In order to improve the portability of basic absorbents monoethanolamine (MEA) and glycine (Gly), both were supported on microporous activated carbon (AC). Chemical modification by alkali-metal ion exchange (of Li, Na, K) was carried out on Gly-based absorbents. All supported absorbents were subjected to CO2 absorption capacity (pure CO2) and selectivity (indoor level) tests. Textural and chemical characterizations were carried out on test sorbents. All impregnation brought about significant reduction of specific surface area and microporosity of the adsorbent. Depreciation in the textural properties was found to result to reduction in pure CO2 sorption. Contrarily, low-level CO2 removal capacity was enhanced as the absorbent dosage increases, resulting in supported 5 molar MEA in methanol solution. Adsorption capacities were improved from 0.016 and 0.8 in raw ACs to 1.065 mmol/g for MEA’s. Surface chemistry via X-ray photoelectron spectroscopy (XPS) of the supported sorbents showed the presence of amine, pyrrole and quaternary-N. In reducing sequence of potency, pyridine, amine and pyrrolic-N were noticed to contribute significantly to CO2 selective adsorption. Furthermore, the adsorption isotherm study confirms the presence of various SNGs heterogeneously distributed on AC. The adsorption mechanism of the present AC adsorbents favored Freundlich and Langmuir isotherm at lower and higher CO2 concentrations respectively.

Key words: Carbon dioxide, MEA, Glycine, Activated carbon, Pre-treatment, Adsorption, Selectivity

1. INTRODUCTION

Monoethanolamine (MEA) is a primary alkanolmine which by virtue of its alkalinity has a high affinity toward CO2. This has resulted in its popular use as CO2 absorbent from combustion processes (where CO2 exists at major levels of ca. 7-15%) such as power generation plants (D’Alessandro et al., 2010). Also, MEA has been reportedly used as a modifier for particulate scrubbing (Jo et al., 2012; Song et al., 2009; Knowles et al., 2006; Gray et al., 2005; Kumar et al., 2003). Alkanolamine molecules generally possess a pair of amino (-NH2) and hydroxyl (-OH) groups (Han et al., 2007). The characteristic -NH2 group gives MEA its basic property which has the ability to react with acidic gases such as CO2 (Caplow, 1968). Nevertheless, MEA has two major intrinsic limitations viz being in liquid phase hinders its applicability to indoor CO2 control and its characteristic pungent smell renders it unappealing for such application (Ahn et al., 2010). However, in our previous work, some degree of reduction in the poignant smell after metal-ion exchange was noticed (Lim et al., 2012).

Amino acids (AA) are N-bearing organic groups that exhibit similar physical and chemical properties as alkanolamines. Each AA molecule has its α-carboxyl carbon bonded to an amino group (-NH2), carboxyl group (-COOH), hydrogen atom and alky side chain (R). There are currently 20 different types of standard AA based on the type of the R group (Mckee and Mckee, 2004). When in aqueous solutions, AA is incapable of reacting with CO2 as the proton from its weakly ionized -COOH (producing a carboxylate) is transferred to the -NH2 (forming -NH3+) resulting in a zwitterion (which possesses both ‘+’ and ‘-’ polarities) (Holst et al., 2008; Lee et al., 2008). Researchers have purported a theory of zwitterions having comparatively excellent affinity toward acidic gases, both strong (SO2, NOx, H2S) and weak (CO2) (Lim et al., 2011; Mckee and Mckee, 2004). The absorption of CO2 by MEA and glycine has been evaluated and reported (Lim et al., 2012, 2011).

In order to avoid the inherent shortcoming of portability aforementioned, we attempted the use of microporous activated carbon (AC) as a support for both MEA and AA. The activation of the glycine’s -NH2 in aqueous solution was carried out by metal-ion exchange before supporting the basic solutions on AC. It was
expected that the activation would form an amino group which could induce a direct reaction with CO₂ as depicted in Fig. 1.

### 2. MATERIALS AND METHODS

Both the glycine (Gly) and alkali metal precursors (hydroxides of Na, Li and K) were reagent-grade procured from Daejeong Chemical, Korea while MEA was supplied by Yakuri, Japan. The pristine and modified absorbents were supported on a commercially available pelletized coconut shell-based AC (WSC-470) purchased from Calgon Corporation, USA. The AC has an average particle diameter of 4.05 ± 1.22 mm. Prior use, the raw AC (RAC) was copiously washed with deionized water (to rid it off of fines) and dried at 120 °C overnight. Based on the experimental plan (Table 1(a)), the first part involves doping of AA (amine concentration of 1-7 molar in aqueous medium) with specific amount of the alkali metal solution (1-5 molar) to initiate metal-ion exchange. For the second part (Table 1(b)), MEA (concentration of 1-7 molar) was prepared in 3 different solvents (without metal ion exchange). Each solution from both sections was subsequently supported on the pre-cleaned AC (AC : AA = 1 : 2 w/v). After mild agitation, the solvent was filtered off before drying the adsorbent at suitable temperature (10 °C below each solvent’s b.p) and store in an evacuated oven prior to further analyses.

After supporting the modified absorbents, changes in textural and chemical properties were investigated.

![Diagram of chemical modification process](image-url)

**Fig. 1.** Schematics showing the chemical modification process of glycine by cation exchange and its significance to CO₂ sorption.

### Table 1(a). Textural characteristics of RAC and glycine supported sorbents.

| Sample ID | AA content (Molar) | Sample description | Surface & pore properties |
|-----------|--------------------|--------------------|--------------------------|
|           |                    |                    | S BET\(^a\) Dp\(^b\) V pure\(^c\) V Meso\(^d\) V Micro\(^e\) FM/T\(^f\) |
| RAC       |                    | Pristine AC support| 1238.9 1.69 0.524 0.062 0.462 88.1 |
| AC-Gly    | 1 molar Gly        | AC+ 1 molar Gly    | 1165.8 1.75 0.511 0.067 0.444 86.9 |
| AC-LiG    | 1 molar Gly        | AC+ 1 molar Gly doped with Li | 1026.9 1.74 0.447 0.059 0.388 86.8 |
| AC-NaG    | 1 molar Gly        | AC+ 1 molar Gly doped with Na | 792.2 1.74 0.345 0.045 0.300 87.0 |
| AC-KG     | 1 molar Gly        | AC+ 1 molar Gly doped with K | 652.6 1.68 0.269 0.023 0.246 91.5 |
| AC-KG 2.5 | 2.5 molar Gly      | AC+ 2.5 molar Gly doped with K | 335.9 1.77 0.149 0.003 0.146 98.3 |
| AC-KG 5   | 5 molar Gly        | AC+ 5 molar Gly doped with K | 263.99 - - - - |

Note: “Gly” is the abbreviation for glycine-supported on AC while “G” is used for metal ion-exchanged glycine.

\(^a\)specific surface area, \(^b\)pore diameter, \(^c\)total pore volume, \(^d\)mesopore volume, \(^e\)micropore volume, \(^f\)fraction of micropore volume
Finally, the pure CO₂ sorption capacity was determined and compared with those reported (without AC support) in our previous work (Lim et al., 2012). Furthermore, the significance of the chemical modification and AC support to low-level CO₂ removal (from indoor spaces) was investigated.

Samples’ surface area and pore properties were examined using Belsorp II mini, BEL Japan, Inc while K-α Thermo-electron was employed for the X-ray photoelectron spectrometric (XPS) examination of the sorbent’s surface chemical properties.

CO₂ being a weak Lewis acid is known to have an appreciable affinity toward electron-rich sites such as surface nitrogen groups (SNGs). The absorbents (MEA and Gly) were used as wet N-rich agents while the AC was used to provide adequate surface area. Fig. 2 provides an overall experimental outline employed in this work.

Pure CO₂ adsorption test was carried out at both standard (ST = 273 K) and room (RT = 298 K) temperatures by supplying CO₂ at increasing concentration under Ar atmosphere (from vacuum to ambient pressure) using the BELsorp mini instrument. A well-calibrated self-assembled setup used in our previous works (Adelodun et al., 2014a, b; Lee et al., 2012) was used for the low-level CO₂ (3000 ppm) adsorption test.

3. RESULTS AND DISCUSSION

3.1 Textural Characterization

Along with sample ID and description, Table 1(a)
provides results of structural analysis of pristine (RAC) and modified/supported glycine and glycine salts while those of MEA samples are listed on Table 1(b).

In general, impregnation of chemical elements on the surface of porous AC pellets brought about depreciation to RAC’s textural properties in terms of $S_{BET}$ and $V_{pore}$. This has been attributed to the blockage of pores as they are occupied by the impregnants’ molecules (Xu et al., 2005). As expected, the derogation of the physical properties increases with the dopant’s concentration. From Table 1(a), it was found that the higher the atomic mass and radius of the alkali metal (K > Na > Li; 39, 23 and 6 g mol$^{-1}$; and 0.227, 0.187 and 0.152 nm respectively), the more intense is the surface derogation induced as evident in the decrease of both $S_{BET}$ and $V_{pore}$. With regard to the solvent used in the preparation of MEA solutions (Table 1(b)), organic solvents tend to induce lesser structural dilapidation despite methanol having a higher molecular weight than water. However, the significance of the molecular weight became obvious when AC doped with ethanol (AC-ME) showed higher drop in $S_{BET}$ and $V_{pore}$ than those comparatively impregnated with methanol (AC-MM). More so, the difference in volatility (determined by boiling point (b.p), i.e. W, 100 > E, 78.3 > M, 64.6 °C) during impregnation and desiccation is believed to contribute to the trend in lowering of the aforementioned textural properties. It was also observed that the lower the boiling point, the lesser the blockage of pores and hence, the higher the $S_{BET}$ and $V_{pore}$. Despite having an obviously much lower b.p than water, ethanol induced more profound blockage of the carbon’s micropore due to its higher molecular weight (Lim et al., 2013b). In this case, we could infer that the impact of molecular size on the structural properties of a microporous support is more significant than volatility.

According to IUPAC, pores with diameter less than 2 nm are classified as micropores. This is the domain where substantial absorption of CO$_2$ molecules occurs (Thompson and Dyer, 1985). As such, micropores greatly contribute to effective mass transfer of CO$_2$ molecules and ultimately become a determinant of absorption efficiency. The proportion of $V_{micro}$ (FM/T%) has been reported to be mainly responsible for CO$_2$ physisorption irrespective of the $S_{BET}$ or $V_{pore}$ (Adelodun et al., 2014a; b; Shafeeyan et al., 2010). As seen here, this property (FM/T%) is determined by the $D_p$, i.e. the narrower the $D_p$, the higher the FM/T%. Increase in concentration of the impregnants was found to increase the $D_p$ as the micropores were eroded, paving way for more functionalities to be tethered on the inner pore walls.

Despite the differences (when glycine was used) in the induced drop of surface and pore properties among the glycimates, all supported samples exhibit a microporous Type I isotherm of N$_2$ adsorption test at 77 K as shown in Fig. 3(a). Similar type was observed with samples treated with 1 molar MEA in different solvents, given in Fig. 3(b). From these figures, we observed that RAC’s smooth Type I isotherm trend was maintained irrespective of the dip in N$_2$ adsorption capacity
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(Lim et al., 2013b; Park et al., 2008). However, as illustrated in Fig. 3(c), increasing concentration of MEA in methanol (MM) resulted in complete blockage/erosion of the micropores, evinced as a Type II non-porous/macroporous isotherm. This high significant effect of M is due to its low molecular size and high volatility of the solvent, enabling its access to the micropores where it condenses (Park et al., 2007). By quantitation, the effect of high concentrations could be seen in Table 1(b) as there was no achievable \( V_{\text{pore}} \) value for AC-MM (7).

In order to ascertain this claim, an investigation into the micropore size distribution was carried out using MP plot (Fig. 4). It is obvious that both glycine- (Fig. 4(a)) and MEA (of low concentration)-supported (Fig. 4(b)) ACs still retained the microporous structure of RAC. In Fig. 4(a), it was observed that Li and K caused reduction at the narrow and wide ultramicropores (\(< 1 \text{ nm}\)) respectively while Na brought about a decrease across board as also seen in a previous work (Adelodun et al., 2014a, b). When compared to RAC and MEA-supported sorbents, glycine induced slight widening of pores while still retaining the dominance of the ultramicropores. However, pronounced drop in micropore volume was shown by MEA samples which was most pronounced with ethanol. This could be attributed to the solvent’s higher molecular weight and less volatility compare to methanol.

Upon increase in concentration of MM (Fig. 4(c)), a much profound reduction of micropores was observed especially in the region of the supermicropores (specifically \( D_p = 1-1.7 \text{ nm} \)). The intensity of the derogation increased with concentration leading to loss of microporosity as presented in Fig. 3(c). Also, the previously non-existing wider pores (\( D_p < 1.7 \text{ nm} \)) which now became evident were derived from the narrowing of neighboring, small mesopores by surface coating thereby resulting in the creation of pseudo-supermicropores (Gregg and Singh, 1982).

### 3.2 Chemical Characterization by XPS

Table 2 illustrates elemental quantitation of pristine and modified absorbent surfaces from XPS analysis. By comparison with RAC, all treated samples showed lowering of %C, indicating some level of derogation caused by surface etching of the pores as observed during textural analysis. Although RAC was found to be devoid of nitrogen content (%N), all modified and supported sorbents exhibited its presence, which was derived from the impregnation on MEA or glycine. Usually, increase in %N is prioritized, however any lowering of %O is also an indication of proper basification of the adsorbent.

Considering the glycine-doped samples, AC-Gly (without metal-ion exchange) sample showed the highest value for %N, whereas when compared to those ion-exchanged, Li tend to negatively impact the carbon structure as a significant drop of %C from 87.2 to 52.7 wt%. A corresponding increase in %O from 13.7 to 45.3 wt%, accompanied by lowering of %N from 3.6 to 2.0 wt% was also observed whilst no significant difference between the other two (AC-NaG and AC-KG). This is in agreement with reports made in previous
works (Lim et al., 2011a; Kumar et al., 2003; Mathonat et al., 1997).

With regard to MEA treatment, we found that the differences in the polarity and molecular weights of the solvent had no impact on the amount of incorporated nitrogen content. Since the results from textural analysis favored methanol amongst the solvents used, the dosage concentration of MM (MEA in methanol) was further upped to 2.5, 5 and 7 M. As expected, the increased concentration ensured improved %N which is believed to enhance the carbon’s basicity (Jang et al., 2009; Plaza et al., 2007). This in turn, could provide more sites for CO₂ binding, thereby enhancing its selective adsorption from low-level atmospheres (Adelodun et al., 2014a, b; Lim et al., 2012a; Arenillas et al., 2005).

The need to identify and quantify the impregnated SNG was imperative prior CO₂ adsorption test. Hence, the XPS-N peak was deconvoluted (N1s, 396-405 eV range). The deconvoluted peaks are depicted in Fig. 5. The SNGs found on the test samples are pyridine-type (BE = 398.4), amine (BE = 399.4), pyrrole (BE = 400.1),

Fig. 5. Deconvoluted N1s-XPS spectra of adsorbents (a) AC-G, (b) AC-LiG, (c) AC-NaG, (d) AC-KG, (e) AC-MM.
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Table 2. Elemental composition of the adsorbents obtained from XPS analysis.

| Samples     | Atomic contents (wt. %) |
|-------------|-------------------------|
|             | C  | O  | N  |
| RAC         | 90.9 | 8.5 | ND |
| AC-Gly      | 82.7 | 13.7 | 3.6 |
| AC-LiG      | 52.7 | 45.3 | 2.0 |
| AC-NaG      | 79.9 | 17.9 | 2.2 |
| AC-KG       | 80.1 | 18.0 | 1.9 |
| AC-MW(1)    | 86.5 | 11.1 | 2.4 |
| AC-ME(1)    | 88.2 | 9.3 | 2.5 |
| AC-MM(1)    | 86.2 | 11.2 | 2.6 |
| AC-MM(2.5)  | 88.3 | 8.1 | 3.6 |
| AC-MM(5)    | 85.7 | 10.1 | 4.2 |
| AC-MM(7)    | 85.7 | 9.8 | 4.5 |

Note: ND means “Not-detected” and it represents values less than 0.01.

quaternary-N (BE = 401.2), and pyridine-N oxides (BE = 402.4) (Biniak et al., 1997).

By overall quantitation, MEA tethered more SNGs than glycine. In counts-per-second (cps), the estimated sum area for the undeconvoluted peaks follow this trend: AC-MM (10,648.8) > AC-NaG (4,651.3) > AC-LiG (4,351.4) > AC-KG (3,509.3). After deconvolution, identified SNGs were quantified and presented in Fig. 6. Previous researches have shown that the lower the BE of the SNG, the higher its relevance and strength toward CO₂ sorption, making pyridine N the most desired in this case (Shafeeyan et al., 2010). Also from these studies, the presence of quaternary and oxygen-containing SNG (such as pyridine-N-oxide) was reportedly detrimental to the sorbent’s CO₂ capture efficiency (Adelodun et al., 2014a, b). This is due to the unavailability of the lone-pair of electrons in quaternary-N and the electro-withdrawing propensity of the pyridine-N-oxide. From our data, we found that there was no specific pattern in the distribution of these SNGs, neither could any trend be accorded to the atomic mass, solvent type nor the reactivity of the alkali metals. Generally, most AA were converted to pyrrolic-N as this was the most impregnated group, followed by amine (unconverted), then quaternary-N and lastly, pyridinic N and its oxides. The used of wet-impregnants has been attributed to the tethering of large amount of undesired quaternary-N (Adelodun et al., 2014a). This is due to the ease of percolation of these agents (unlike gas-phase amination) to the inner graphene layers where atomic carbons are substituted by nitrogen. This occurs via its 1S² free electro-pair involves in a dative covalent bonding with adjacent carbon atom thereby losing its ability to serve as a Lewis base. The significant lowering of the amount of pyridine-N oxide in AC-MM seems favorable, but this was accompanied in lowering of the desired pyridines and elevation in the concentration of the undesired quaternary-N. Judging by the available data, Gly impregnation performed better than MEA in this respect. Therefore, the metal ion-substitution performance follows the trend: AC-KG > AC-Na > AC-LiG. However, the relevance of these observations to the adsorption of different levels of CO₂ needed to be affirmed.

4. ASSESSMENT OF CO₂ ADSORPTION

4.1 Quantitation of Adsorption Amount

Pristine and supported AA were subjected to CO₂ adsorption tests in order to assess the relevance of both the chemical modification and AC support. Fig. 7 provides the comparison of CO₂ adsorption amount amongst the adsorbents. At a glance, it was noticed that chemical modification of the AC pellets resulted in reduction of adsorption capacity of pure CO₂ (Fig. 7(a)). This is attributed to the surface coverage and pore blockage by the absorbents as earlier found with textural properties assessment. This observation is similar to those reported by Xu (2003) and Park (2007) (Park et al., 2007; Xu et al., 2003). It has been initially reported that when the surface of AC is chemically modified by the chemical impregnation, there often exist reduction in the S BET and microporosity which would eventually deplete the adsorption capacity of the adsorbent (Adelodun et al., 2014a, b; Adelodun and Jo, 2013). However, such depreciation is often compensated for by enhanced selective remov-
al of the sorptive of interest (from low-level concentrations). Here, AC-LiG was the only sample that retains the pure CO$_2$ adsorption capability of RAC whilst increased concentration among showed stepwise decrease as well (Jang and Park, 2010). By comparison amongst the choice of solvents, methanol fair the most (AC-MM(1)) while ethanol (AC-ME(1)) proved the worst. This justified the choice of methanol in further examination as the concentration was optimized. As expected, adsorption at 273 K was higher than those at room temperature (298 K). This is generally characteristic of physical adsorption phenomena which are exothermic as they are favored at lowered temperature (Kim et al., 2010; Beruto et al., 1984). Exceptions to this were those samples with high concentrations of MM (i.e. AC-MM(5) and (7)). Here, we opine the occurrence of endothermic process while the possibility of a systematic error could not be entirely rule out as well, because the magnitude of the difference was not consistent with the concentration of the impregnants.

When compared to our previous work where these solutions were used for CO$_2$ absorption without support (Lim et al., 2012), we found that AC support significantly improved the CO$_2$ capture from 0.8 mmol/g (maximum value by Na-Gly) to ca. 2.2 mmol/g by AC-LiG, as shown in Fig. 7(a), being the maximum value obtained in current work.

Furthermore, the samples were tested for low-level (selective) CO$_2$ adsorption (Fig. 7(b)) and mirror image of the trend with pure CO$_2$ feed was observed. Almost all samples showed some improvement over RAC’s low-level adsorption capacity (0.016 mmol/g) except for AC-G, with which mere improvement upon ion-exchange treatment was noticed. Although, potassium
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(AKG) faired best amongst the alkali metals, increase in K concentration led to decrease in CO2 selective adsorption. From here, it is best to conclude that the investigative experiment of supporting metal-ion exchanged glycine on AC was a failure and not recommended as it neither improved the AC storage (pure CO2 capacity) nor selective separation (indoor CO2 control) abilities. As initially found with pure CO2 adsorption test, the choice of methanol faired best amounts the solvents used for preparing MEA (AC-MM > AC-ME > AC-MW) with an optimum concentration of 5 molar, as a depreciation was observed upon further concentration (i.e with 7 molar). This optimized sample (AC-MM(5)) recorded the highest 3000 ppm CO2 selective capacity of 1.065 mmol/g, an enhancement factor of ca. 66.6 compared to RAC. From this result, we infer that the choice of methanol as a solvent for preparing MEA solution, supported on AC is best suited for using the AA absorbent for scrubbing of indoor CO2 which wouldn’t have been possible if not for the AC support that improves portability and ease of handling.

By relating the CO2 adsorption results to the chemical characterization of supported adsorbents, it was observed that the absorption capacities of ACs modified with glycine substituted with alkali metal also increased accordingly with increase in surface basicity. Furthermore, it is deemed that the difference in absorption capacities despite of impregnation of identical 1 M glycine salt was influenced by the alkali metals, injected as substituents for activation of amines.

In inference, enhancement of basicity is responsible for chemical absorption of the sorptive as while pure CO2 absorption capacities is driven by available micropores, which is an important factor for physical absorption (Lim et al., 2013b; Diaz et al., 2008; Lee and Jo, 2008).

4.2 Adsorption Isotherm Study

Investigation into the adsorption pattern of newly fabricated sorbents is necessary in order to understand the trend of CO2 removal as the molecules collect onto the sorbent. Customarily, Langmuir (1916) and Freundlich (1906) isotherm models are primarily used to investigate the basis of most adsorption processes. They were therefore used in this work. The isotherm plots of CO2 adsorption at 273 and 298 K of selected samples are given in Fig. 8. Each sub-figure (8(a)-(f)) expresses the fitting of experimental adsorption data to
both models so as to understand the nature of the adsorbent’s surfaces as well as the mechanism of CO₂ separation at the interphase.

The isotherm model plots made from the fittings of experimental data of CO₂ adsorption for all samples are provided in supporting document (S1). All the samples showed a Type I isotherm. The fitting of representative samples are displayed in Fig. 8 with the extrapolated isotherm parameters provided in Table 3 (Refer to S2 for detailed parameters for all test samples). The error function used in this work is average relative error (ARE) due to its better robustness compared to the most conventional coefficient of determination (R²).

It was identified that the adsorption mechanism randomly follows either Langmuir or Freundlich model as evidenced by the obtained ARE values. Such irregularity does not enable a straight-forward conclusion for describing the sorption behavior of the samples based of their respective treatment methods. However, we noticed that the strength of adsorption (indicated by the magnitude of Kₙ and n) increases with decrease in qₘₐₓ. This is in agreement with the observation made during the quantitation of CO₂ adsorption amount at both pure and low levels. This shows that as the concentration of the active SNG increases, their distribution increases, heterogeneously covering more surfaces of the pore walls which led to lowering of CO₂ uptake at higher pressure (concentration). By comparing RAC with the sample with highest 3000 ppm CO₂ adsorption selectivity (AC-MM(5) in Fig. 7(d)), one could see a significantly high adsorption trend at low partial pressure (between 0-0.2 atm) which reached ca. 1.4 mmol/g (LNG_298 K). The adsorption trend was steady throughout the adsorption process despite of increasing CO₂ concentration, which indicates that all the available sites of adsorption had been occupied at P/Pₒ of about 0.05 (5000 ppm). When compared to sample with similar preparation concentration (i.e. AC-KG (5) in Fig. 5(c)), one would notice that despite both showing similar adsorption trend at maximum P/Pₒ, they exhibit quite different propensities at lower level. This was responsible for the exceptional low-level (3000 ppm) CO₂ adsorption prowess of AC-MM(5) sample over all others (Adelodun et al., 2014b).

Hence, the adsorption isotherm study confirms the presence of various SNGs which were heterogeneously distributed on AC, yet the non-conformity of the theoretical adsorption parameters suggest that the absorbents were simply coated on the AC and the CO₂ removal mechanism was not a clear-cut adsorption process. Although, the error estimation results favored Freundlich isotherm at lower CO₂ concentration while Langmuir is favored at high levels.

### 5. CONCLUSION

- The supporting of glycine and MEA on microporous activated carbon via wet impregnation method led to depreciation in the carbon’s specific surface area and microporosity as the nitrogen content was improved;
- Alkali metal-ion exchanged glycine evinced more depreciation in structural properties than other samples. As per the choice of solvent for the preparation of MEA, methanol was found most suitable. In most cases, there was degradation of S_BET and microporosity with AC-MM(7) and AC-KG(5) showing the worst physical properties;
- XPS analysis reveals that AC-KG possesses the most significant SNGs (pyridine and amine) for CO₂ adsorption;
- Pure CO₂ adsorption capacity of RAC was not improved by any treatment. However, supporting the absorbents on AC brought about a significant increase in CO₂ sorption (i.e from 0.8 mmol/g to 2.2 mmol/g) when compared with absorption results from our previous work. More importantly, low-level CO₂ adsorption was most significantly enhanced

### Table 3. Isotherm parameters obtained by fitting isotherm models to the experimental data.

| Temp. (K) | Langmuir | Freundlich |
|----------|----------|------------|
|          | kₙ       | qₘₐₓ      | ARE (%) | kₚ       | n          | ARE (%) |
| RAC      |          |           |         |          |            |         |
| 273      | 2.36     | 4.32      | 11.58   | 3.27     | 1.63       | 0.96    |
| 298      | 1.72     | 3.36      | 6.36    | 2.38     | 1.41       | 4.30    |
| AG-Gly   |          |           |         |          |            |         |
| 273      | 1.38     | 3.87      | 6.06    | 2.50     | 1.33       | 4.24    |
| 298      | 1.22     | 3.28      | 3.60    | 2.06     | 1.27       | 6.21    |
| AC-KG(5) |          |           |         |          |            |         |
| 273      | 3.39     | 1.36      | 7.92    | 1.18     | 1.83       | 4.16    |
| 298      | 3.70     | 1.03      | 15.59   | 0.88     | 1.80       | 3.37    |
| AC-MM(5) |          |           |         |          |            |         |
| 273      | 154.00   | 1.12      | 3.67    | 1.45     | 2.76       | 22.31   |
| 298      | 92.10    | 1.39      | 7.51    | 1.81     | 2.75       | 23.43   |
from 0.016 to 1.065 mmol.g by AC-MM(5) sample.
• The adsorption isotherm study shows the presence of heterogeneous distribution of various SNGs on AC resulting in inconclusive results, proving that the absorbents were simply coated on the AC and the CO₂ removal mechanism was not a clear-cut adsorption process. However, error estimation results revealed that Freundlich isotherm is more favored than Langmuir at low concentration and vice versa.
• Consequently, AC-MM(5) could be further improved as it shows to be the most efficient sample for the control of low-level CO₂ such as indoor scenarios.

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| Temp. (K) | Langmuir | Freundlich |
|----------|----------|------------|
|          | k_L     | q_max AER (%) | k_F  | n | AER (%) |
| RAC      | 273     | 2.36 4.32 11.58 | 3.27 | 1.63 | 0.96 |
|          | 298     | 1.72 3.36 6.36  | 2.38 | 1.41 | 4.30 |
| AG-Gly   | 273     | 1.38 3.87 6.06  | 2.50 | 1.33 | 4.24 |
|          | 298     | 1.22 3.28 3.60  | 2.06 | 1.27 | 6.21 |
| AC-LiG   | 273     | 2.32 4.09 8.66  | 3.35 | 1.42 | 8.76 |
|          | 298     | 2.04 3.21 8.83  | 2.48 | 1.40 | 6.51 |
| AC-NaG   | 273     | 3.19 3.10 14.28 | 2.60 | 1.73 | 1.58 |
|          | 298     | 1.66 2.98 6.31  | 2.11 | 1.39 | 4.22 |
| AC-KG    | 273     | 3.05 3.45 10.19 | 2.97 | 1.66 | 3.84 |
|          | 298     | 3.11 2.53 13.08 | 2.11 | 1.39 | 2.33 |
| AC-KG(2.5) | 273   | 3.35 2.51 8.37  | 2.19 | 1.77 | 4.46 |
|          | 298     | 3.94 1.57 19.04 | 2.14 | 2.31 | 5.83 |
| AC-KG(5) | 273     | 3.39 1.36 7.92  | 1.18 | 1.83 | 4.16 |
|          | 298     | 3.70 1.03 15.59 | 0.88 | 1.80 | 3.37 |
| AC-MW(1) | 273     | 4.04 1.95 18.62 | 1.70 | 1.92 | 3.80 |
|          | 298     | 3.70 1.86 19.92 | 1.51 | 2.06 | 4.45 |
| AC-ME(1) | 273     | 4.45 1.49 21.45 | 1.26 | 2.29 | 3.71 |
|          | 298     | 3.08 1.39 19.81 | 1.01 | 2.23 | 9.27 |
| AC-MM(1) | 273     | 1.38 3.34 7.55  | 2.07 | 1.41 | 0.89 |
|          | 298     | 4.81 1.91 17.89 | 1.49 | 3.03 | 10.62 |
| AC-MM(2.5) | 273   | 10.51 1.64 13.58 | 1.84 | 2.26 | 14.00 |
|          | 298     | 19.25 1.41 21.29 | 1.47 | 4.15 | 9.97 |
| AC-MM(5) | 273     | 154.00 1.12 3.67 | 1.45 | 2.76 | 22.31 |
|          | 298     | 92.10 1.39 7.51  | 1.81 | 2.75 | 23.43 |
| AC-MM(7) | 273     | 71.11 0.94 2.74  | 1.23 | 2.44 | 24.09 |
|          | 298     | 97.69 1.03 2.58  | 1.31 | 2.55 | 21.73 |
Fig. 15. Correlation of experimental data for CO₂ adsorption isotherms; LNG: Langmuir equation, FRD: Freundlich equation. (a) RAC, (b) AC-Gly, (c) AC-LiG, (d) AC-NaG, (e) AC-KG(1), (f) AC-KG(2.5), (g) AC-KG(5), (h) AC-MW(1), (i) AC-ME(1), (j) AC-MM(1), (k) AC-MM(2.5), (l) AC-MM(5), (m) AC-MM(7)).
Fig. 1S. Continued.