Emissions of CO$_2$ from industrial, agricultural, residential and commercial activities [1,2] are major sources of climate change. They have gained attention in recent years [3] as the concentration of CO$_2$ increases from 278 ppm to about 405 ppm from 1970 to 2017 as measured by Global Monitoring Division of NOAA/Earth System Research Laboratory [4]. Various CO$_2$ removal methods such as absorption [5-7], membrane separation [8,9], cryogenic distillation [10] and adsorption [11-15] have been developed. Among these techniques, adsorption on solid adsorbent is a promising alternative method due to the potential of handling higher throughput for regeneration [18]. Adsorbents such as zeolites [19-22], siliceous compounds [19,23], metal-organic frameworks [24-26], hydrotalcites [27,28], activated carbons [29,30] and metal oxides [27] have been investigated, however they have inherent limitations. Consequently, it is essential to develop a cost effective adsorbent for CO$_2$ gas.

Alum sludge is a by-product from water treatment plant processes comprising coagulation, flocculation, filtration and/or purification [31,32]. The water treatment residual or waterworks sludge contains high amount of aluminium as its compounds are used as a coagulant in coagulation-flocculation process. The management of this sludge has become important environmental issue due to stringent environmental regulation and increasing public awareness [33]. About 80,000 tons of alum sludge waste is produced annually from water treatment plants [34] and can be a huge problem if it is not properly disposed. Aluminum based waterworks sludge has been utilized as a solid-based adsorbent for heavy metal, dye, phosphorus and sulphur dioxide adsorptions [35-44]. As far as we aware, there is no reports on aluminium based waterworks sludge as the CO$_2$ adsorbent, therefore we embarked a study to evaluate this sludge for this purpose. This report describes the effectiveness of reusing drinking water treatment plant sludge as carbon dioxide adsorbent. The sludge collected from a local drinking water treatment plant. It was dried and characterized using scanning electron microscope-energy disperse X-ray (SEM-EDX), Fourier transform infrared spectrometer (FTIR) and thermogravimetric analysis (TGA). Investigations of the effects of temperature, flow rate, concentration of CO$_2$ and adsorbent dosage on CO$_2$ adsorption capacity were performed using a fixed bed column at a pressure of 1 bar. The maximum capacity of 32.56 mg/g was found which was higher than that of some reported adsorbents.

**Keywords:** Aluminium-based sludge, Drinking water treatment plant sludge, Carbon dioxide, Adsorption.
of CO₂ adsorption using dried fresh aluminium based waterworks sludge. The effects of adsorbate flow rate and concentration of adsorbate, temperature of adsorption and adsorbent dosage on the CO₂ uptake were investigated.

### EXPERIMENTAL

Aluminium based waterworks sludge was supplied by a local waterworks in Malaysia. It was dried in an oven at 110 °C for 24 h, cooled to room temperature and grounded using a mortar, sieved into 250-500 µm particle sizes and kept in an air tight container. High purity of carbon dioxide (99.99 %) and helium (99.99 %) gases were purchased from LINDE gas company.

**Adsorption experiments:** Aluminium based waterworks sludge adsorbent column was prepared by packing the adsorbent in a 200 mm × 20 mm glass column. Prior to adsorption, the column was heated at 100 °C for 30 min in helium gas flow (4 L/min). The temperature of the column was then adjusted to desired adsorption temperature and gas mixture sample (CO₂ in He) from the mixing chamber (250 mL of round bottom flask with 3 necks) was immediately passed through the adsorption column. The CO₂ detector (KANE 100-1, UK) was used to determine the influent and effluent CO₂ concentrations at 1 min interval. The concentrations of CO₂ were used to estimate the adsorption capacity, \( q \) (mg/g) [45], using eqns. 1 and 2.

\[
q = FC\frac{t_o}{W} \quad (2)
\]

where \( t_o \) is total time of sorption (min), \( C_o \) is CO₂ concentration fed into the fixed column (% v/v), and \( C_t \) is CO₂ concentration measured at the outlet of fixed-bed column (% v/v), \( F \) is feed flow rate (mL/min), \( W \) is adsorbent dosage (g), and \( t \) is time (min).

Table-1 shows the parameters studied while Fig. 1 shows the schematic diagram of experimental set-up of CO₂ adsorption.

The adsorption temperature range selected covers a typical post flue gas desulphurization range of 318-328 K and vehicle exhausts.

### RESULTS AND DISCUSSION

**Characterization of aluminium based waterworks sludge adsorbent:** Fig. 2a shows the SEM micrograph of aluminium based waterworks sludge adsorbent. The image shows that the sludge particles are of different form and type. Similar characteristics of waterworks sludge has been reported earlier [46]. The micrograph also showed that the sludge particles are in agglomeration forms. However, this surface morphology of aluminium based waterworks sludge particles are different compared to that of dewatered Irish alum sludge, ferric and alum water treatment residuals (FARs) and water clarifier sludge [47].

The EDX spectrum shows the peaks of Al, Si, O, K, and Fe at 1.5, 1.75, 0.5, 3.3 and 0.65 keV, respectively. Quantitative analysis of the data shows that the sludge consists of 27.62 % of Al, 9.48 % of Fe, 28.17 % of Si, 28.74 % of O and 5.98 % of K (Fig. 2b). High aluminium content in aluminium based waterworks sludge is expected as aluminium sulphate is used as coagulant for the water treatment. The presence of Si, O, K, and Fe may be originated from dissolved and suspended minerals in the raw water as a result of its interaction with rocks, organic matters, living organisms and atmosphere.

The FTIR spectrum of aluminium based waterworks sludge (Fig. 3) shows peaks at 3687, 3620, 3382, 1638, 1000, 790, 679, 522, 480 and 409 cm⁻¹. The water treatment residuals are mixtures of aluminum hydroxides and either iron or CaCO₃ that also contain sediments, activated carbon and/or polymers [31]. Based on the FTIR spectrum, the absorption bands of silica appear at 1000, 1500, and 480 cm⁻¹ which are attributed to asymmetric stretching vibration of Si-O-Si, symmetric stretching vibration of Si-O-Si and bending vibration of O-Si-O, respectively. The absorption bands of Al(OH)₃ at 500, 1638, and 3382 cm⁻¹ are corresponding with Al-O stretching vibration, bending vibration of water molecules chemically associated with Al(OH)₃ as well as OH stretching of Al(OH)₃, respectively.

### TABLE-1

**PARAMETERS INVESTIGATED IN THE CO₂ ADSORPTION**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (mL/min)</td>
<td>60</td>
</tr>
<tr>
<td>Concentration of CO₂ (% (v/v))</td>
<td>0.10</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>303</td>
</tr>
<tr>
<td>Adsorbent dosage (g)</td>
<td>10</td>
</tr>
</tbody>
</table>
The position and intensity of Si-O-Si stretching band (Fig. 3) gives an indication of the nature of silicate network. For amorphous silica, this peak occurs at approximately 1000 cm\(^{-1}\). Spectral bands at peaks 3687 and 3620 cm\(^{-1}\), corresponding to free hydroxyl ions of red ochre and kaolinite [48]. The peaks at 1543 and 1458 cm\(^{-1}\) could be due to bending vibration of water molecules of silica [49]. The peak at 998 cm\(^{-1}\) is probably due to Si-O-Al stretching vibration, while at 910 cm\(^{-1}\) may indicate the presence of Al-O-H stretching vibration of kaolinite and red ochre [48]. It can be observed that the peaks at 790 and 679 cm\(^{-1}\) are most probably due to symmetric stretching of Si-O of kaolinite and quartz [49,50]. Peak at 522 cm\(^{-1}\) matches to that of Si-O-Al of kaolinite and quartz [48]. The peak at 452 cm\(^{-1}\) is assigned as Si-O-Al stretching vibration of kaolinite [50], while the band at 409 cm\(^{-1}\) in spectrum shows the presence of Si-OH wagging mode of silica [49].

The sludge used was also characterized by TGA and its profile was reported in earlier publication [51]. The results showed that the sludge degrades in three stages. First degradation is attributed to the thermodesorption of physically adsorbed water molecules from the sludge while the second degradation may be attributed by the conversion of aluminium hydroxide and other metal hydroxides such as iron, silicon and potassium into their oxides and water as shown in eqns. 3-5, respectively. The aluminium hydroxide degrades at 150-200 °C and then continues to degrade until 550 °C [52].

\[
\begin{align*}
2\text{Al(OH)}_3 & \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \\
2\text{KOH} & \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \\
2\text{Fe(OH)}_3 & \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}
\end{align*}
\] (3) (4) (5)

The weight loss after 300 °C corresponds to silanol condensation [53]. The silanol condensation reaction during heating of sludge can be presented as given in eqn. 6:

\[
2\text{SiOH} \rightarrow \cdots -\text{Si}–\text{O}–\text{Si}– \cdots + \text{H}_2\text{O}
\] (6)

**CO\(_2\) adsorption studies**

**Effect of feed flow rate:** The effect of feed flow rates from 60 to 90 mL/min on CO\(_2\) adsorption was investigated at 303 K and the results are presented as breakthrough curves (Fig. 4a). The results revealed that the breakthrough is at shorter time for higher flow rate and this can be explained by the fact that residence time of the gas in fixed bed decreases as the flow rate is increased although the transport of CO\(_2\) molecules onto the sorbent surface is enhanced [54,55]. The adsorption capacities of 9.28, 5.54, 4.22 and 2.92 mg-CO\(_2\)/g were recorded at the flow rates of 60, 70, 80 and 90 mL/min, respectively (Table-2).

**Table-2**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Value</th>
<th>(q) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow rate (mL/min)</td>
<td>60</td>
<td>9.28 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>5.54 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.22 ± 0.41</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>2.92 ± 0.38</td>
</tr>
<tr>
<td>Initial feed concentration (%)</td>
<td>0.10</td>
<td>13.65 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>16.07 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>17.94 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>23.05 ± 0.16</td>
</tr>
<tr>
<td>Adsorption temperature (K)</td>
<td>303</td>
<td>10.64 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>8.500 ± 0.36</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>4.860 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>2.510 ± 0.23</td>
</tr>
<tr>
<td>Adsorbent dosage (g)</td>
<td>10</td>
<td>8.620 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>32.56 ± 0.07</td>
</tr>
</tbody>
</table>
Effect of CO₂ initial concentration: The effect of CO₂ initial concentration on adsorption of CO₂ by aluminium based waterworks sludge was investigated for various concentrations of CO₂ (0.1, 0.15, 0.02 to 0.3 % (v/v)) at 303 K and the adsorption capacities are 13.65, 16.07, 17.94 and 23.05 mg/g, respectively (Table-2), showing that increasing the initial concentration of CO₂ increases in the adsorption capacity. The breakthrough curves are displayed in Fig. 4b. The general pattern of the breakthrough curves, as expected, increase CO₂ initial concentration reduces the breakthrough time. This can be explained, as the influent concentration of CO₂ is increased, CO₂ loading rate also increases [45], thus enhances the amount of available CO₂ molecules for CO₂ adsorption by the column and subsequently reduces the saturation time [1]. On the other hand, molecules of CO₂ are dispersed at smaller rate due to the decrease of diffusion coefficient or mass transfer, hence reduces the breakthrough time [45].

Effect of adsorption temperature: Effect of adsorption temperature on CO₂ adsorption capacity of aluminium based waterworks sludge was studied from 303 to 353 K. The breakthrough curves (Fig. 4c) display the typical trend of effect on CO₂ adsorption capacity. It is observed that breakthrough time at lower adsorption temperature was longer as compared to that at the higher adsorption temperature, showing that the amount of CO₂ adsorbed per gram on aluminium based water-works sludge decreases with the increase of adsorption temperature.
The CO₂ adsorption capacities are 10.64, 8.50, 4.86 and 2.51 mg-CO₂/g at 303, 318, 328 and 353 K, respectively, as shown in Table-2. The adsorption capacity decreases 76.41 % when the adsorption temperature is increased from 303 to 353 K. The results also revealed that the adsorption of CO₂ using aluminium based waterworks sludge is an exothermic process which is favourable at lower temperature. The exothermic behaviour of aluminium based waterworks sludge adsorbent towards CO₂ is similar to that of diethanolamine activated alumina beads (DAAB) and MgO/Al₂O₃ applied for CO₂ capture [1,54]. This is due to the fact that increasing the temperature leads to an increase in kinetics energy of CO₂ molecules which enhances the diffusion rate of the molecules resulted in the decrease of the adsorption of CO₂ molecules on adsorbent.

Effect of adsorbent dosage: Fig. 4d shows the breakthrough time increases when the dosage is increased and hence adsorption capacity is improved. Table-2 shows that the adsorption capacities are 8.62 and 32.56 mg/g at sludge dosage of 10 g and 20 g, respectively. This finding is in accordance with the trend using modified activated alumina as CO₂ adsorbent [56].

Comparison of adsorption capacity of aluminium based waterworks sludge: The adsorption capacity of 20 g of aluminium based waterworks sludge for CO₂ adsorption at 303 K, feed flow rate of 60 mL/min, 0.10 % CO₂ concentration in the feed with balance of helium, with particle sizes of 250-500 μm was compared with other reported adsorbents (Table-3). The sorption capacity exhibited by aluminium based waterworks sludge was 32.56 mg/g (0.74 mmol/g) which was higher than carbon nitrogen enriched porous carbon used by previous workers [57]. The adsorption capacity of the sludge is comparable with activated UiO-66 [58]. However, the adsorption capacity of sludge is lower than that of DAAB and Zr-MOF [1,26].

Conclusion

Aluminium based waterworks sludge is found to be potential adsorbent for CO₂ emission reduction. Its adsorption capacity is high due to presence of aluminium hydroxide which enhance CO₂ chemisorption. Adsorption temperature, adsorbent dosage, flow rate and initial concentration of CO₂ affects the adsorption capacity of the adsorbent. The maximum adsorption capacity of 32.56 mg/g was found when the adsorption on 20 g of sludge was carried out with 0.10 v/v % of CO₂ at flow rate and adsorption temperature of 60 mL/min and 303 K, respectively.

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