A Systematic Review of Amino Acid-Based Adsorbents for CO₂ Capture

Nur Syahirah Mohamed Hatta 1, Mohamed Kheireddine Aroua 1,2,3, Farihahusnah Hussin 1,3,* and Lai Ti Gew 3,4

1 Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Engineering and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia; nur.m227@sunway.edu.my (N.S.M.H.); kheireddine@sunway.edu.my (M.K.A.)
2 Department of Engineering, Lancaster University, Lancaster LA1 4YW, UK
3 Sunway Materials Smart Science and Engineering (SMS2E) Research Cluster, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia; janeg@sunway.edu.my
4 Department of Biological Sciences, School of Medical and Life Sciences, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia
* Correspondence: fariah@sunway.edu.my

Abstract: The rise of carbon dioxide (CO₂) levels in the atmosphere emphasises the need for improving the current carbon capture and storage (CCS) technology. A conventional absorption method that utilises amine-based solvent is known to cause corrosion to process equipment. The solvent is easily degraded and has high energy requirement for regeneration. Amino acids are suitable candidates to replace traditional alkanolamines attributed to their identical amino functional group. In addition, amino acid salt is a green material due to its extremely low toxicity, low volatility, less corrosive, and high efficiency to capture CO₂. Previous studies have shown promising results in CO₂ capture using amino acids salts solutions and amino acid ionic liquids. Currently, amino acid solvents are also utilised to enhance the adsorption capacity of solid sorbents. This systematic review is the first to summarise the currently available amino acid-based adsorbents for CO₂ capture using PRISMA method. Physical and chemical properties of the adsorbents that contribute to effective CO₂ capture are thoroughly discussed. A total of four categories of amino acid-based adsorbents are evaluated for their CO₂ adsorption capacities. The regeneration studies are briefly discussed and several limitations associated with amino acid-based adsorbents for CO₂ capture are presented before the conclusion.

Keywords: CO₂ capture; CO₂ adsorption; amino acid; solid sorbent

1. Introduction

An increasing trend of global carbon dioxide (CO₂) emissions has become a major concern that affects global warming in the economic recovery phase following the COVID-19 pandemic. According to the report by Global Energy Review 2021, the global energy-related CO₂ emission was projected to increase by 4.8% in 2021 from 31.5 GtCO₂ to 33.0 GtCO₂ in 2020, driven by a growing demand for coal, oil, and gas [1]. The Global Carbon Budget 2021 estimated the total anthropogenic emission to reach 39.4 GtCO₂ in 2021—an increase of 1.4 GtCO₂ in comparison to 38.0 GtCO₂ in 2020 [2]. The Sustainable Development Goal 13 (SDG13: Climate Action) set by the United Nations has highlighted the aim to secure global net zero carbon emissions by 2050 by limiting the rise of global temperature to 1.5 °C by 2030 [3]. Carbon capture and storage (CCS) technology plays an important role in addressing the CO₂ emissions from point sources [4] since the first CCS project was implemented for natural gas processing in 1972 [5]. Most CCS technology could reduce nearly 85–95% of CO₂ produced by a power plant [6]. Nevertheless, this relatively high percentage of CO₂ reduction will contribute only up to 21% of the reduction from the global CO₂ emissions [7], indicating a clear need to improve the current CCS technology.
In general, CCS technology involves three main processes, namely (1) the separation of CO$_2$ from the flue gas stream, (2) the transportation of the captured CO$_2$, and (3) the CO$_2$ sequestration or storage (the process of storing CO$_2$, typically by ocean storage or industrial fixation into carbonates) [6]. Pre-combustion, post-combustion, and oxyfuel combustion are three basic approaches of CCS. Pre-combustion CO$_2$ capture occurs before the combustion process by converting the fuel into a mixture of CO and H$_2$ through gasification and the reforming process. The products will then use the water–gas shift reaction in the presence of water vapour and steam supplied to produce CO$_2$ and H$_2$, which is ready to be separated, compressed, and transported for sequestration [7,8]. This approach utilises less energy and water consumption compared to post-combustion but poses high auxiliary system requirement, which increases the overall plant cost [9–11]. Post-combustion CO$_2$ capture occurs after the combustion process by means of several separation techniques such as absorption using liquid solvents, membranes, and cryogenics, and adsorption using solid materials and calcium looping cycle [12]. Adsorption has several advantages, such as easy operation, low operating cost, low energy penalty, and less corrosion issue compared to chemical absorption [13]. However, the development of adsorbent material with high adsorption capacity that can compete with conventional absorption methods remains an open challenge. Calcium looping (CaL) is an alternative option that has continuously gained attraction for post-combustion CO$_2$ capture. The method involves two steps: (1) carbonation, where the calcium oxide (CaO) reacts with CO$_2$ from flue gas to produce calcium carbonate (CaCO$_3$), and (2) calcination, where the solid CaCO$_3$ is calcined to regenerate the CaO. The regenerated sorbent will be fed back into the carbonator and the whole process continues repeatedly (looping) [14]. Although a high purity of CO$_2$ can be achieved by this method, the operating temperature, especially for the regenerator (calciner) is very high (900 $^\circ$C) [14]. In addition, the amount of NO$_x$ emissions should be taken into consideration as the heat source for the regenerator is commonly supplied through the oxyfuel combustion of coal [15].

Oxyfuel combustion CO$_2$ capture consumes pure oxygen to burn fossil fuels during the combustion process instead of air. This approach can produce flue gas with high CO$_2$ concentration in exchange with high capital cost and energy demand for air separation unit [8]. To date, pre-combustion and post-combustion CO$_2$ capture have been well-established at full-scale plants, while oxyfuel combustion capture is still limited to pilot-scale operations [11]. Apart from these three basic approaches, chemical looping is another emerging CO$_2$ separation technique, which can be viewed as an advanced form of oxyfuel combustion [16]. This approach offers indirect combustion of air with the aid of a metal oxide, typically copper oxide (CuO) as a solid oxygen-carrier, thus removing the need for an expensive air separation unit [17]. However, the process development is still in its early phase, which requires extensive research for future large-scale operation [17,18]. It is noteworthy that direct CO$_2$ capture from the atmosphere is also essential, although most CCS technology is focused on reducing the CO$_2$ from point sources and industries. Recently, an interesting review by Krzywanski et al. [19] reported that over 3.5 billion tonnes of CO$_2$ per annum can be captured directly from the atmosphere through walls and roofs covered with ivy plants via a photosynthesis reaction. The excellent properties of ivy plants that require low maintenance and are easily adapted in various climatic zones make the technology a potentially sustainable method for CO$_2$ capture, with zero harmful effects on humans and the environment [19,20]. Table 1 compares the advantages and disadvantages of the aforementioned technology for CO$_2$ capture.
Table 1. Summary of advantages and disadvantages of various carbon capture technology.

<table>
<thead>
<tr>
<th>Carbon Capture Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Refs</th>
</tr>
</thead>
</table>
| Pre-combustion            | • Well-established technology;  
• Removal of CO$_2$ from fuels occurs before the combustion and is completed using partial oxidation;  
• Low energy demand for CO$_2$ separation process due to high CO$_2$ concentration;  
• Less water consumption compared to post-combustion. | • High capital and operating costs compared to conventional coal plants due to complex installation and high auxiliary system requirement;  
• Plant shutdown may be required in case of process failure, feed problems and corrosion;  
• Limited commercial availability of integrated gasification combined cycle (IGCC). | [9–11] |
| Post-combustion           | • Widely adopted in chemical processing industries and coal-fired plants;  
• Captures CO$_2$ from flue gas after combustion by physical or chemical processes (absorption, adsorption, membrane, cryogenic, and calcium looping);  
• Easily retrofitted to existing power plants (cost-effective);  
• Resulted in lowest impurities content compared to pre- and oxyfuel combustion. | • Low CO$_2$ concentration affects the capture efficiency;  
• Pre-treatment is essential to minimise oxides (NOx and Sox), water vapour, and particulate matter from the gas stream;  
• Large equipment and cooling systems requirement due to high temperature (120–180 $^\circ$C) and low partial pressure of CO$_2$ (~0.15 bar) in the gas stream. | [9,10,21–24] |
| Oxyfuel combustion        | • Commonly applied for the pulverized coal (PC) and circulating fluidised bed (CFB) boilers;  
• This technology uses pure oxygen to burn the primary fuel to produce a flue gas with high CO$_2$ concentration;  
• Low temperature purification process;  
• Cost-effective and simple in process as well as able to achieve high CO$_2$ removal efficiencies. | • High-efficiency drops, energy penalty, costly, and corrosion problem may also arise;  
• No full-scale establishment to date. | [11,25,26] |
| Chemical looping combustion| • Applicable for CO$_2$ capture with variety of gaseous, liquid, and solid fuels;  
• Fuel is combusted without direct contact with air using solid oxygen carrier (metals such as CuO)—less energy demand for air separation) and low parasitic load;  
• Substantially reduced energy penalty when integrated with membrane-assisted chemical looping reforming technology. | • Highly endothermic nature of the gasification process;  
• High capital cost of gasification unit due to high requirement of gasification rate;  
• The process is still under development and not suitable for large-scale operation. | [14,17,18,27] |
Table 1. Cont.

<table>
<thead>
<tr>
<th>Carbon Capture Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Refs</th>
</tr>
</thead>
</table>
| Calcium looping combustion (Post-combustion) | - Suitable for coal-fired combustors;  
- CO₂ separation process occurs via carbonation reaction between CaO and CO₂ to form carbonates (CaCO₃);  
- Low cost of natural limestones and dolomites;  
- Improved flexibility of CO₂ process for retrofitting option and has high potential for scale-up. | - Extremely high temperature capturing (600–700 °C) and regeneration (calcination) (900 °C) processes;  
- Nox emission from regenerator is relatively high;  
- No full-scale establishment to date. | [14,15,28–31] |
| Direct air capture by photosynthesis (Mainly focused on virgin ivy plants) | - CO₂ capture process occurs directly from the atmosphere through walls and roofs covered with plants, algae, cyanobacteria;  
- High adaptability of ivy plants widen its applicability in various climatic zones;  
- Safe and clean technology. | - Different ivy species have unique strategies of climbing (to vertical or horizontal surfaces) that may cause negative effect on building structure;  
- Limited amount of CO₂ captured depending on the area of greenery and plant type. | [19,20,32]     |

To date, the most mature and scalable technology in CCS is post-combustion CO₂ capture associated with chemical absorption using alkanolamines, also known as amine technology, despite its high regeneration energy and capital investment cost [33]. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are still preferred in most industries [34]. Adsorption by solid sorbent can be a viable alternative for removal of CO₂, which could eliminate corrosion problems and substantially reduce regeneration energy requirements faced by the conventional amine system [35,36]. There are several types of solid material that can be used as adsorbents for CO₂ capture; for instance, activated carbon, zeolite, molecular sieve, silica (mesoporous or nanoporous), nanoparticle, metal oxides framework, and graphene [37]. However, each type of adsorbent has its own limitations and shortcomings. Adsorbent with porous carbon materials is required to produce high CO₂ adsorption performance because it possesses high specific surface, high porosity, easy surface functionalisation, and is able to achieve high adsorption capacity [38]. Furthermore, surface modification by physical or chemical activation method is needed to enhance the physical and chemical properties of porous carbon material. Chemical activation is commonly used to produce better surface modification of porous carbon material and to enhance CO₂ adsorption capacity [39]. The selection of activating agent is important in the synthesis and modification of solid carbon material. Activating agents have great influence on pore development and the enhancement of surface characteristics of adsorbent. Developing a green activating agent which could both produce a high adsorption capacity and does not bring harm to the environment and human health is needed.

Amino acid-based solvents have attained considerable attention to be used as an activating agent to modify surface properties of adsorbents due to several advantages, such as high biodegradability, no formation of toxic intermediates, low volatility, high resistance towards thermal and oxidative degradation, high surface tension, and less corrosion issues [40,41]. In addition, amino acids contain both an amino group (similar to conventional amines) and a carboxyl group, which contribute to the effective adsorption of CO₂ [42]. Amino acid salt can be used directly as an activating agent for solid material.
Alternatively, it can be modified by combining with ionic liquids, inorganic strong alkali, and organic amine-based solvent, or used as an adding activator to enhance amino acid performance. Then, modified amino acid will be impregnated with solid material to produce an effective adsorbent to capture CO\(_2\). The precipitation formation at a high concentration of amino acid, due to its low solubility in aqueous solution, creates a limitation because it potentially causes a decrease in mass transfer and damage to equipment. In a positive view, the precipitation could also bring reduce the energy requirement of the regeneration system [40]. There are many studies reported on the performance of various types of amino acid salts, comparing their physical and chemical properties, exploring their absorption kinetic abilities and discussing their CO\(_2\) absorption performance [40–42]. Nonetheless, there is a lack of studies that focus on the performance of amino acid-based solid sorbent for CO\(_2\) adsorption. Table 2 summarises the overview of recent available reviews reported for CO\(_2\) absorption and literature studies for CO\(_2\) adsorption in the field of CO\(_2\) capture using amino acid.

<table>
<thead>
<tr>
<th>Most Available Studies Reported on the Utilisation of Amino Acid as Capturing Agent for CO(_2) Absorption</th>
<th>Lack of Studies Focus on Performance of Amino Acid-Based Solid Sorbent for CO(_2) Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary of review: Detailed studies on the reaction kinetics of amino acid and performance of amino acid as capturing agent in CO(_2) absorption. Reported by Sang Sefidi and Luis [43];</td>
<td>Summary of literature studies (research articles) performed on CO(_2) adsorption using amino acid as solid sorbent such as:</td>
</tr>
<tr>
<td>Summary of review: Discussed physicochemical properties of 20 amino acids as alternative solvent for CO(_2) absorption. Reported by Ramezani et al. [40];</td>
<td>• Hiremath et al. [45] developed novel adsorbent by modifying silica with amino acid functionalised ionic liquids to increase adsorption capacity of CO(_2);</td>
</tr>
<tr>
<td>Summary of review: Focused on the absorption kinetics and industrial challenges for applying amino acid solvent in large-scale processes. Reported by Hu et al. [44];</td>
<td>• Reported by Pires et al. [46], modified montmorillonite clay with amino acids for enhancing adsorption capacity;</td>
</tr>
<tr>
<td>Summary of review: Discussed thermodynamics study and absorption kinetics of various types of amino acid for CO(_2) capture. Reported by Zhang et al. [42].</td>
<td>• Uehara et al. [47] investigated the textural properties and adsorption performance of mesoporous silica impregnated with amino acids;</td>
</tr>
<tr>
<td></td>
<td>• Huang et al. [48] modified mesoporous silica surfaces using amino acid ionic liquid to enhance its CO(_2) adsorption capacity.</td>
</tr>
</tbody>
</table>

**Scope of this Review**

The specific objectives of this review are as follows:

- To provide information on the physical and chemical properties of amino acids associated with their contribution as CO\(_2\) capturing agent for enhanced CO\(_2\) adsorption performance of solid sorbents after the surface modification process (Section 3.1).
- To summarise the currently available amino acid-based adsorbents and to compare their CO\(_2\) adsorption capacities upon being immobilised into solid materials. In this review, the amino acid-based adsorbents were classified into four adsorbent categories according to the existing form of modified amino acids: (1) amino acid ionic liquid (AAIL), (2) solid amino acid or amino acid salt, (3) strong alkaline amino acid salt, and (4) amino acid blended with amine solvent (Section 3.2).

It is important to note that this review uses specific keywords for searching the literature, and that the search has been conducted by following an established method for systematic review (Section 2), namely Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA). Although it is widely used among researchers, this method has a limitation in that some of the related articles that do not have the matched keywords in the title or abstract might be omitted.

This systematic review presents up-to-date findings on the state-of-the-art adsorption technology using amino acid-based adsorbent in the field of CO\(_2\) capture. Amino acid is naturally non-toxic and has been reported as one of the potential green solvents. The application of amino acid as an activating agent could enhance the solid material properties,
leading to high adsorption capacity. There is little existing literature that reports on the performance of amino acid-based adsorbents, and none with a systematic or comprehensive review. It is worth mentioning that there is one recent publication signifying the potential of amino acids as promising ligands for synthesis of bio-based metal organic frameworks (Bio-MOFs) [49].

The information provided in the present review will be beneficial for researchers who are doing their studies in this field. In addition, this systematic review will provide a guideline for future research and help a wide range of readers including academicians, researchers, and industry professionals to gain a better understanding on the current research topic. The challenges and limitations of the technology related to amino acid-based adsorbents are briefly discussed in Section 4.

2. Review Methodology

2.1. Information Sources and Search Methods

The methodology adopted for this study followed a standard guideline for conducting a systematic review, namely Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) [50]. The first step was to refer to the search strategy to compile all the published journal articles related to the concerned topic. This study aimed to review all the scientific information on the application of amino acids in CO$_2$ capture by adsorption from 2012 to 2022. Based on the topic “amino acid-based adsorbents for CO$_2$ capture”, two categories of keywords were selected, which are: (category 1) for the field of application (carbon capture) and (category 2) the type of capturing agent used for the application (amino acid-based adsorbents). These keywords were then combined with Boolean operators and truncation symbol (*) to develop a “search string”. Search string was used to provide better input and information suitability, in relevance to the aim of this review paper. Table 3 summarises the selected keywords and the developed search string that was used to search for the relevant articles from two databases, namely Web of Science and Scopus. The search outcome showed a limited number of studies previously conducted on this topic over the past ten years; the figure was between 412 and 488 publications, thus indicating the significance of conducting this systematic review.

Table 3. Selection of keywords and search string for literature search.

<table>
<thead>
<tr>
<th>Keywords (category 1)</th>
<th>Carbon dioxide capture; carbon capture; CO$_2$ capture; CO$_2$ adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keywords (category 2)</td>
<td>Amino acid; adsorbent; solid sorbent</td>
</tr>
<tr>
<td>Search string used in database Web of Science</td>
<td>ALL = (“Carbon dioxide capture*” OR “Carbon capture*” OR “CO$_2$ capture*” OR “CO$_2$ adsor*”) AND “amino acid*”)</td>
</tr>
<tr>
<td>Search string used in database Scopus</td>
<td>TITLE-ABS-KEY(“Carbon dioxide capture*” OR “Carbon capture*” OR “CO$_2$ capture*” OR “CO$_2$ adsor*”) AND “amino acid*”)</td>
</tr>
</tbody>
</table>

Note: Truncation symbol (*) at the end of a term allows it to be searched in both singular and plural nouns.

Figure 1 presents the number of documents published annually. An almost similar trend can be observed from both databases, in which the number of documents increased from 2012 to 2019 and then started to decrease slightly, which could be due to the lack of research activities during the COVID-19 pandemic. Nevertheless, the number of documents published in recent years (excluding 2022) is still high, thus highlighting the relevance of the topic that will be discussed in this review.
2.2. Eligibility Criteria for Screening Process

Figure 2 shows the PRISMA flowchart of this review for searching and screening of the literature studies. The second step of the PRISMA method after keyword-based search is the screening process, which is further divided into two steps. The first screening process was performed by automation in each database system (Web of Science and Scopus). The articles’ information was then exported in CSV format file using Microsoft Excel to remove any duplicate publications. The selected articles was restricted to only research articles published in the English language from 2012 to 2022, up to February 20. Reports in the form of conference papers, conference reviews, proceeding papers, review articles, book chapters, data papers, meeting abstracts, early access, and editorial materials were excluded. The second screening process was conducted by reading the title and abstract of each record, and excluding those articles that are irrelevant to the specific topic (application of amino acid for CO\textsubscript{2} capture via adsorption technology). The full-text reports obtained after the screening (n = 49) were assessed independently for eligibility. The following information was extracted: physical and chemical properties of amino acid functionalised adsorbents, adsorption isotherm, thermodynamic, CO\textsubscript{2} adsorption capacity, and regeneration studies.

Records identified from databases:
- Web of Science (n = 488)
- Scopus (n = 412)

First screening process:
- Records screened (n = 900)

Second screening process:
- Records screened by title and abstract (n = 514)

Full-text reports assessed for eligibility (n = 49)

Total studies included in this review (n = 41)

Reports excluded:
- Duplicate records (n = 227)
- Non-English articles
  - Web of Science (n = 2)
  - Scopus (n = 12)
- Publication year before 2012
  - Web of Science (n = 30)
  - Scopus (n = 47)
- Non-journal articles
  - Web of Science (n = 108)
  - Scopus (n = 70)

Reports excluded:
- Not related to amino acid-based adsorbents (n = 465)

Reports excluded:
- Not related to amino acid-based adsorbents (n = 8)

Figure 2. PRISMA flowchart for searching and screening literature.
2.3. Co-Occurrence of Keywords Analysis

Selecting and analysing keywords is an important part of a research paper and another way to identify research gaps in related fields. This might be beneficial to researchers to manoeuvre the research direction, and it gives an idea as to which topic or field needs to be emphasised upon. It also gives an idea as to which topic requires new research, particularly in the field of amino acid-based adsorbents for CO\(_2\) capture. The analysis also helps in highlighting the hotspot areas of the research in a specific field. In this study, VOSviewer version 1.6.17 was used to generate a keyword co-occurrence network. The threshold for each keyword occurrence was 15. The top 10 most used keywords extracted from Scopus between 2012 and February 2022 are ‘carbon dioxide’, ‘amino acids’, ‘amino acid’, ‘co2 capture’, ‘ionic liquids’, ‘absorption’, ‘solvents’, ‘carbon capture’, ‘ethanolamines’, and ‘amines’. In Figure 3, each keyword is represented as a circle or a node. The larger the circle or node, the greater the weight (frequency of keyword occurrence), demonstrating the number of publications in which these keywords appeared. Node colours show that the keywords were categorised under the same cluster or group. A group with the highest number of keywords will be assigned as the first cluster (Cluster 1), which highlight the hottest spot of the research area. The connection of each of the keywords to other keywords is represented by a curve. Thicker lines provide information on the link strength of the co-occurrence of two connected keywords, indicating the number of scientific articles in which the keywords appeared together. The distance between the keywords indicates the relatedness of the keywords. In general, the closer two keywords are located to each other, the stronger the relatedness of these keywords. It is important to mention that a smaller number of keywords in one group or cluster indicate a smaller number of publications, and there is a chance that the researcher needs to venture in this field. Based on the keywords analysis, it demonstrated that only a few publications discussed amino acid-based adsorbents and that more research is needed on this topic.

In Figure 3, there are four clusters identified which are: (1) the application of amino acids in CO\(_2\) absorption, (2) studies on kinetics between amino acid and CO\(_2\) in gas–liquid system, (3) enzyme-based CO\(_2\) capture, and (4) the application of amino acids in CO\(_2\) adsorption. The distance between the keywords in Cluster 4 is far away from each other compared to the keywords in Cluster 1 and Cluster 2, which belong to CO\(_2\) absorption. The results clearly highlight the gap in the field of CO\(_2\) capture using amino acid. The occurrence of keywords ‘silica’ and ‘amino acid ionic liquids’ in the adsorption cluster shows that most publications reported for CO\(_2\) capture via adsorption utilised amino acid ionic liquids in modifying the properties of solid sorbent, most likely to be silica. Interestingly, six out of ten most-cited articles are related to amino acid ionic liquid immobilised into porous solid materials (Table 4). The other four articles reported on the development of new amino acid-based adsorbents using different approaches such as direct heating into mesopore channels \[51\], forming amino acid-complex with surfactant or polymer \[52\], adding amino acid ligand for chiral metal organic framework (MOF) \[53\], and thermal polymerisation \[54\]. This finding strongly suggests that the potential application of amino acid-based adsorbents for CO\(_2\) capture is fairly recognised.
Amino Acid as CO2 Capturing Agent

Alkanolamines are popular absorbents in conventional technology for CO2 capture from gas processing, mostly primary and secondary amines attributed to their amino group that can react rapidly with CO2 to form carbamates [55]. However, an amine-based absorbent has several drawbacks such as high regeneration energy and corrosion problem. Amino acids (AAs) are gaining more attention lately, as they can eliminate the corrosion problem and reduce the cost associated with high energy requirements for solvent regeneration [56]. In addition, investigations on CO2 capture by using AA-based solid sorbents have been considerably less than amine-based solid sorbents. AA has similar amine (-NH2) functional group to alkanolamine, hence similar reactions are expected to occur between the CO2 and amino groups of the compound [57]. Furthermore, the toxic level of AA-based solvent was reported to be none or much lower than amines depending on the type of solvent incorporated with the amino acid, which makes them ideal as an environmentally friendly CO2 capturing agent. It is important to understand the physical and chemical properties of the AA in order to capture CO2 effectively, regardless of whether they are being used as liquid absorbent or functionalised solid adsorbents.

Table 4. Top ten most-cited articles in the field of amino acid-based adsorbents for CO2 capture.

<table>
<thead>
<tr>
<th>Title</th>
<th>First Author</th>
<th>Year</th>
<th>TC a</th>
<th>TC b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino acid-functionalized ionic liquid solid sorbents for post-combustion carbon capture.</td>
<td>Wang, X.</td>
<td>2013</td>
<td>96</td>
<td>90</td>
</tr>
<tr>
<td>Preparation and CO2 sorption/desorption of N-(3-aminopropyl)aminoethyl tributylphosphonium amino acid salt ionic liquids supported into porous silica particles.</td>
<td>Ren, J.</td>
<td>2012</td>
<td>88</td>
<td>85</td>
</tr>
<tr>
<td>Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO2 capture.</td>
<td>Wang, X.</td>
<td>2013</td>
<td>83</td>
<td>76</td>
</tr>
<tr>
<td>Highly reversible CO2 capture using amino acid functionalized ionic liquids immobilized on mesoporous silica.</td>
<td>Hiremath, V.</td>
<td>2016</td>
<td>59</td>
<td>57</td>
</tr>
<tr>
<td>Carbon-supported ionic liquids as innovative adsorbents for CO2 separation from synthetic flue-gas.</td>
<td>Erto, A.</td>
<td>2015</td>
<td>47</td>
<td>43</td>
</tr>
<tr>
<td>Development of amino acid and amino acid-complex based solid sorbents for CO2 capture.</td>
<td>Jiang, B.</td>
<td>2013</td>
<td>46</td>
<td>43</td>
</tr>
<tr>
<td>Post-combustion CO2 capture: On the potentiality of amino acid ionic liquid as modifying agent of mesoporous solids.</td>
<td>Balsamo, M.</td>
<td>2018</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Sustainable Preparation of Bio-Based Polybenzoxazine Resins from Amino Acid and Their Application in CO2 Adsorption.</td>
<td>Shi, W.</td>
<td>2019</td>
<td>23</td>
<td>23</td>
</tr>
</tbody>
</table>

TC a and TC b = total citations (TC) from database Scopus and Web of science, respectively.
3. Amino Acid as CO\(_2\) Capturing Agent

Alkanolamines are popular absorbents in conventional technology for CO\(_2\) capture from gas processing, mostly primary and secondary amines attributed to their amino group that can react rapidly with CO\(_2\) to form carbamates [55]. However, an amine-based absorbent has several drawbacks such as high regeneration energy and corrosion problem. Amino acids (AAs) are gaining more attention lately, as they can eliminate the corrosion problem and reduce the cost associated with high energy requirements for solvent regeneration [56]. In addition, investigations on CO\(_2\) capture by using AA-based solid sorbents have been considerably less than amine-based solid sorbents. AA has similar amine (\(-\text{NH}_2\)) functional group to alkanolamine, hence similar reactions are expected to occur between the CO\(_2\) and amino groups of the compound [57]. Furthermore, the toxic level of AA-based solvent was reported to be none or much lower than amines depending on the type of solvent incorporated with the amino acid, which makes them ideal as an environmentally friendly CO\(_2\) capturing agent. It is important to understand the physical and chemical properties of the AA in order to capture CO\(_2\) effectively, regardless of whether they are being used as liquid absorbent or functionalised solid adsorbents. In this review, the role of AA as CO\(_2\) adsorbent will be discussed. Moreover, AA can combine with amine group, ionic liquid, and alkali solvent to produce a highly efficient adsorbent to capture CO\(_2\).

3.1. Physical and Chemical Properties of Amino Acid-Based Adsorbents

3.1.1. Molecular Weight and Protonation Constant

Table 5 summarises the molecular weight (MW) and protonation constant (pKa) of 20 basic amino acids (AAs). These two parameters have strong influence in the reaction performance of sorbents with CO\(_2\). For amine-modified CO\(_2\) adsorbent, a low MW adsorbent demonstrated slightly higher CO\(_2\) uptake compared to the one with high MW [58]. A similar trend is expected for the AA-based adsorbents due to identical amino functional groups that contribute to high adsorption capacity. Therefore, glycine with the lowest MW (75.07 g/mol) is assumed to be the best at capturing CO\(_2\) among the 20 basic AAs. Dong et al. [59] reported that the CO\(_2\) uptake of the glycine-functionalised covalent triazine framework BCK-CTF-Gly reached 245 mg/g (5.57 mmol/g) at 1 bar and 0 \(\degree\)C. In another study using various amino acid ionic liquids (AAILs) immobilised into porous support polymethylmethacrylate (PMMA), the adsorption capacity of (EMIM)(Gly)-PMMA was the second highest (0.88 mmol/g) after (EMIM)(Lys)-PMMA (1.06 mmol/g) when tested under the same operating temperature of 30 \(\degree\)C [60]. Both studies evidently showed that a low MW of AA-based adsorbents resulted in a moderately high adsorption capacity. However, Ouyang et al. [61] reported opposite findings where the HCP(St-DMDAAC)-Trp displayed superior CO\(_2\) capacity of 60.7 wt% (13.8 mmol/g) under the conditions at 0 \(\degree\)C and 1 bar, regardless of higher MW of tryptophan (204.23 g/mol) compared to glycine, histidine, and aspartic acids that were also grafted into hyper-crosslinked polymer (HCP) in the same study. Nevertheless, the author presumed that the highest grafted amount of tryptophan led to its exceptional performance [61]. Furthermore, Li et al. [62] found that the CO\(_2\) sorption capacity was influenced by both MW and the molecular structure of the adsorbent (branched vs. linear).

Protonation constant or pKa is a major physiochemical parameter for AAs that helps in analysing the reaction mechanisms and molecular structure in an aqueous solution. As shown in Table 5, the AAs have high pKa values between 8–10, which are similar to typical alkanolamine solutions [64]. This indicates that the existence of the primary amine group in AA solutions allowed them to react with CO\(_2\) at a high chemical reactivity [42]. As pKa measures the strength of an acid or a base (tendency to dissociate in aqueous solution), pH measures the acidity or basicity of the solution (concentration of hydrogen ions). The difference in pH value may influence the adsorbent’s performance due to the different chemical forms of AA, which will be discussed in Section 3.1.3. However, the effect of different pH levels on the CO\(_2\) adsorption capacity is rarely discussed in the literature.
Pires et al. [46] conducted an experiment using the Arg-, His-, and Gly-based adsorbents prepared at two different pHs (5 and 7). In the study, the adsorption capacities were higher for all adsorbents prepared at pH 5 (up to 0.8 mmol/g) compared to the one prepared at pH 7 (<0.3 mmol/g) [46]. In general, alkaline pH is commonly favoured to react with acidic CO\(_2\) molecules. The selection of pH was based on the isoelectric point of the amino acid used in the study. In this case, lower pH favours the protonation of the amino groups for ion exchange with the cation of montmorillonite (MMT) clay. As a result, the amount of protonated amino acid increased thus increasing the percentage of intercalated amino acid in the MMT layer [46]. Nevertheless, it is assumed that the final pH of adsorbents are within the alkaline region due to basic properties of the clay, although they were not reported in the study.

### Table 5. List of basic 20 amino acids.

<table>
<thead>
<tr>
<th>Amino Acid (AA)</th>
<th>3-Letter Symbol</th>
<th>Molecular Weight</th>
<th>Molecular Formula</th>
<th>pKa</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>Ala</td>
<td>89.1</td>
<td>C(_3)H(_7)NO(_2)</td>
<td>10.01, 9.87 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Arginine</td>
<td>Arg</td>
<td>174.2</td>
<td>C(_4)H(_14)N(_2)O(_2)</td>
<td>12.48, 9.04 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Asparagine</td>
<td>Asn</td>
<td>132.12</td>
<td>C(_4)H(_8)N(_2)O(_3)</td>
<td>8.80 (^a)</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>Asp</td>
<td>133.11</td>
<td>C(_4)H(_7)NO(_4)</td>
<td>10.16, 9.60 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Cysteine</td>
<td>Cys</td>
<td>121.16</td>
<td>C(_3)H(_7)NO(_2)S</td>
<td>8.18 (^c)</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>Glu</td>
<td>147.13</td>
<td>C(_5)H(_9)NO(_4)</td>
<td>9.97, 9.67 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Glutamine</td>
<td>Gln</td>
<td>146.15</td>
<td>C(_5)H(_10)N(_2)O(_3)</td>
<td>9.13</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Glycine</td>
<td>Gly</td>
<td>75.07</td>
<td>C(_2)H(_5)NO(_2)</td>
<td>9.77, 9.78 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Histidine</td>
<td>His</td>
<td>155.16</td>
<td>C(_4)H(_9)N(_2)O(_2)</td>
<td>9.33</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>Ile</td>
<td>131.18</td>
<td>C(_4)H(_13)NO(_2)</td>
<td>9.68</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Leucine</td>
<td>Leu</td>
<td>131.18</td>
<td>C(_4)H(_13)NO(_2)</td>
<td>9.75</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Lysine</td>
<td>Lys</td>
<td>146.19</td>
<td>C(_5)H(_11)NO(_2)O(_2)</td>
<td>10.67, 8.95 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Methionine</td>
<td>Met</td>
<td>149.21</td>
<td>C(_5)H(_11)NO(_3)S</td>
<td>9.2, 9.21 (^a)</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>Phe</td>
<td>165.19</td>
<td>C(_9)H(_11)NO(_2)</td>
<td>9.29, 9.31 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Proline</td>
<td>Pro</td>
<td>115.13</td>
<td>C(_3)H(_8)NO(_2)</td>
<td>10.76, 10.6 (^a)</td>
<td>[42,43,63]</td>
</tr>
<tr>
<td>Serine</td>
<td>Ser</td>
<td>105.09</td>
<td>C(_3)H(_7)NO(_3)</td>
<td>9.15 (^a)</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Threonine</td>
<td>Thr</td>
<td>119.12</td>
<td>C(_4)H(_8)NO(_3)</td>
<td>9.12 (^a)</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>Trp</td>
<td>204.23</td>
<td>C(_9)H(_12)N(_2)O(_2)</td>
<td>9.39</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>Tyr</td>
<td>181.19</td>
<td>C(_9)H(_11)NO(_3)</td>
<td>9.11</td>
<td>[43,63]</td>
</tr>
<tr>
<td>Valine</td>
<td>Val</td>
<td>117.15</td>
<td>C(_5)H(_11)NO(_2)</td>
<td>9.72</td>
<td>[43,63]</td>
</tr>
</tbody>
</table>

\(^a\) Amino acids with L-AA configuration, pKa determined at 25 °C. \(^b\) \(\beta\)-alanine; \(^c\) pKa determined at 30 °C.

### 3.1.2. Functional Groups

Amino acid (AA) consists of amino groups mainly amine (–NH\(_2\)) and carboxyl (–COOH) groups with a general R side chain in their structure (Figure 4) that facilitates the CO\(_2\) capturing process via chemical adsorption (chemisorption) [65–68]. In general, CO\(_2\) molecules are physically adsorbed onto the solid surface through physisorption or chemisorption. In terms of physisorption, solid porous materials with large pores around tens of nanometers are in favour for providing fast transport of CO\(_2\) molecules onto the adsorbent surfaces and for pore filling, resulting in better performance for CO\(_2\) capture [69,70]. The examples of porous materials include metal organic frameworks (MOFs), zeolites, mesoporous silica, clay-based adsorbents, porous polymers, porous carbons, and porous metal oxides [69,70]. Surface functionalisation or doping of these porous materials with a basic functional group [71] such as amine is one of the keys to improve the CO\(_2\) chemisorption [56,70,72], leading to superior adsorption capabilities.
A recent study by Huang et al. [65] revealed that the presence of –NH₂ in amino acid ionic liquid (AAIL) led to high CO₂ capacities. This is because the amine group has a strong affinity towards CO₂ to bind together via chemisorption [66], and it is undoubtful that amine technology has been regarded as a mature technology for CO₂ capture for decades. Jiang et al. [52] interpreted that the presence of multiple amino groups in the arginine-based adsorbent Arg-PMMA resulted in higher CO₂ capacity compared to His-, Orn-, Asp-, and AEE-based adsorbents. A similar result was observed in Ren et al. [67] where the Sorb-Lys
displayed the highest CO$_2$ adsorption capacity (1.87 mmol/g), as it was the only adsorbent tested that had four amino groups in the chemical structure. In contrast, Aquino et al. [68] claimed that the type of amino group is more important compared to the number. In this case, an in-depth study is necessary to understand the mechanism of these adsorbents. Meanwhile, the carboxyl group is beneficial for physisorption, as it increases the binding energy [66], which could be an advantage for AA compared to traditional amine solution.

Fourier transform infrared (FTIR) analysis [45,46,59,61,75,76] and nuclear magnetic resonance (NMR) spectroscopies [65] can be used to determine the functional groups in the compound by analysing any changes of peaks, intensities, and chemical shifts reflected in the spectrum by the vibration or stretching of these chemical groups before and after amino acids functionalisation. This characterisation analysis is conducted to verify the successful grafting or impregnation of AAs. For example, in a study by Xu et al. [75], the peaks in the IR spectra of ionic liquid (N$_{2222}$)(Gly) at ~1000 cm$^{-1}$ and ~3300 cm$^{-1}$ indicated the stretching vibration of C–N and N–H bond while the peak at ~1386 cm$^{-1}$ and ~1572 cm$^{-1}$ were both attributed to C = O bond. For the solid material PDVB, the peak at ~3000 cm$^{-1}$ was assigned to C–H bond. After the functionalisation, the modified adsorbent showed the sum of the peaks existed in both AAIL and PDVB, and the intensities increased with increasing AAIL loading [75]. The FTIR analysis might also provide strong evidence on the reactions between the AA functional groups and CO$_2$ although it was hardly reported in previous works. There are several reports that compared the infrared spectrum of the raw adsorbent with the one after CO$_2$ adsorption [67,74,76,77]. For instance, in a study by [74], the FTIR analysis was conducted for adsorbent taurine, namely TAU, before and after CO$_2$ adsorption. It is noteworthy that taurine is a nonessential amino acid (not included in the 20 basic essential amino acids) that contains sulphur or sulphonyl hydroxide group (–S(=O)$$_2$$(OH)) in its chemical structure, instead of carboxyl group (–COOH). The presence of this functional group along with amine (–NH$_2$) improved the affinity for CO$_2$ adsorption, as evidenced in the reported literature [74]. Before CO$_2$ adsorption, the characterisation peaks were determined at 1342 cm$^{-1}$, 1210 cm$^{-1}$ and 1043 cm$^{-1}$, representing the bonds of (–C–N–), (–N–H–) and (–S–O–). After adsorption, the peaks’ intensities reduced for (–C–N–) and (–S–O–) while the bond for (–N–H–) disappeared. A similar test was conducted for adsorbent sarcosine SAR. It was observed that the peak of (–N–H–) bond was shifted from a lower (1554 cm$^{-1}$) to a higher region (1645 cm$^{-1}$) of spectrum while an intense new peak was formed at 766 cm$^{-1}$ which was attributed to (–O–H–) bond. All these findings indicate clear evidence of the bond formation between the amino acids and CO$_2$ [74]. Furthermore, in another study by Shao et al. [78], elemental analysis and X-ray photoelectron (XPS) were also performed to determine the amount of nitrogen (N) and sulphur (S), and the state of N and S in the sample, respectively. The presence of the heteroatom-containing groups could enhance the chemisorption process of CO$_2$ [78]. In conclusion, a complete characterisation of surface chemical properties is strongly recommended for a newly developed adsorbent to further understand the mechanism of CO$_2$ capture. Although functionalising AA into solid porous materials enhanced the CO$_2$ adsorption capacity compared to raw adsorbent (without AA functionalisation), the effect of multiple amino groups, the position of the functional group in adsorbent, and the structural configuration of the R side chain of AA are still unclear due to limited references on this specific area, which define the gap in this field of CO$_2$ capture.

3.1.3. Reaction and Adsorption Mechanism of Amino Acid with CO$_2$

Amino acids (AAs) are potential solvents for CO$_2$ separation processes. Kinetic analysis will provide the information on the nature of adsorption process (chemical and physical) as well as the reaction rate [28]. In this field of CO$_2$ capture, the kinetic analysis of CO$_2$ adsorption is often described based on the fitting of experimental data with one or more kinetic models, such as double exponential model [48,60,79], pseudo-first order [80], pseudo-second order [80], Avrami’s fractional-order [81], Elovich [80], and intra-particle diffusion [80]. Among those reported in literature, double exponential model
was frequently adopted and fitted well with most AA-based adsorbents. A well-fitted data using this model indicated that the adsorbent undergoes two sorption processes, namely (1) fast CO$_2$ adsorption on the adsorbent surfaces and (2) CO$_2$ diffusion into the adsorbent [79]. This can be observed through the fitted curve with rapid exponential weight gain in the first stage, followed by slow weight change represented by an almost plateau region [60]. Additionally, adsorption isotherms help in describing the interaction between adsorbate and adsorbent related to monolayer or multilayer adsorption, which can be interpreted using well-established adsorption isotherm equations such as Langmuir, Freundlich, Dubinin Radushkevich, and Temkin. Most importantly, this analysis is required for the interpretation of thermodynamic parameters, such as enthalpy or heat of adsorption, entropy, and Gibbs energy [82]. This type of data is important for effective design of the adsorption system and to optimise both adsorption mechanism pathways and expression of the surface properties [82]. Based on literature, the adsorption isotherm and thermodynamic qualities of AA-based adsorbents were rarely analysed previously but have gained an interest by some groups of researchers for the past few years. Several studies revealed that these adsorbents were best fitted with the Freundlich isotherm model [28,61,73]. Therefore, extended research focusing on the thermodynamic and kinetic studies, such as Raja Shahrom et al. [80], is highly encouraged, mainly for potential adsorbents.

The chemical form of AA is strongly dependent on the pH of the aqueous solution. The presence of amino and carboxyl groups in AAs will determine their chemical form, and whether they are acidic, basic, or neutral [83]. Figure 6 displays the change in chemical forms of amino and carboxyl groups of one of the AAs (glycine) between the pH range of 0–14. In both acidic and neutral types of AA, amino groups exist in the form of -NH$_3^+$, which is less reactive than the deprotonated form (-NH$_2$) at basic condition [84]. Based on Figure 6, the pH of the AA solvent should be adjusted to >pH 10 to fully deprotonate the amino groups in order to capture CO$_2$ effectively. This is in line with the typical range of pH reported in the literature (pH 10–11) [45,85].

![Figure 6. Change in chemical forms of amino and carboxyl groups of glycine between the pH ranges of 0 to 14 at 25 °C (reproduced with permission from Guo et al. [84], published by American Chemical Society (2013)).](image-url)
Equations (1) and (2) show a reaction scheme for 1:2 stoichiometry between CO$_2$ and AA in the gas–liquid phase. This reaction mechanism is known as the zwitterion mechanism. The first step involves the reaction between 1 mol of AA (NH$_2$ species) and 1 mol of CO$_2$ that forms a carbamic acid (Equation (1)). This carbamic acid proceeds to react with another NH$_2$ species of AA to form carbamate ion (Equation (2)). Under humid conditions, additional reaction might take place to form bicarbonate, as described in Equation (3) [56].

$$\text{R-NH}_2 + \text{CO}_2 \rightleftharpoons \text{R-NHCOOH} \quad \text{(Carbamic acid)} \quad (1)$$

$$\text{R-NHCOOH} + \text{R-NH}_2 \rightleftharpoons \text{R-NHCOCO}^- + \text{R-NH}_3^+ \quad \text{(Carbamate ion)} \quad (2)$$

$$\text{R-NH}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_3^+ + \text{HCO}_3^- \quad \text{(Bicarbonate ion)} \quad (3)$$

The chemical reaction between amino acid (AA) supported adsorbent and CO$_2$ is still unclear due to the lack of understanding in the reaction mechanism between AA and CO$_2$ in the gas–solid phase. It is believed that the reaction stoichiometry mechanism between CO$_2$ and amino group in the AA-based adsorbent follows the 1:2 ratio (mol of CO$_2$ to mol of NH$_2$ of AA) or the 1:1 stoichiometry to directly form carbamate, or both [77]. For instance, Uehara et al. [60] synthesised two different types of amino acid-functionalised ionic liquid (AAIL) immobilised into polymethylmethacrylate (PMMA) to investigate the roles of cation on the CO$_2$ adsorption capacity and to study the reaction mechanism of the adsorbents. In the study, the CO$_2$ uptake of the adsorbents when converted to mol-CO$_2$/mol-AAIL implied that the reaction between CO$_2$ and amino group of AA-supported solid sorbent occurred in a similar manner to the stoichiometric reaction in the absorption system. However, the results for the adsorption capacity of the adsorbents in the unit of mmol/g unit were in the opposite order, indicating that the performance of AAIL-based adsorbent also depends on the cation of the AAIL [60], and not only on the type of AA and solid support. In addition, it is worth mentioning the significant findings in a study conducted by Al-Terkawi et al. [86]. In this study, the reaction between solid powder L-lysine and CO$_2$ was investigated through a milling experiment. The commercially available L-lysine was milled in a planetary mill reactor under a CO$_2$ flow condition at 5 bar and then analysed by thermogravimetric analysis (TGA). The results obtained from the TGA curve depicted that a mass loss of the product at temperature range of 25 $^\circ$C to 75 $^\circ$C is equivalent to the mass of one water molecule released from ammonium carbamate reported in previous literature [87], supported by additional analysis by powder X-ray diffraction (XRD) and elemental analysis [86].

3.1.4. Surface Morphology and Structural Property

One of the important properties of adsorbents is surface structure property, which includes surface morphology, surface area, and porosity. Porous materials have an advantage in retaining the CO$_2$ molecules, as the gases are diffused onto the adsorbents’ surfaces by physisorption, provided with appropriate proportion of mesopore and micropore of the supports [88]. The morphological surface is commonly conducted to observe the effect of amino acid (AA) functionalisation. In most cases, this will reduce the amount of Brunauer–Emmett–Teller (BET) surface area and pore volume of the support materials as the AA fills the pores. Table 6 recaps the BET surface areas, pore volumes, and pore sizes of reported amino acid-based adsorbents before and after functionalisation. By increasing the loading of AA solution into the support, more active sites are available for interaction with CO$_2$, however it also increases the chance of pore blocking. The phenomenon of pore blocking could be due to insufficient pore size to accommodate the AA into the support [52]. For example, low water insolubility of arginine caused uneven distribution of the AA solution into the support and resulted in low CO$_2$ capacity of less than 0.5 mmol/g [52]. Figure 7a,b reveal the SEM images of the Arg-PMMA and its inside structure, respectively. The inset image in Figure 7a reveals the image of large microsized crystal particle of arginine that led to pore blocking. Meanwhile, in studies using amino acid ionic liquid (AAIL) supported on PMMA, it was found that the optimum capacity of CO$_2$ adsorbed was attained at loading
between 48.7–50 wt% [79,81]. Figure 7c displays the SEM images of (EMIM)(Lys)-PMMA surface structure at optimum loading of 48.7% with the presence of unblocked pores, indicating uniform distribution of AAIL [79]. The close image of the cross-sectional structure of the adsorbent in Figure 7d further verified that the interior porous structure of the PMMA was retained even after the AAIL functionalisation [79].

Table 6. Surface area, pore volume, and diameter of raw supports and amino acid-based adsorbents.

<table>
<thead>
<tr>
<th>Sample of Raw Supports and Amino Acid (AA)-Based Adsorbents</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>547</td>
<td>1.34</td>
<td>-</td>
<td>[79]</td>
</tr>
<tr>
<td>(EMIM)(Lys)-PMMA</td>
<td>0.77–94</td>
<td>0.01–0.50</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>527</td>
<td>1.12</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(EMIM)(Lys)-PMMA</td>
<td>38–327</td>
<td>0.35–0.93</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(P&lt;sub&gt;4444&lt;/sub&gt;)(Lys)-PMMA</td>
<td>37–256</td>
<td>0.32–0.99</td>
<td>-</td>
<td>[60]</td>
</tr>
<tr>
<td>(P&lt;sub&gt;4444&lt;/sub&gt;)(Lys)-PMMA</td>
<td>9.0–378</td>
<td>0.02–1.04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>570.70</td>
<td>1.15</td>
<td>9.17</td>
<td>[81]</td>
</tr>
<tr>
<td>PMMA-(N&lt;sub&gt;1111&lt;/sub&gt;)(Gly)</td>
<td>7.26–316.76</td>
<td>0.05–0.96</td>
<td>11.41–29.80</td>
<td></td>
</tr>
<tr>
<td>OMS</td>
<td>583</td>
<td>0.8</td>
<td>5.54</td>
<td>[45]</td>
</tr>
<tr>
<td>OMS-IL (AA)</td>
<td>294–325</td>
<td>0.77–0.79</td>
<td>9.6–10.9</td>
<td></td>
</tr>
<tr>
<td>MMT</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>AA-modified MMT</td>
<td>9–35</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HCP(St-DMDAAC)</td>
<td>864.1</td>
<td>1.20</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>HCP(St-DMDAAC)-AA</td>
<td>433.8–662.5</td>
<td>0.47–0.60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Al-raw</td>
<td>166</td>
<td>0.47</td>
<td>10.0</td>
<td>[77]</td>
</tr>
<tr>
<td>Al-(Emim)(Gly)</td>
<td>83–140</td>
<td>0.23–0.40</td>
<td>8.8–11.5</td>
<td></td>
</tr>
<tr>
<td>MCM-41</td>
<td>1213</td>
<td>0.83</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>(Emim)(Lys)-MCM-41</td>
<td>36</td>
<td>0.11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SBA-15</td>
<td>725</td>
<td>0.94</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>(Emim)(Lys)-SBA-15</td>
<td>33–265</td>
<td>0.05–0.58</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>UiO-66</td>
<td>1508</td>
<td>0.987</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td>(Emim)(Gly)/UiO-66-5%</td>
<td>1102</td>
<td>0.736</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MOF/GO</td>
<td>1080</td>
<td>0.462</td>
<td>0.461</td>
<td>[88]</td>
</tr>
<tr>
<td>MOF/GO-Arg</td>
<td>956</td>
<td>0.430</td>
<td>0.420</td>
<td></td>
</tr>
<tr>
<td>BCK-CTF-400-5</td>
<td>1969</td>
<td>1.39</td>
<td>-</td>
<td>[59]</td>
</tr>
<tr>
<td>BCK-CTF-Gly</td>
<td>1720</td>
<td>1.09</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PDVB</td>
<td>845.8</td>
<td>2.65</td>
<td>-</td>
<td>[75]</td>
</tr>
<tr>
<td>(N&lt;sub&gt;2222&lt;/sub&gt;)(Gly)@PDVB</td>
<td>3.0–127.4</td>
<td>0.01–0.71</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MCF</td>
<td>677</td>
<td>2.22</td>
<td>-</td>
<td>[76]</td>
</tr>
<tr>
<td>MCF-AA</td>
<td>33–47</td>
<td>0.26–0.38</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Activated carbon (AC)</td>
<td>767.97</td>
<td>0.37</td>
<td>1.94</td>
<td>[90]</td>
</tr>
<tr>
<td>AC-AAIL (arg, lys, gly)</td>
<td>24.16–288.18</td>
<td>0.0169–0.17</td>
<td>2.22–2.66</td>
<td></td>
</tr>
</tbody>
</table>
Overall, as shown in Figure 7, the AA and AAIL structures could not be observed clearly in the cross-sectional structure of the adsorbent, as they were dominated by the rough structure of PMMA microspheres [79]. Therefore, the information of BET surface area, pore volume, and size are helpful to support this structural analysis. The information on the ratio of micropore to total pore volume provides an early assumption on the effectiveness of the adsorbents. Dong et al. [59] has reported an increase in CO$_2$ uptake from 145 mg/g (3.29 mmol/g) to 245 mg/g (5.57 mmol/g) when the ratio of micropore volume increased from 0.35 to 0.50 after glycine functionalisation. Alternatively, it is worth using a simulation to predict the CO$_2$ capacity for the initial stage. A blocked model developed by Xia et al. [89] showed that the results obtained were closer to the experimental results when compared to the random model (without blocked pore). For validation, experimental works are still required due to many possibilities for the blocked channels to occur in a real condition, which counts as the drawback of simulation models. Nonetheless, explicit SEM images can be attained for some adsorbents using different support material, such as mesoporous silica SBA-15 [47].

3.1.5. Thermal Stability

In post-combustion carbon capture, the temperature of the flue gas from a power plant is commonly cooled prior to adsorption, however it is preferred in most separations that the adsorbents must be able to operate under a relatively high temperature of a minimum of above room temperature up to ~150 °C [91]. Thermal stability plays an important role in minimising the decomposition of the adsorbent throughout the adsorption process [58]. This property will determine the adsorbent lifetime depending on its frequency of replacement after multiple CO$_2$ adsorption–desorption (regeneration) cycles [92]. Likewise, thermal stability has been considered as one of the selection criteria for solid adsorbents due...
to its direct impact on the economics for any potential adsorbents to be commercialised [93]. The stability over the extensive regeneration cycle may help in early prediction of the cost-effectiveness of the adsorbent while promising its sustainability, as it can reduce the frequency of solid wastes generation. In a previous work, amino acid (AA) salts (sodium glycinate) showed a faster degradation rate as compared to alkanolamines [94].

However, amino acid ionic liquid (AAIL), namely (EMIM)(Lys), exhibited reasonably good thermal stability at approximately 200 °C [79]. In another study, a similar observation was made for all adsorbents (various AAILs grafted onto ordered mesoporous silica) that were stable up to 250 °C, although their weight loss seemed to decrease gradually at higher temperature [45]. A recent study by Uehara et al. [47] reported high thermal stability up to 700 °C for the adsorbents ((EMIM)(Lys) loaded into different supports of both SBA-15 and MCM-41). Nevertheless, a slow reduction in CO₂ adsorption capacities was observed throughout 10 cyclic CO₂ adsorption–desorption cycles with a maximum of 35%, which was presumed to be due to incomplete desorption of CO₂, weight loss of AAIL, or a combination of both [47]. In a real application such as a coal power plant, another concern is the presence of water vapour in the flue gas stream typically around ~20% that can degrade the silica supports such as SBA-15 and MCM-41 when exposed to elevated temperature [68,95].

All findings in this section (Section 3.1) indicate that the CO₂ capturing performance of the AA-based adsorbents should not be predicted solely based on the properties of AAs. For example, in the case of AA-complexes and AAILs, their physical and chemical properties will be influenced by the constituents of the complex materials or ionic liquid itself. The properties of AA can be a guideline in selecting the most suitable AA to be functionalised into the supports or other materials. However, further investigations are still required to determine the effectiveness of the final adsorbents prepared.

3.2. Performance of Amino Acid-Based Adsorbents for CO₂ Capture

Solid amine sorbents are known to have advantages over liquid absorbents in reducing the energy penalty in CO₂ capture technology, yet it remains an option due to some drawbacks, including low adsorption capacity [56]. Remarkably, the effectiveness of aqueous amino acid (AA) for CO₂ capture has been critically reviewed in the past three consecutive years [40,42,43]. However, there is no review currently available on the role of AA as CO₂ adsorbents despite several published works that have been performed in developing AA functionalised adsorbents. This review paper is the first review on the performance of various types of AA-based adsorbents published from 2012 to 2022. The performance evaluation mainly focuses on the CO₂ adsorption capacity, however some information on the adsorption mechanisms, thermodynamic, and regeneration studies were also discussed in brief.

3.2.1. Amino Acid Ionic Liquid-based Adsorbents

Amino acid (AA) salts and ionic liquids are among the ideal solvents utilised to capture CO₂ owing to their high selectivity towards the acid gases [96]. Amino acid ionic liquid (AAIL) has been reported as a potential candidate for CO₂ capture [97] and sometimes is regarded as a “green solvent” [98]. However, not all AAILs are non-toxic [99]. One major problem of using IL as a liquid absorbent is slow CO₂ sorption and desorption rates due to its high viscosity [60]. Therefore, utilising AAIL as a surface modifier could overcome the high viscosity issue. This can be conducted by introducing AAIL into a solid porous support that has a large specific surface area and sufficient pore volume. Stronger chemical bonding between the CO₂ molecules and surface functional groups (–NH₂) of the support will provide greater efficiency in CO₂ adsorption capacity [100]. In previous studies, immobilising different types of AA anions into solid support materials demonstrated much more rapid CO₂ sorption than unsupported or pure AAILs [60].

Table 7 shows the adsorption performance of AAIL-based adsorbents. The lysine-functionalised ILs were commonly reported as exhibiting the highest CO₂ adsorption
Energies 2022, 15, 3753

capacity (0.61–1.87 mmol/g) compared to other AAILs [45,60,67,76,90,101]. Ren et al. [67]
interpreted that the effectiveness of Sorb-Lys was attributed to being the only adsorbent
with four amino groups in comparison to Sorb-Ala, Sorb-Gly, Sorb-His, and Sorb-Asp
that consist of three amino groups. A comparative study on the efficiency of multiple
amino groups confirmed that an introduction of one additional amino group successfully
increased the adsorption capacity of the AAIL-based adsorbent from 1.06 mmol/g to
1.50 mmol/g [65]. In another study, the authors emphasised that the interaction between
the amino groups with CO2 molecules could be hindered by the complex side chains of
amino acids [60]. The lys- and gly-based adsorbents with a simple linear side chain attached
with primary amino groups resulted in better adsorption capacities (0.88–1.06 mmol/g)
compared to histidine and arginine (0.28–0.63 mmol/g) with a complex structure [60], as
shown in Figure 8. Similar observations were made in Wang et al. [79] where (EMIM)(Lys)PMMA demonstrated the highest adsorption capacity of 1.67 mmol/g followed by gly-,
al- and arg-based adsorbents with the capacities of 1.53 mmol/g, 1.38 mmol/g, and
1.01 mmol/g, respectively.

![Chemical structure of L-lysine, L-glycine, L-arginine, and L-histidine.](image)

Figure 8. Chemical structure of L-lysine, L-glycine, L-arginine, and L-histidine.

Special cases using polymer containing materials such as poly(VBTMA)(Arg) [80]
and porous-P(VBMI)(Gly)) [102] showed promising results with excellent CO2 uptake
of 7.91 mmol/g and 3.75 mmol/g, respectively. Raja Shahrom et al. [90] also reported
exceptional CO2 adsorption capacity between 24–30 mmol/g for AAIL of (vbtma)(gly),
(vbtma) (lys), and (vbtma) (arg) when supported onto activated carbon but operated at a
high pressure condition of 20 bar. Polymeric capturing technology containing AAs could
be the next generation of solid adsorbents due to the intriguingly high CO2 adsorption
capacity of >3 mmol/g. Khatri et al. [103] described that the effectiveness of CO2 capture
can be achieved if the adsorbent exhibits high adsorption capacity of >1 mmol/g, has
a long-term regeneration capability, and low energy requirement during regeneration.
However, an adsorption capacity of at least 3 mmol/g is required in order to compete
with the absorption technologies [104] or between 2 mmol/g and 4 mmol/g to reduce the
overall cost [105]. More details on the application of polymer-containing materials for CO2
capture can be found in the report by Sattari et al. [106].

Table 7. Amino acid ionic liquid (AAIL)-based adsorbents (from 2012 to 2022).

<table>
<thead>
<tr>
<th>AAIL-Based Adsorbent</th>
<th>Ratio of AAIL (wt%)</th>
<th>Synthesis Method</th>
<th>Operating Conditions</th>
<th>Adsorption Mechanism</th>
<th>Thermodynamic</th>
<th>Adsorption Capacity (mmol/g)</th>
<th>Regeneration Cycle</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorb-Lys</td>
<td>50</td>
<td>Impregnation</td>
<td>25 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.87</td>
<td>4 cycles (3.1% drop)</td>
<td></td>
</tr>
<tr>
<td>Sorb-Ala</td>
<td>50</td>
<td>Impregnation</td>
<td>25 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.46</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sorb-Gly</td>
<td>50</td>
<td>Impregnation</td>
<td>25 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.65</td>
<td>4 cycles (5.7% drop)</td>
<td>[67]</td>
</tr>
<tr>
<td>Sorb-His</td>
<td>50</td>
<td>Impregnation</td>
<td>25 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sorb-Asp</td>
<td>50</td>
<td>Impregnation</td>
<td>25 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(EMIM)(Gly)-PMMA</td>
<td>50</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>E_a = 6.8 kJ/mol</td>
<td>1.53</td>
<td>5 cycles</td>
<td></td>
</tr>
<tr>
<td>(Ala)-PMMA</td>
<td>50</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.38</td>
<td>-</td>
<td>[79,</td>
</tr>
<tr>
<td>(EMIM)(Arg)-PMMA</td>
<td>50</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>1.01</td>
<td>-</td>
<td>101</td>
</tr>
<tr>
<td>(EMIM)(Lys)-PMMA</td>
<td>48.7</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>Double exponential model (DE)</td>
<td>E_a = 4.1–4.3 kJ/mol</td>
<td>1.67</td>
<td>14 cycles (4% drop)</td>
<td></td>
</tr>
</tbody>
</table>
Table 7. Cont.

<table>
<thead>
<tr>
<th>AAIL-Based Adsorbent</th>
<th>Ratio of AAIL (wt%)</th>
<th>Synthesis Method</th>
<th>Operating Conditions</th>
<th>Adsorption Mechanism</th>
<th>Thermodynamic</th>
<th>Adsorption Capacity (mmol/g)</th>
<th>Regeneration Cycle</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe60-I900 (Emim)(Gly)</td>
<td>-</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 15% CO₂</td>
<td>Freundlich</td>
<td></td>
<td>0.502</td>
<td>5 cycles</td>
<td>[107]</td>
</tr>
<tr>
<td>RGC30 (Emim)(Gly)</td>
<td>-</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 15% CO₂</td>
<td>Freundlich</td>
<td></td>
<td>0.426</td>
<td>5 cycles</td>
<td></td>
</tr>
<tr>
<td>MCF-Arg</td>
<td>-</td>
<td>Impregnation</td>
<td>75 °C, 1 bar 15% CO₂</td>
<td>-</td>
<td></td>
<td>0.63, 0.42 b,c</td>
<td>10 cycles</td>
<td></td>
</tr>
<tr>
<td>MCF-Lys</td>
<td>-</td>
<td>Impregnation</td>
<td>75 °C, 1 bar 15% CO₂</td>
<td>-</td>
<td></td>
<td>1.38, 1.30 b, 1.27 c</td>
<td>10 cycles</td>
<td></td>
</tr>
<tr>
<td>MCF-Gly</td>
<td>-</td>
<td>Impregnation</td>
<td>75 °C, 1 bar 15% CO₂</td>
<td>-</td>
<td></td>
<td>0.58, 0.39 b, 0.44 c</td>
<td>10 cycles</td>
<td></td>
</tr>
<tr>
<td>OMS-IL(Ala)</td>
<td>Grafting</td>
<td>25 °C, 1 bar 99% CO₂</td>
<td>Adsorption rate = 0.047 mmol/min</td>
<td>Freundlich</td>
<td></td>
<td>Eₐds = 67.72 kJ/mol Eₐdes = 78.1 kJ/mol</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>OMS-IL(Lys)</td>
<td>Grafting</td>
<td>25 °C, 1 bar 99% CO₂</td>
<td>Adsorption rate = 0.05 mmol/min</td>
<td>Freundlich</td>
<td></td>
<td>ΔH = −370.9 kJ/mol ΔS = 4.57 J/mol.K Eₐ = 3.08 kJ/mol, 6.72 kJ/mol</td>
<td>0.61, 0.56 d</td>
<td>10 cycles</td>
</tr>
<tr>
<td>OMS-IL(Gly)</td>
<td>Grafting</td>
<td>25 °C, 1 bar 99% CO₂</td>
<td>Adsorption rate = 0.06 mmol/min</td>
<td>Freundlich</td>
<td></td>
<td>Eₐds = 76.14 kJ/mol Eₐdes = 90.64 kJ/mol</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>OMS-IL (Pro)</td>
<td>Grafting</td>
<td>25 °C, 1 bar 99% CO₂</td>
<td>Adsorption rate = 0.06 mmol/min</td>
<td>Freundlich</td>
<td></td>
<td>Eₐds = 85.15 kJ/mol Eₐdes = 106.1 kJ/mol</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>PMMA-(N1111)(Gly)</td>
<td>Impregnation</td>
<td>35 and 75 °C, 1 bar 10% CO₂</td>
<td>Avrami’s fractional-order kinetic model</td>
<td></td>
<td></td>
<td>2.14, 1.58</td>
<td>10 cycles</td>
<td></td>
</tr>
<tr>
<td>PMMA-(N2222)(Gly)</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 15% CO₂</td>
<td>-</td>
<td>Freundlich isotherm, Pseudo-first order kinetic model</td>
<td>ΔH = −30.3 kJ/mol (chemical) ΔS = −91.14 kJ/mol.K ΔG = (−3.16 to +0.27) kJ/mol Eₐ = 7.23 kJ/mol</td>
<td>3.23–7.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-(vbtma) (gly)</td>
<td>Impregnation</td>
<td>25 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AC-(vbtma) (lys)</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AC-(vbtma) (arg)</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.28</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Emim)(Ala)-PMMA</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.63</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Emim)(BALA)-PMMA</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.88</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Emim)(His)-PMMA</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.63</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Emim)(Lys)-PMMA</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>0.88</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(AEMIM)(Lys)-PMMA</td>
<td>Impregnation</td>
<td>30 °C, 1 bar 2.3% CO₂</td>
<td>DE kinetic model</td>
<td>DE kinetic model</td>
<td></td>
<td>1.06</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AC-(vbtma) (gly)</td>
<td>Impregnation</td>
<td>25 °C, 20 bar</td>
<td>Freundlich isotherm</td>
<td>Freundlich isotherm</td>
<td>ΔH = −33 kJ/mol (chemical) ΔS = −41.36 J/mol.K ΔG = (−3.16 to +0.27) kJ/mol Eₐ = 7.23 kJ/mol</td>
<td>3.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porous-P(VBMI)(Gly)</td>
<td>Impregnation</td>
<td>25 °C, 10 bar</td>
<td>-</td>
<td>-</td>
<td>ΔH = −2.5 e</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(N2222)(Gly)#PDVB</td>
<td>Impregnation</td>
<td>75 °C, 1 bar 10% CO₂</td>
<td>-</td>
<td>-</td>
<td>ΔH = −1.2 e</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
AAIL-Based Adsorbent | Ratio of AAIL (wt%) | Synthesis Method | Operating Conditions | Adsorption Mechanism | Thermodynamic | Adsorption Capacity (mmol/g) | Regeneration Cycle | Refs
--- | --- | --- | --- | --- | --- | --- | --- | ---
(APMIM) (Lys)-loaded PMMA | 50 | Impregnation | 30 °C, 1 bar 15% CO$_2$ | DE kinetic model, Freundlich | $\Delta H = 44$ kJ/mol | 1.45 | - | [48]

a $E_a$ is activation energy, $\Delta H$ is enthalpy, $\Delta S$ is entropy, $\Delta G$ is Gibbs energy.
b,c Water vapor content of 2.5% and 10.6%, respectively. d Under CO$_2$ inlet concentration of 15%.
e Estimated reading from the graph. f Values converted from unit mg/g to mmol/g.

### 3.2.2. Naturally Occurring Solid Amino Acid-based Adsorbents

In a study by Chatterjee et al. [74], the performance of naturally occurring solid amino acids (AAs) in capturing CO$_2$ was evaluated. Among eight AAs studied, taurine exhibited the highest CO$_2$ adsorption capacity of 3.25 mmol/g, followed by sarcosine (2.85 mmol/g) and valine (2.29 mmol/g). It was also found that the order of adsorption rate and capacity for all AAs were influenced by the molecular size as well as the presence of electronegative atom in the chemical structure of some of the AAs (in this case, sulphur in taurine). Nevertheless, the experiment was conducted under the inlet concentration of pure CO$_2$ (99%), which was incomparable for post-combustion application. Although the author suggested the reusability of these AAs, the results from the regeneration study showed a gradual decrease in CO$_2$ capturing performance of about ~20% after 10 cycles [74]. This phenomenon could relate with the lack of thermal stability of AAs, as discussed in Section 3.1.5. This limitation could be enhanced by immobilising the amino acids into suitable support materials or by modifying the AA solvents before the immobilisation process.

AA can be immobilised into support materials via two classical methods used for solid amine sorbents [56]. The popular technique is a simple wet impregnation method, which involves physical mixing of the solid support materials and AA solution for a certain period, followed by evaporation to remove the excess solution or solvent [52,108]. Impregnation can also be performed via dry impregnation by immersing the support in a fixed amount of solvent to fill the pores, unlike wet impregnation that utilises a large volume of solvent [109]. Another method is grafting, which covalently links the AA to the support by condensation reaction, which provides more thermal stability during the regeneration cycles [56]. In a comparative study between impregnated and grafted amine adsorbents, it was revealed that impregnation allows amine to diffuse easily into the pores of the support, thus it exhibited outstanding adsorption capacity [110]. This finding is also in line with the review conducted by Fatima et al. [109], highlighting the efficiency of impregnated samples compared to grafted samples, however this method may result in the deposition of a larger and thicker layer of solvent on the external surface of the supports, causing some pores to be blocked and further reducing the active sites to interact with CO$_2$ molecules [111].

Table 8 shows the performance of AA impregnated or grafted adsorbents in terms of adsorption capacity. The overall results indicated undesirably low adsorption capacity <1.0 mmol/g in regard to impregnated or grafted samples, which would not be feasible for practical industrial application, except for two adsorbents. This could be due to the lack of water solubility of AA that resulted in a non-uniform distribution of the AA within the porous support leading to low CO$_2$ adsorption capacity [52]. The effectiveness of the two exceptional AA adsorbents, HCP(St-DMDAAC)-Trp and BCK-CTF-Gly, was highly attributed to the excellent CO$_2$ capturing performance of the support materials themselves, owing to the high pore volume, abundant microporosity, and large BET surface area (864–1969 m$^2$/g) [59,61]. The hyper-crosslinked polymer HCP(St-DMDAAC) was able to capture CO$_2$ up to 28.4 wt% without AA functionalisation and increased significantly to 60.7 wt% (13.8 mmol/g) after functionalisation with tryptophan [61]. Meanwhile, the CO$_2$ uptakes of the covalent triazine framework BCK-CTF were 145 mg/g (3.29 mmol/g) and 245 mg/g (5.57 mmol/g) before and after functionalisation with glycine [59]. Both
adsorbents also have good regenerative performance between 6 and 10, cycles which advocates for their potential application of CO₂ capture for larger scale.

Table 8. Amino acid impregnated or grafted into various types of support materials.

<table>
<thead>
<tr>
<th>Amino Acid (AA)</th>
<th>Support Materials</th>
<th>Content of AA (wt%)</th>
<th>Synthesis Method</th>
<th>Operating Conditions</th>
<th>Adsorption Mechanism</th>
<th>Thermodynamic</th>
<th>Adsorption Capacity (mmol/g)</th>
<th>Regeneration Cycles</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arginine ethyl ester</td>
<td>Polymethylmethacrylate (PMMA) microsphere</td>
<td>20</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>[52]</td>
</tr>
<tr>
<td>Arginine Aspartic acid</td>
<td></td>
<td>10–50</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>0.2–0.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ornithine</td>
<td></td>
<td>20</td>
<td>Impregnation</td>
<td>40 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>L-arginine</td>
<td>Mesoporous TiO₂ beads</td>
<td>-</td>
<td>Grafting</td>
<td>30 °C, 1.2 bar</td>
<td>Langmuir</td>
<td>-</td>
<td>0.62 e</td>
<td>-</td>
<td>[68]</td>
</tr>
<tr>
<td>L-glutamine</td>
<td></td>
<td>-</td>
<td>Grafting</td>
<td>30 °C, 1.2 bar</td>
<td>Langmuir</td>
<td>-</td>
<td>0.43 f (at 1.5 bar)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Arginine</td>
<td>Montmorillonite (MMT) clay</td>
<td>-</td>
<td>Intercalation</td>
<td>25 °C, 8 bar</td>
<td>-</td>
<td>-</td>
<td>0.8 c, d, 0.5 c, e</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>Glycine</td>
<td></td>
<td>-</td>
<td>Intercalation</td>
<td>25 °C, 8 bar</td>
<td>-</td>
<td>-</td>
<td>0.5 c, d, 0.2 c, e</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>L-Histidine</td>
<td></td>
<td>-</td>
<td>Intercalation</td>
<td>25 °C, 8 bar</td>
<td>-</td>
<td>-</td>
<td>0.5 c, d, 0.2 c, e</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tryptophan</td>
<td>Porous microsphere HCP(St-DMDAAC)</td>
<td>5.4</td>
<td>Grafting</td>
<td>0 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>13.8</td>
<td>6 cycles (5% drop)</td>
<td>[61]</td>
</tr>
<tr>
<td>Glycine</td>
<td>BCK-CTF-400-5 a</td>
<td></td>
<td>Grafting</td>
<td>0 °C, 1 bar</td>
<td>-</td>
<td>-</td>
<td>Qₑ = 28.4 kJ/mol Qₐ = 33.3 kJ/mol</td>
<td>5.57 f, 2.66 f</td>
<td>10 cycles</td>
</tr>
</tbody>
</table>

a BCK-CTF-400-5 = Bis(4-cyanophenyl)ketone (BCK) synthesised at 400 °C using 5 mol equivalent ratio of ZnCl₂/BCK. b Qₑ = isosteric heat of adsorption. c Estimated value read from graph; d, e Samples prepared at pH 5 and pH 7, respectively. f Values converted from mg/g to mmol/g.

3.2.3. Strong Alkaline Amino Acid Salt-based Adsorbents

Aqueous AA-based potassium salt solutions were found to be more effective in capturing CO₂ as compared to commercial monoethanolamine (MEA) due to additional hydrolysis reaction with CO₂ as a result of unstable carbamate formation unlike MEA [112]. Potassium lysinate (K-Lys) also demonstrated a higher CO₂ loading capacity than MEA [113]. Immobilising potassium AA salt into porous support is expected to enhance the CO₂ capacity. Nevertheless, no publication was found on the application of AA-based potassium salt solvent for surface modification of porous support except for Lim et al. [114] and Shao et al. [78] up to the date this review was conducted. In this study, the author investigated the effect of metal-ion exchange involving the doping of aqueous AA with alkali metal solution such as potassium hydroxide (KOH) to deprotonate -NH₃⁺ groups of AA to -NH₂ prior to impregnation into activated carbon (AC). However, the adsorption capacity of potassium glycinate-supported AC adsorbent (AC-KG) failed to improve the capacity of raw AC at all molar concentrations of 1–5 [112]. This could be due to the heterogeneous distribution of surface nitrogen groups (SNGs) of the AA-based potassium solvent that simply coated the surface of AC leading to low adsorption capacity [112]. The most recent study adopted a different approach in preparing the adsorbent known as a facile two-step synthesis strategy, which involves the pyrolysis of the AA-thiourea mixture and KOH activation to generate a highly porous adsorbent [78]. As a result, an impressive performance was exhibited by the adsorbent with maximum adsorption capacity of 3.54 mmol/g and 5.54 mmol/g at 25 °C and 0 °C, respectively, under 1 bar pressure [78].

3.2.4. Blended Amine and Amino Acid-based Adsorbents

Surface modifiers for solid amine sorbents for CO₂ capture are commonly sourced from organic chain alkanolamines or amine polymers (for impregnation method) and silane amines (for grafting method) [115]. This includes polyethyleneimine (PEI)-based adsorbents. Recently, a PEI-impregnated alginate adsorbent synthesised in a capsule form was reported for the first time, exhibiting high adsorption capacity but in a different
application (gold recovery) [116]. This type of adsorbent is strongly recommended to be further investigated for CO₂ capture due to its large number of amine groups. Furthermore, the blended solvent of hexamethylenediamine (HDMANa) + sodium glycinate (NaGly) [117] and MEA + sodium glycinate [118] demonstrated higher CO₂ loading capacities compared to NaGly. The kinetic study of the former blended solvent also showed high overall constant rate [119]. However, increasing the concentration of AA salt solution in the blended solution led to an increase in corrosion rate as reported in several articles [118,119], which is unfavourable for industrial application. Therefore, these promising blended solutions can be utilised as alternative surface modifiers for the development of new solid sorbents for CO₂ capture.

3.2.5. Other Amino Acid-based Adsorbents

Due to emerging technology of solid adsorbents, several approaches have been adopted or developed to enhance the adsorption capacity of amino acid (AA)-based adsorbents. This includes the development of new AA-based metal organic frameworks (MOFs) [53,88,120,121] or zeolite framework [122], AA-crosslinked polymer or complex [54,123,124], AA-nanohybrid [85] or nanoparticles anchored with AA-based ligand [125], co-doping the heteroatoms, such as nitrogen, sulphur, and oxygen [78,126], and N-doping via hydrothermal self-assembly or direct heating [51,127]. A recent trend in the application of zeolites [128,129] and MOFs [130] for CO₂ capture showed that superior adsorption capacity was mostly >3 mmol/g after surface modification or with the aid of a catalyst. This further advocate their potentiality as solid support materials, despite the high cost of the materials. Nevertheless, it is important to note that the potential of those materials could be exploited without sufficient understanding of the properties of AA before incorporating the AA with the frameworks. For instance, Xia et al. [89] investigated the performance of AAIL-MOF composite using two types of AAILs, which are 1-ethyl-3-methylimidazolium glycinate ((Emim)(Gly)) and 1-ethyl-3-methylimidazolium phenylalanate ((Emim)(Phe)), incorporated into two different Zr-based MOFs, namely UiO-66 and NU-1000, at different loading. The results revealed that the CO₂ capacity of raw adsorbent was higher (~ 2.5 mmol/g, 1 bar) than modified adsorbents at all loadings for both solid materials, due to the failure of these AAILs to disperse uniformly into the solid framework [89]. Almost similar findings were observed in another study by Erto et al. [107] using two different types of commercial activated carbons (F600-900 derived from coal and RGC30 derived from sawdust) impregnated with (Emim)(Gly). The adsorption capacities for these adsorbents were slightly reduced after the functionalisation but showed improvements at higher temperatures of 50 °C and 80 °C [107].

In another study by Philip and Henni [122], opposite findings were reported using the zeolite framework (ZIF-8) incorporated with (Emim)(Gly). The CO₂ uptake of the modified adsorbents were enhanced significantly from 0.6 mmol/g to 1.4 mmol/g under the same pressure condition of 1 bar [122]. Furthermore, silica is another promising support material for AA-based adsorbents despite its sensitivity under humid conditions or in the presence of water vapour. A study conducted by [47] prevailed impressive performance using two types of mesoporous silica (MCM-41 and SBA-15) impregnated with 1-Ethyl-3-methylimidazolium lysine (EMIM)(Lys). In addition, extensive studies have been performed by this group of researchers, exploring the effect of expanding adsorbents’ pore sizes to accommodate a sufficient volume of AAIL [47,131], the effect of the added and remained surfactants [47], the roles of cation and anion of AAIL [60], and the effect of the presence of water vapour [132]. All these findings indicate that apart from excellent properties of activating agent and solid porous materials, the synthesis and modification method also influenced the CO₂ adsorption performance, and it thus requires considerable attention among the researchers who are working in this specific area to avoid undesired phenomenon such as pore blockage which leads to low CO₂ uptake.
3.3. Regeneration Studies

There are few review articles focused on regeneration performance for CO\textsubscript{2} adsorption. For instance, Plaza et al. [133], Raganati et al. [12], Raganati and Ammendola [134], and Dhoke et al. [135] presented a comprehensive review on various type of regeneration mode for CO\textsubscript{2} adsorption and stated that each regeneration mode has its own advantages and disadvantages. In this section, the important point will be discussed. There are two main regeneration strategies for CO\textsubscript{2} adsorption; temperature swing adsorption (TSA) [129,136–138] and pressure swing adsorption (PSA) [138–140]. In TSA application, the temperature is increased at an approximately constant pressure. There are two regeneration modes associated with the TSA approach, which are non-isothermal purge and isothermal purge. In the non-isothermal mode, both heating operation and feed switching are activated at the same time. After the adsorption process is complete, the column is heated to the selected desorption temperature and the column feed is switched to pure nitrogen (N\textsubscript{2}) flow to purge the bed. Comparatively, in the isothermal mode, the purging step occurs at a constant temperature. After the adsorption step, the inlet and outlet of the column are closed with two-way valves before the temperature is raised to the desired desorption temperature. The N\textsubscript{2} gas stream is then fed into the column for purging once it reaches the set temperature [134].

In PSA application, the pressure is reduced by using large particles or structured packings, in the case of the fixed bed reactor depending on the reactor configuration [135]. However, the term vacuum swing adsorption (VSA) or vacuum pressure swing adsorption (VPSA) is commonly used in post-combustion CO\textsubscript{2} capture. This is because the pressure used for the desorption is normally reduced to below atmospheric pressure due to the uneconomical pressurised step for large quantities of flue gas [135]. A conventional VSA regeneration mode consists of four simple operations, which are feed gas pressurisation, adsorption, forward blowdown, and reverse evacuation. Among the above processes, TSA is mostly preferred as it provides an option for energy integration with existing utilities at power plants (low pressure steam, waste heat, or cooling tower) [136]. Conversely, in a study by Ammendola et al. [129], the energy penalty of TSA outweighed the sorbent regeneration performance, indicating the need for an in-depth assessment before this CO\textsubscript{2} adsorption technology can be commercially deployed and economically acceptable. Alternatively, a combined use of two or more regeneration modes could be beneficial. For instance, Plaza et al. [133] have conducted an experiment to compare the performance of TSA, VSA, and combination of these two modes, namely vacuum and temperature swing adsorption (VTSA). Based on the critical review, VTSA displayed the highest productivity up to 1.9 molkg\textsuperscript{−1}h\textsuperscript{−1} with maximum CO\textsubscript{2} recovery of 97%, followed by VSA (1.7 molkg\textsuperscript{−1}h\textsuperscript{−1}; 87% CO\textsubscript{2} recovery) and TSA (0.8 molkg\textsuperscript{−1}h\textsuperscript{−1}; 40% CO\textsubscript{2} recovery). Detailed discussion on the benefits and drawbacks of each regeneration mode as well as other type of mode such as electric or electrothermal swing adsorption (ESA) can be found in this previous review [135,141].

Details on reactor configuration have been reviewed by authors Dhoke et al. [135] and Raganati et al. [12]. In general, there are three basic concepts of reactor configuration for adsorption-based CO\textsubscript{2} capture at low temperature, which are fixed bed, fluidised bed, and moving bed reactors. Fixed bed reactor can be further classified into two reactor designs, which are conventional fixed bed reactor or structured fixed bed reactor. This type of reactor is simple in operation and is an ideal selection for PSA regeneration mode because of its poor heat transfer properties. However, it requires a large amount of adsorbent pellets in the case of conventional reactor, or structured packings in the case of structured and packed reactor, in order to reduce a great amount of pressure drop [135]. An alternative to fixed bed reactor configuration is a moving bed reactor. Traditionally, the moving bed reactor comprises more than one interconnected section and reactor instead of one reactor column [12]. Although all sections and reactors are operated at the same fixed conditions (steady-state), the design for this reactor is more complex than fixed bed reactors, which is unfavourable in most industries. Due to their complex configuration, a suitable regeneration mode...
would be TSA, although it is less efficient compared to the fixed bed reactor with PSA mode [142]. Apart from the moving bed reactor, another reactor configuration, the fluidised bed reactor, is a promising technology for CO₂ capture application, similar to the structured and packed fixed bed reactor depending on the number of stages of the reactor column. Multistage fluidised bed reactor is said to enhance the working adsorption capacity by reducing the overall internal back mixing (number of sorbents recirculation), leading to significant energy saving capabilities [135]. This type of reactor will provide an excellent application when combined with the TSA mode. Meanwhile, a sound-assisted fluidised bed reactor could be an option in the case of specific adsorbent materials with fine particles and powders [134]. For the combined regeneration modes such as VTSA, a novel swing adsorption reactor cluster (SARC) was developed in the past few years by a group of researchers [143]. This reactor consists of four multistage reactors and each reactor is responsible for carbonation, evacuation, regeneration, and cooling processes. A sound knowledge of this novel technology is available in recent publication [143]. Nevertheless, the technology readiness level and suitability for combined use with potential adsorbents remain an open challenge.

In the present review of amino acid-based adsorbents, the number of regeneration cycles for these adsorbents have been reported in several research articles (Tables 7 and 8). The highest number of cycles was 14 [79], and most adsorbents showed high stability with 10 regeneration cycles in average [25,41,49,54,59], advocating the potential application of AA-based adsorbents. However, these articles only discussed the regeneration performance without in-depth analysis of regeneration mode and reactor configuration. As a matter of fact, solid adsorbents are most likely to behave differently under realistic dynamic conditions, considering a non-equilibrium multi-component mixture of flue gas stream as well as different types of gas–solid contact systems used in real post-combustion CO₂ processes [12]. Subsequently, an appropriate combination of reactor configuration, regeneration mode, and adsorbent selection will significantly enhance the overall CO₂ adsorption performance in large-scale or industrial applications. Moreover, the number of cycling times and the energy consumption can be reduced, thus increasing the productivity of the process. Therefore, by taking into account all these aspects, it is possible to establish a promising adsorption-based CO₂ capture technology that is economically viable. This will attract more researchers, industrial experts, and engineers to be involved in the future implementation of this technology process.

4. Challenges and Limitations Associated with Amino Acid-Based Adsorbents for CO₂ Capture

Although amino acids are known as a green sorbent material and are a promising candidate for enhancing CO₂ adsorption capacity of solid sorbents, there are limitations and challenges that must be addressed before these adsorbents can be viably commercialised. Furthermore, the feasibility of this technology depends on various parameters, including the type and source of amino acid, type of solid materials, adsorption capability under real dynamic conditions, reactor configuration, and economic aspects. This defines the limitation of CO₂ capture adsorption process for commercial deployment as more factors must be considered to optimise the adsorbent functionalities and to scale-up the process for industrial application. Therefore, extensive research and development studies in the following area are highly encouraged:

(i) Adsorption Mechanism

There is lack of data published on the interaction mechanism between amino acid and CO₂ adsorption. Most available information on the mechanism between CO₂ and amino acid (AA) addressed in previous literature is for CO₂ absorption. Although the mechanism of CO₂ for solid AA-based adsorbent is believed to follow a similar ratio stoichiometry mechanism of 1:2 such as in the case for CO₂ absorption, it is still insufficient to validate the assumption. More studies on adsorption of CO₂ by AA are essential for better understanding of the adsorption mechanism to optimise the CO₂ adsorption
performance of solid adsorbents. This also helps in the development of novel amino acid-based adsorbents.

(ii) Pilot Scale CO₂ Adsorption Processes

There are several limitations for commercialising CO₂ adsorption using solid adsorbents. The most significant challenges are related to the technical aspect, such as adsorption set up or equipment installation, and the economical aspect, such as raw materials. The combined selection of the adsorbents with a suitable reactor configuration as well as the regeneration mode should be performed in a pilot-scale for early investigation on the practicality of the technology. Several criteria need to be considered to have a possible large-scale system, such as developing low-cost raw material, cost effective technology with high regeneration performance, high selectivity towards CO₂, and insensitivity to some other trace contaminants found in a typical flue gas. Currently, there is no study reported that focuses on AA-based adsorbents for CO₂ capture for large-scale application. Therefore, more studies need to be conducted in this area.

(iii) Life Cycle Assessment and Economic Impact Analysis

The life cycle assessment (LCA) is an assessment tool standardised by the International Organisation for Standardisation for general practices to analyse the environmental impacts and benefits of a product or technology in its entire life-cycle stages [144]. This method quantifies the emissions of greenhouse gases (GHG) associated with each process in the system boundaries, especially for CO₂ gases. The principle of LCA involves four phases: (1) the definition of goal and scope, (2) life cycle inventory analysis (LCI), (3) life cycle impact assessment (LCIA), and (4) interpretation [144]. During the first stage, a system boundary covering the entire life cycle from cradle-to-grave (from raw material acquisition to end of life of the product or service) is developed to define the required processes and life cycle stages prior to LCI analysis [145]. In accordance with the UN’s Sustainable Development Goals (SDG13), it is important to perform the LCA for AA-based adsorption technology. This will determine the efficiency of the technology in reducing carbon footprint. Although AA is naturally non-toxic, there is no guarantee that the AA-based adsorbents possess the same properties, especially AAIL-based adsorbents. In addition, an economic impact assessment (EIA) is also required in relation to cost and amount of energy used. Figure 9 shows the general framework of a system boundary with the common stages of a product’s life cycle [146], and Figure 10 presents a possible framework of the five life cycle stages of an adsorbent.

![Figure 9](image-url) General framework of a system boundary for life cycle assessment (reproduced with permission from Hernandez et al. [146], published by Elsevier (2019)).
5. Conclusions

The urgency to mitigate the climate change problem associated with continuously increasing CO$_2$ emissions into the atmosphere has facilitated unprecedented amounts of research to improve the efficiency of various potential carbon capture and storage (CCS) technologies. One of the CO$_2$ separation techniques that has gained attraction among the researchers is CO$_2$ capture via adsorption using solid sorbents (adsorbents). Although there are many works reported on the development of novel adsorbents to enhance the CO$_2$ adsorption capacity, not all of them are green materials. Amino acid is one of the green solvents reported in most publications. Hence, it is suitable to be used as an activating agent to modify solid materials properties to enhance the selectivity of CO$_2$ during the capturing process, attributed to its reactive functional groups, mainly amine (-NH$_2$). This paper has presented the fundamental properties of amino acids and discusses how they contribute to the enhancement of solid sorbent properties. It has endeavoured to report the performance of the amino acid-based adsorbents that have been published in the past ten years and to discuss the challenges and limitations of these adsorbents. This systematic review will help in filling the gap of the research in the field of CO$_2$ capture and facilitate the development of the specific area of adsorption technology.

In this systematic review, the literature data from two databases (Web of Science and Scopus) were collected according to the preferred method of reporting items for systematic reviews, namely Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) as described in Section 2. It was found that the information related to the application of amino acid in CO$_2$ adsorption is indeed lacking in this field of CO$_2$ capture,
which clearly highlighted the research gap in this field, illustrated through the keywords-based mapping analysis. In addition, out of 412 records from Scopus and 488 records from Web of Science obtained using the developed search string, there were only 66 review articles (22—Scopus; 44—Web of Science) without removing the duplicate records. Most of the review papers discussed on the amino acids as a potential solvent for CO$_2$ capture. None of the papers reviewed on amino acid application in CO$_2$ adsorption, except for one recent publication [49] that briefly discussed the potential of amino acid as one of the ligands for the synthesis of bio-based metal organic frameworks (Bio-MOFs), which supports the relevance of the topic of the present review. Based on the keywords analysis and top ten most cited research articles, the hotspot area of research in this specific topic is the immobilisation of amino acid ionic liquids into solid porous materials. This is in line with the emerging technology of ionic liquids that can be tuned to improve their properties for a specific task, thus they are sometimes referred as task-specific ionic liquids (TSILs).

In Section 3.1, the physical and chemical properties of amino acid-based adsorbents were discussed thoroughly, in terms of molecular weight and protonation constant, functional groups, reaction and adsorption mechanisms between amino acid and CO$_2$, surface morphology and structural property, as well as thermal stability. In-depth review in this section can conclude that the low molecular weight of amino acid was favoured for high CO$_2$ adsorption capacity depending on the chemical structure of the adsorbent. In Section 3.2, the performance of the adsorbent with linear side chain structure such as lysine- and glycine-based adsorbents prevailed for higher adsorption capacity (1–2 mmol/g) compared to the adsorbent with a branched-side chain. The complex structure of amino acid side chain could hinder the reaction between the amino groups and CO$_2$ molecules. Moreover, the presence of multiple amino groups in the adsorbent also revealed significant improvement of CO$_2$ adsorption capacity. In this review, the amino acid-based adsorbents were classified into four adsorbent categories according to the existing form of modified amino acids: (1) amino acid ionic liquid (AAIL), (2) solid amino acid or amino acid salt, (3) strong alkaline amino acid salt, and (4) amino acid blended with amine solvent (Section 3.2). Based on the information extracted from the currently available amino acid-based adsorbents, most research focused on the impregnation of amino acid ionic liquids (AAILs) into solid porous materials such as polymethyl methacrylate (PMMA). Although these modified solid sorbents showed an improvement of adsorption capacity in comparison to raw adsorbent materials, it is still insufficient to be considered for scale-up operation. In order to compete with the conventional adsorption technology, the adsorption capacity of the adsorbent must achieve at least 3 mmol/g. Recent trends in the development of solid sorbent materials has pinpointed the advantage of porous materials such as MOFs, zeolites, and hyper crosslinked polymers (HCPs) for CO$_2$ capture. In the present review, it was also found that these adsorbents showed outstanding adsorption capacities (up to ~13 mmol/g) when incorporated with an amino acid-based activating agent, which suggests an interesting topic to be explored with promising results for future research. Nevertheless, the drawback of these adsorbents could lie on the availability and cost of raw materials as well as the preparation methods. Currently, very limited information is available related to strong alkaline amino acid salt adsorbent and blended amine–amino acid salt adsorbent, which could also be a potential topic of interest.

In Section 4, the challenges and limitations associated with amino acid-based adsorbents for CO$_2$ capture were summarised. It is important to note that the effectiveness and the feasibility of the technology to be commercially viable depends on various parameters and aspects such as type and source of amino acid, type of solid materials, adsorption capability under real dynamic conditions, reactor configuration, and economic aspects. In this systematic review, most relevant limitations were briefly discussed which include: (1) the lack of understanding of reaction between amino acid and CO$_2$ in gas–solid phase system, (2) the need for consideration to build a pilot-scale adsorption process, and (3) the necessity of conducting the life cycle analysis as well as economic assessment for these adsorbents. To summarize, among four categories of amino acid-based adsorbents presented in this
review, amino acid ionic liquid (AAIL) has an advantage over solid naturally occurring amino acids, attributed to their properties that can be tuned for a specific task. Based on all findings in this systematic review, these AAILs are most suited to be incorporated with mesoporous silica via impregnation, which is in agreement with the result of keywords co-occurrence analysis. Nonetheless, more studies are required in order to optimise the performance of these adsorbents. The potential areas of research would be the development of novel AA-based adsorbents, the optimisation of promising AA-based adsorbents, thermodynamics and adsorption mechanisms, and in-depth regeneration studies associated with regeneration mode and reactor configuration, followed by the development of a pilot-scale operation. The authors hope that this review could provide a useful addition to the current prominent adsorption technology for CO$_2$ capture.

**Author Contributions:** Writing—original draft preparation, N.S.M.H.; writing—review and editing, F.H. and L.T.G.; supervision, M.K.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Ministry of Higher Education, Malaysia, under Fundamental Research Grant Scheme (FRGS/1/2020/TK0/SYUC/01/2).

**Acknowledgments:** The authors would like to thank Sunway University, Malaysia for the Publication Support Scheme and Ministry of Higher Education, Malaysia for the Fundamental Research Grant Scheme (FRGS/1/2020/TK0/SYUC/01/2). The first author (Mohamed Hatta, N.S.) would also like to thank Sunway University for providing the PhD scholarship for her postgraduate study.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


27. Khan, M.N.; Cloete, S.; Amini, S. Efficient Production of Clean Power and Hydrogen Through Synergistic Integration of Chemical Looping Combustion and Reforming. Energies 2020, 13, 3443. [CrossRef]


34. Hasan, S.; Abbas, A.J.; Nasr, G.G. Improving the Carbon Capture Efficiency for Gas Power Plants through Amine-Based Absorbers. Sustainability 2021, 13, 72. [CrossRef]


56. Ünveren, E.E.; Monkul, B.O.; Sanoglan, Ş.; Karademir, N.; Alper, E. Solid amine sorbents for CO₂ capture by chemical adsorption: A review. *Petroleum 2017*, *3*, 37–50. [CrossRef]


Wang, X.; Akhmedov, N.G.; Duan, Y.; Luebeke, D.; Li, B. Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO₂ capture. J. Mater. Chem. A 2013, 1, 2978–2982. [CrossRef]


Wang, X.; Li, Y.; Xiao, H.; Pan, Y.; Liu, J. Hydrothermal synthesis of nitrogen-doped ordered mesoporous carbon via lysine-assisted self-assembly for efficient CO₂ capture. RSC Adv. 2020, 10, 2932–2941. [CrossRef]


130. Younas, M.; Rezakazemi, M.; Daud, M.; Waizir, M.B.; Ahmad, S.; Ullah, N.; Ramakrishna, S. Recent progress and remaining challenges in post-combustion CO$_2$ capture using metal-organic frameworks (MOFs). *Prog. Energy Combust. Sci.* 2020, 80, 100849. [CrossRef]


141. Tian, J.; Shen, Y.; Zhang, D.; Tang, Z. CO$_2$ capture by vacuum pressure swing adsorption from dry flue gas with a structured composite adsorption medium. *J. Environ. Chem. Eng.* 2021, 9, 106037. [CrossRef]


