | $5.0 \times 10^{-8}$   |
| Linear equation                            |                               | $E$ (J/mol)   | 3162.28                |
| $\ln Q_e = \ln Q_s - K_{ad} \varepsilon^2$ | $\ln Q_e$ vs. $\varepsilon^2$ | $R^2$   | 0.5908                 |

The X-ray diffractograms are shown in Figure 3. The peaks were observed in all samples correspond to the rhombohedral phase of hematite,  $\alpha\text{-Fe}_2\text{O}_3$  with lattice parameters  $a=5.0356$  and  $b=c=13.7489$  (matched with JCPDS number 33-0664). A higher intensity of the peaks for  $\alpha\text{-Fe}_2\text{O}_3$  compared to bulk  $\alpha\text{-Fe}_2\text{O}_3$  due to more crystallite formation through the hydrolysis method. No additional peaks after being exposed to  $\text{CO}_2$ , but the peak intensities reduce might be due to the carbonate formation after being exposed to  $\text{CO}_2$  for only one hour. It is not similar as  $\text{FeCO}_3$  since it can be detected by XRD (Mendoza et al. 2019).  $\text{Fe}_2(\text{CO}_3)_3$  formation is thermodynamically unstable due to high polarizing power with high charge density, which is a triply charged ion. Hence, a greater distortion of the

carbonate ( $\text{CO}_3^{2-}$ ) ion's electron cloud (Lahuri et al. 2022b). According to Fajan's rule, induced covalent character on ionic compound increases with an increase in charge on the cation, which  $\text{Fe}^{3+}$  will be less ionic compared to  $\text{Fe}^{2+}$  (Sattler 2011). The carbonate might be generated in the form of carbonate complexes such as bidentate carbonate (Hakim et al. 2016a). Nevertheless, the reduction in peak intensities is noteworthy to further explore since numerous works reported the potential of  $\alpha\text{-Fe}_2\text{O}_3$  as a  $\text{CO}_2$  adsorbent (Lahuri et al. 2017; Mendoza et al. 2019). After TPD at  $650^\circ\text{C}$ , the peak intensities were slight increases compared to after being exposed to  $\text{CO}_2$ . This indicates that adsorbed  $\text{CO}_2$  was partially removed at  $650^\circ\text{C}$ . The limitation of the XRD analysis should be supported by further surface analyses such as FTIR spectroscopy and FESEM-EDX.

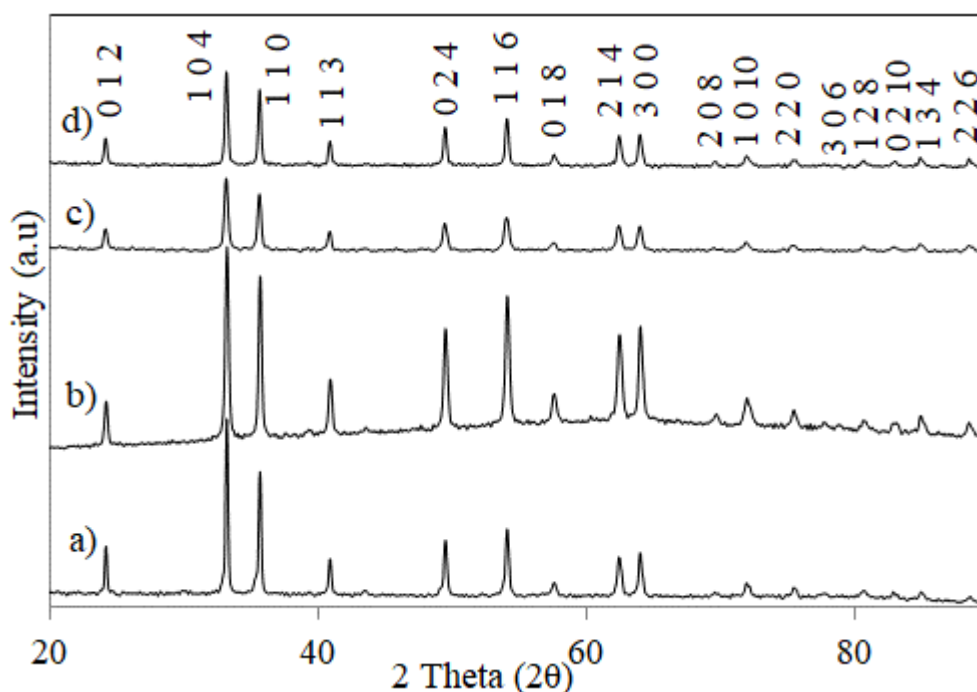


FIGURE 3. XRD pattern for a) bulk  $\alpha\text{-Fe}_2\text{O}_3$ , b)  $\alpha\text{-Fe}_2\text{O}_3$ , c)  $\text{CO}_2$  adsorption on  $\alpha\text{-Fe}_2\text{O}_3$ , for 1 hour and d)  $\text{CO}_2$ -TPD for  $\alpha\text{-Fe}_2\text{O}_3$  at desorption temperature of  $650^\circ\text{C}$

The IR spectra for the fresh  $\alpha\text{-Fe}_2\text{O}_3$  and after  $\text{CO}_2$  exposure at 4, 12 and 24 hours are shown in Figure 4. Table 2 shows the vibrational mode assignments of the IR spectra. There is no peak indicating the carbonate formation on bulk  $\alpha\text{-Fe}_2\text{O}_3$  except the physisorption  $\text{CO}_2$  ( $2347\text{ cm}^{-1}$ ) and  $\text{CO}_2$  bound to metal ion ( $2388\text{ cm}^{-1}$ ) were appeared for all samples (Lahuri Lahuri & Yarmo 2022b).

Unlike bulk  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$  easily adsorb  $\text{CO}_2$  from the atmosphere due to the presence of absorption bands of  $1041$  and  $1627\text{ cm}^{-1}$  that are associated with C-O and O-C-O asymmetry stretch, respectively, for carbonate compound (Baltrusaitis et al. 2011; Lahuri & Yarmo 2022b). These peaks were observed to be prominent after 4 hours of  $\text{CO}_2$  exposure and onward. A similar trend is

observed for the absorption band at 789 and 915  $\text{cm}^{-1}$  that are associated with Fe-O-H (Hakim et al. 2016a, 2016c). A higher intensity of the absorption band of 915  $\text{cm}^{-1}$  after 24 h  $\text{CO}_2$  adsorption ascribed to the traces moisture content in the gas feed. The absorption bands at 623, 668 and 682  $\text{cm}^{-1}$  were assigned for bend  $\text{CO}_2$  (Isokoski, Poteet & Linnartz 2013; Kazansky et al. 1999; Mutch et al. 2016). The absorption bands at 423, 443

and 456  $\text{cm}^{-1}$  correspond to the Fe-O bond for  $\alpha\text{-Fe}_2\text{O}_3$  (Mohanraj & Sivakumar 2017; Qin et al. 2011; Tadic et al. 2019). The inconsistency of the fingerprint region in IR spectra might be due to the presence of the moisture content in the sample. The  $\text{CO}_2$  exposure could lead to the traces moisture from the gas feed to adsorb onto sample and interfere the Fe-O related peaks. Therefore, the peak intensities that associated with Fe-O-H also increases.

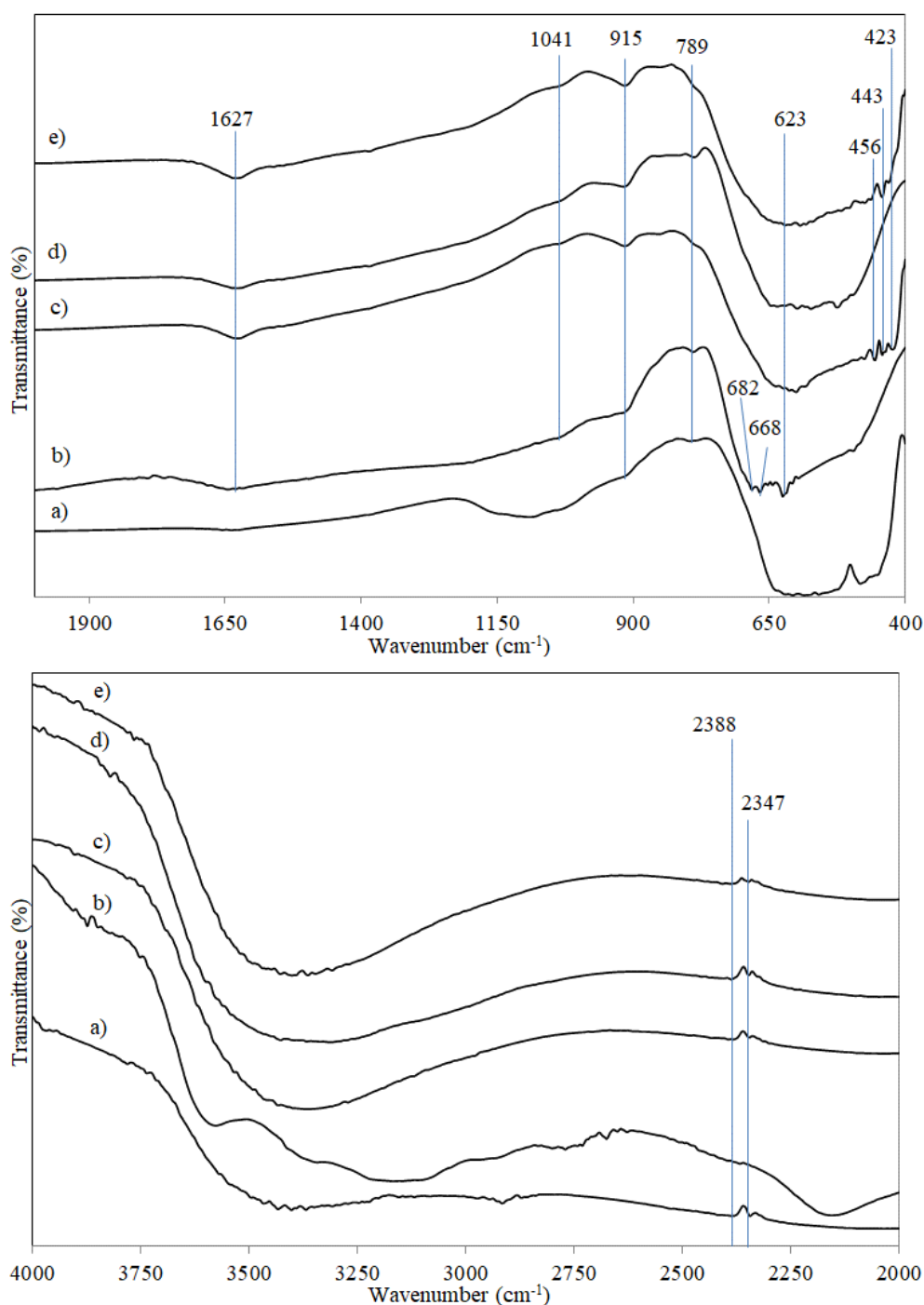


FIGURE 4. IR spectra for a) bulk  $\alpha\text{-Fe}_2\text{O}_3$ , b)  $\alpha\text{-Fe}_2\text{O}_3$ , c) 4 hours of  $\text{CO}_2$  adsorption on  $\alpha\text{-Fe}_2\text{O}_3$ , d) 12 hours of  $\text{CO}_2$  adsorption on  $\alpha\text{-Fe}_2\text{O}_3$ , e) 24 hours of  $\text{CO}_2$  adsorption on  $\alpha\text{-Fe}_2\text{O}_3$

TABLE 2. Mode assignments of IR absorption bands

| Vibrational mode assignments       | Experimental frequencies (cm <sup>-1</sup> ) | Literature references (cm <sup>-1</sup> ) |
|------------------------------------|--|---|
| Fe-O bond                          | 423, 443 and 456                             | 420, 440 and 456                          |
| Bend CO <sub>2</sub> (C=O)         | 623, 668 and 682                             | 625, 666 and 682                          |
| Fe-O-H                             | 789, 915                                     | 796, 918                                  |
| C-O                                | 1041   | 1040                                      |
| Asymmetry O-C-O                    | 1627   | 1635                                      |
| Physisorption CO <sub>2</sub>      | 2347   | 2344                                      |
| CO <sub>2</sub> bound to metal ion | 2388   | 2383                                      |

Figure 5 shows the morphology of the fresh  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and after being exposed to CO<sub>2</sub> for 4, 12, and 24 hours. The identification of the elemental composition

was analyzed quantitatively using EDX. It is noteworthy to observe the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> synthesized by the hydrolysis method generates a nano coral shape. Although a similar

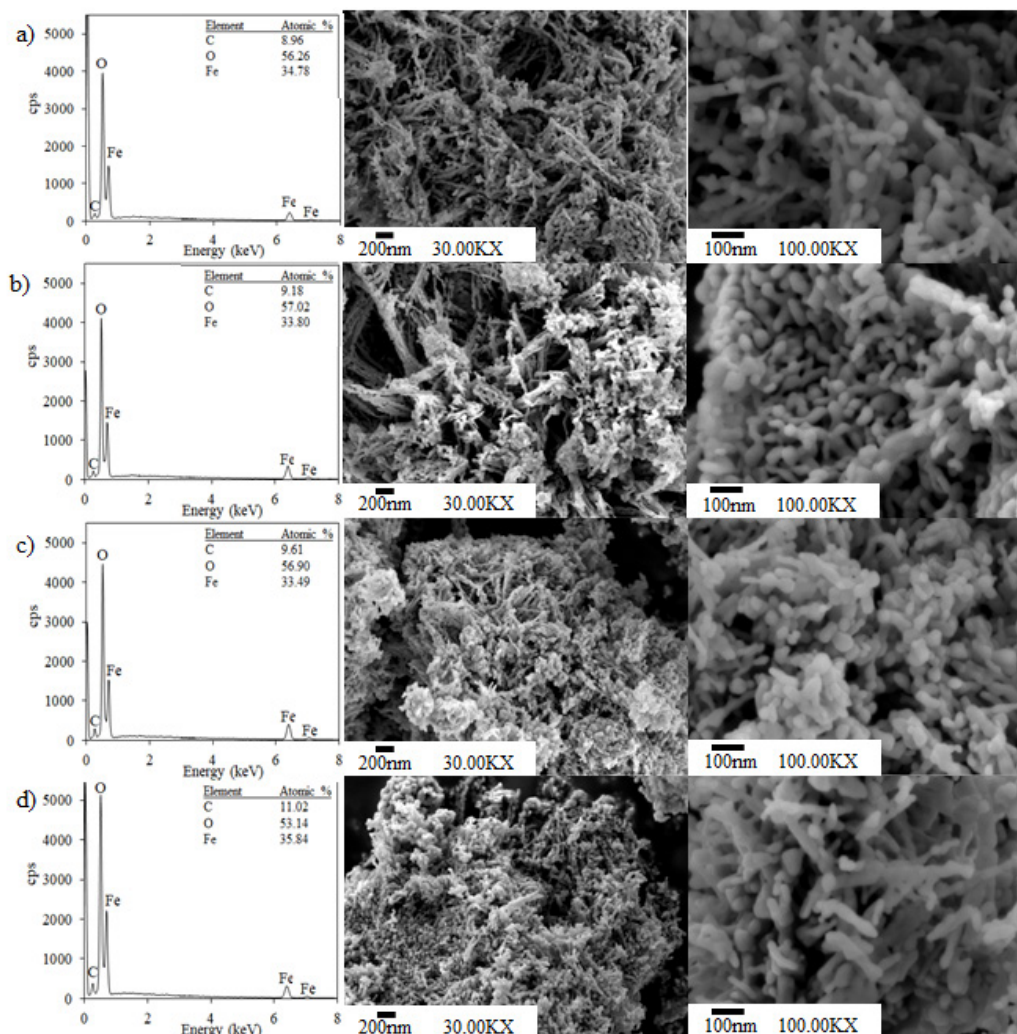


FIGURE 5. FESEM-EDX micrographs for a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, b) 4 hours of CO<sub>2</sub> adsorption on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, c) 12 hours of CO<sub>2</sub> adsorption on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and d) 24 hours of CO<sub>2</sub> adsorption on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>



sonication assisted method was employed, a different precursor, precipitation agent and pH controller compared to Chen, Chen and Liu (2016) result in a different shape of iron(III) oxide. A coral-like morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was reported to possess a significantly larger surface area compared to a nanorod shape (Kment et al. 2017) which could enhanced the adsorption capacity. The micrograph for the long CO<sub>2</sub> exposure on the nano coral-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> of 4, 12 and 24 hours were indistinct. The O element showed a general increase in the atomic % over the time except for 24 hours ascribed to the regional factor during the area was scanned. Nevertheless, the C element increases proportionally over the CO<sub>2</sub> adsorption time indicating the capability and potential of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to adsorb CO<sub>2</sub> for a long period.

#### CONCLUSIONS

The hydrolysis method was used to synthesize  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with the precursor concentration of 2 M of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and calcination temperature of 450 °C. The CO<sub>2</sub> adsorption isotherm at 25 °C showed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> obtain an adsorption capacity of 8.66 cm<sup>3</sup>/g (17.00 mg/g) which is higher than bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The experimental data was analyzed using adsorption isotherm models such as Langmuir, Freundlich, Temkin and D-R. Experimental CO<sub>2</sub> adsorption isotherm at 25 °C fit well for all isotherm models but it was found the best fit with Freundlich isotherm model with an R<sup>2</sup> value of 0.9129. This implies the CO<sub>2</sub> adsorption process is favorable by having multilayer adsorption on the heterogeneous surface. The surface analyses were conducted for fresh  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and after being exposed to CO<sub>2</sub>. The XRD pattern showed lower intensities of the peaks might be due to the formation of the complexes carbonate. The IR spectra showed a greater intensity from 4 to 24 hours of CO<sub>2</sub> exposure, especially for the C-O and asymmetry O-C-O stretches for carbonate compound. The hydrolysis method was confirmed to generate a nano coral reef shaped of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> that was observed through FESEM-EDX. The carbonate formation onto nano coral-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was not distinct but the increment of the C element indicates the capability and potential of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in a long CO<sub>2</sub> adsorption time.

#### ACKNOWLEDGEMENTS

The authors wish to express gratitude for the research work supported by Universiti Putra Malaysia (GP-IPB/2019/9671302, GP/2020/9692700), 6300940 grant award under OCIM Sdn. Bhd. to Universiti Putra Malaysia and 230.PKIMIA.6711923 grant award under

Ministry of Higher Education to Universiti Sains Malaysia.

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