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# Improved Hydrogel as Potential Carbon Dioxide Adsorbent

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Hydrogel is a versatile material that vastly used in various applications. In this study, the carbon dioxide capture properties of hydrogels were further improved with the infusion of amine. Three types of superabsorbent hydrogel namely polyacrylic acid (AAc), sodium polyacrylate (SAP) and polyacrylamide (AAm) were synthesized via simple solution polymerization with the aid of ammonium peroxodisulphate (APS) as the initiator and N,N'-methylenebis (acrylamide)(MBA) as the crosslinker. Diethanolamine (DEA) loading AAm hydrogel has recorded 0.9 mmol $CO_2$ captured/ g hydrogel and monoethaolamine (MEA) loading AAm hydrogel has captured 1.7 mmol $CO_2$ / g hydrogel. An increment up to 2.2 mmol $CO_2$ captured/ g hydrogel was obtained when the ratio of hydrogel to amine loading was increased to 1:4 from 1:1. In term of regeneration of the adsorbent, this amine infused hydrogels maintained its maximum adsorption capacity until third cycle. The amine infused hydrogel provide a facile platform for developing solid sorbents for $CO_2$ capture.

## 1. Introduction

Carbon dioxide ($CO_2$) has been regarded to be a major greenhouse gas for global warming which has been a serious environmental concern. The constant increment of $CO_2$ emission to the atmosphere arising from burning of fossil fuels has led to unprecedented global warming and significant climate change. In year 2020, the global $CO_2$ emission was estimated at 34.81 x $10^9$ t and this value keep increasing every year (Jaganmohan, 2022). With the rising of $CO_2$ emission, it has also led to the rising environmental concerns. Over the years, physical or chemical approaches to capture and store $CO_2$ have been introduced as a solution to the increasing $CO_2$ emission. This technology is known as $CO_2$ capture and storage (CCS). However, operational capacity of CCS facilities worldwide which dated from 2002 to 2021 was only at 36.6 x$10^6$ t/y.
Some prominent techniques to capture $CO_2$ are amine scrubbing, oxyfuel combustion, pre and post $CO_2$ combustion capture, absorption and adsorption. Among these selections, amine scrubbing is the widely accepted traditional technology owing to its applicability in industrial processes such as syngas purification and $H_2S$ removal (Varghese and Karanikolos, 2020). Amine scrubbing has been used to separate $CO_2$ from natural gas and hydrogen since 1930 (Rochelle, 2009). However, there were obvious limitations and challenges of amine scrubbing for $CO_2$ capture, which are massive energy demands associated with regenerating liquid amines, low absorption capacity, and severe corrosion on facilities for long term usage (Xu et al., 2018). To overcome the limitations of amine scrubbing for $CO_2$ capture, it was proposed the utilisation of amine aqueous solutions such as monoethanolamine (MEA) and diethanolamine (DEA) by infusing it into hydrogel. This alternative is known as amine infused hydrogel.
Hydrogel is a part of the gels group where its properties can be modified in response to an environment stimulus such as light, heat and pH. The hydrogel has been used in numerous applications in the role of membrane, drug delivery, biosensors, coating and adsorbent. Particularly, the hydrogels possess three dimensional (3D) cross-linked polymer matrices that can take in and keep massive quantities of liquids. Hydrogels are generally prepared based on the hydrophilic monomers, in any case hydrophobic monomers are sometimes used in the hydrogel preparation to regulate the properties for specific applications. The tuneable properties, hydrophilic surface and the ability to absorb a large amount of liquid of hydrogel make it widely used in various application. Attribute to the versatility of hydrogel, there are various of material to choose from to synthesised hydrogel, either synthetic or natural polymer. These polymers have their own properties depending on their chemical

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composition. Thus, this study aims to investigate the $CO_2$ capture performance of three type hydrogels namely AAc, SPA and AAm. These hydrogels were then infused with amine to facilitate the $CO_2$ capture performance. The influences of amine type, hydrogel to amine loading ratio, and adsorbent regeneration were also explored to gain a deeper understanding of the $CO_2$ capture by the amine infused hydrogel.

## 2. Experimental

### 2.1 Material

Acrylic acid (99 %), sodium hydroxide pallet, acrylamide (AR), MEA (EMSURE) and DEA (EMSURE) were supplied by Merck. AR grade ammonium peroxodisulphate (APS) was supplied by R&M Chemicals. N,N'-methylenebis(acrylamide)(MBA) (99 %), was purchased from Sigma-Aldrich. A synthesis-grade of monomers and cross-linker were used as-received without further purification. Distilled water was used throughout this research work as the polymerization medium.

### 2.2 Synthesis of AAm, AAc and SPA hydrogel

The synthesis of hydrogel was conducted in 500 mL three-necked round bottom flask via solution polymerization. A water bath at 65 °C was utilised to ensure all component mixture was received proper heat distribution from water bath to the reactor. The reactor was equipped with a thermocouple, nitrogen gas inlet and vent condenser as illustrated in Figure 1. The mixture was stirred using magnetic bar to ensure proper mixing. Synthesis of hydrogel was started by heating up the mixture of monomer and distilled water in the reactor. Once the solution reached 60 °C, the cross linker was added into the monomer solution. The initiator was added to the reactor after swirling it for 10 minutes. Before the reactor was removed from the heat source, the mixture was stirred until it solidified as a hydrogel. Then, the obtained hydrogel was cut into smaller pieces and dried at 50 °C for 5 h. The formulation of the hydrogels was tabulated in Table 1.

*Table 1: The formulation of the hydrogels*

| Hydrogels | AAm | AAc | SPA |
|---|---|---|---|
| Monomer | 30 g of acrylamide | 30 g of acrylic acid | 100 g of sodium acrylate (90 % degree of naturalization) |
| MBA (crosslinker) | 1 wt% | 1 wt% | 1 wt% |
| APS (initiator) | 0.25 wt% | 0.25 wt% | 0.5 wt% |
| Distilled water (solvent) | 70 g | 70 g | n.a |

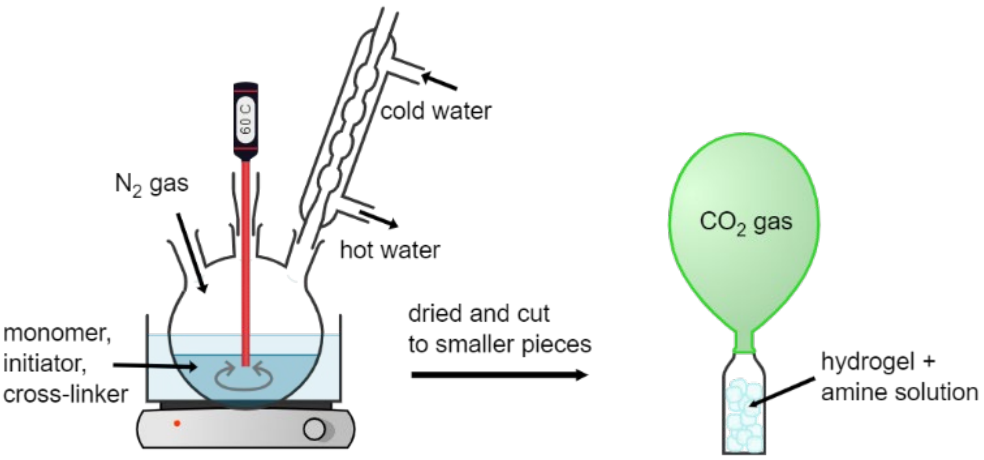


*Figure 1: Schematic diagram of amine infused hydrogel preparation for CO2 capture analysis Fourier Transform Infrared (FTIR) analysis*

Perkin -Elmer Spectrum One, FTIR-frontier were used to assess FTIR spectra of all sample. Wave resolution was 4 $cm^{-1}$, and the wavenumber ranged from 400 to 500 $cm^{-1}$. The hydrogel samples are prepared by vacuum oven-drying them for five hours at 50 °C. The samples were thinly cut, and the attenuated total reflectance (ATR) method was used.

### 2.3 Degree of swelling

Degree of swelling of the hydrogels, DS is defined as ratio of absorbed liquid eight to dry gel weight (Stoševski et al., 2015). Distilled water was used to measure the swelling behavior of hydrogels in the two types of 30 wt% amines solution which were MEA and DEA. The Eq(1) was utilised to calculate DS.

$$DS = \frac{W_s - W_d}{W_d} \quad (1)$$

where $W_s$ is the weight of swollen hydrogel and $W_d$ is the dry weight of the hydrogel. Hydrogel were swollen in distilled water and two different amine which were MEA and DEA.

### 2.4 $CO_2$ capture analysis

The experimental procedure of $CO_2$ capture capacity was adapted from Xu et al., (2018). Two study was conducted to determine the effect of type of amine (MEA and DEA) and the effect of amine loading. Firstly, 0.5 g of dry AAc, SPA or AAm hydrogels with size around 0.2 cm were weight and added into the 10 mL sample bottles together with 0.5 g of 30 wt% of amine solution (either MEA or DEA). The initial mass of swollen hydrogel and sample bottle was recorded prior the $CO_2$ adsorption analysis. A balloon filled with purified $CO_2$ gas were connected to the sample bottles mouth. Snoop test was done to ensure the $CO_2$ gas was not leaking. The $CO_2$ capture capacity were measured gravimetrically using balance; the mass difference of the samples before and after $CO_2$ capture as recorded at 5 min for first half an hour and continue with every 15 min time interval until the samples saturated. All the experiments were performed at ambient condition.
The effect of amine loading was investigated by using 30 wt% of MEA solution. Ratio of AAc, SPA and AAm hydrogel/ MEA solution were varied at 1:1 and 1:4. The experiment was repeated for three times to obtain average $CO_2$ adsorption capacity.

### 2.5 Regeneration of amine infused hydrogels

For the first cycle, 30 wt% MEA infused AAc, SPA and AAm hydrogels underwent the $CO_2$ capture experiment at ambient conditions. After that, the $CO_2$-loaded sample was placed in a drying oven at 95 °C for 1 h (Xu et al., 2018). The samples were weight before and after the regeneration process and distilled water was added to the heated sample to make up the evaporative water loss. The samples were cooled to the ambient temperature before the repetition of $CO_2$ capture was performed. Five cycles of adsorption and desorption cycle were performed to evaluate the regeneration ability of these amine infused hydrogels.

## 3. Results and discussions

### 3.1 Functional group of hydrogels

Figure 2 shows the FTIR spectra of AAc, SPA and AAm hydrogel. All hydrogel shows characteristic carbonyl bonds (C=O) from 1,555 to 1,755 $cm^{-1}$. These bonds are typical in amide, carboxylic acid and ketones which are commonly forms the basis of polymer structures. The amide functional group in AAm hydrogel was located at 1,654 $cm^{-1}$, which was also confirmed by the two N-H stretches of primary amine from 3,000 to 3,300 $cm^{-1}$, corresponds to the symmetric N-H stretch and asymmetric N-H stretch in lower wavenumber and higher wavenumber.

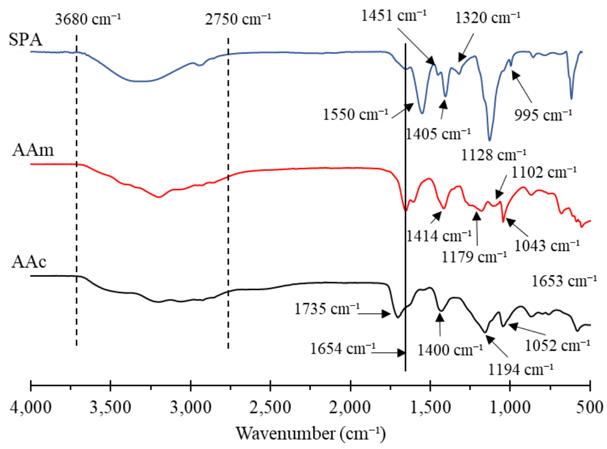


*Figure 2: The FTIR spectras of AAc, SPA and AAm hydrogel.*

Meanwhile, the characteristic peak of AAc was confirmed from the presence of strong saturated C=O stretch at 1,735 $cm^{-1}$ and C-O-H in-plane bend and 1400 $cm^{-1}$. In SPA, since the carbonyl bond exist as a negatively charged carboxylate, two intense peaks were observed resulted from the dipole moment of C=O and C-O bond. The stretching at 1,550 $cm^{-1}$ was attributed to asymmetric C-O 'bond and a half' stretch and and 1,405 $cm^{-1}$ represents symmetric C-O 'bond and a half' stretch. Similar finding was reported by Magalhães et al. (2012). Hydrogen bondings were responsible for the structural integrity of all hydrogels. The presence of negatively charged oxygen in SPA and AAc and nitrogen in AAm made them capable to form intermolecular interactions. These intermolecular forces could be elucidated from the hydrogen bond stretches at the -OH region (3,300 $cm^{-1}$) (Novak and Grdadolnik, 2021). In the case of AAc and SPA, the carboxylic or carboxylate bond can exist as dimers, which can form hydrogen bonds between themselves.

### 3.2 Degree of swelling

The easily evaporated property of amine had caused some researchers to impregnate the amine solution into the host such as carbon (Gholidoust et al. 2017) and hydrogel (Xu and Wood, 2018). It must be noted that hydrogel was dried after the synthesis to facilitate its storage and transportation. Thus, swelling degree and ability of hydrogel to retain the liquid is important to be studied in $CO_2$ capture analysis to ensure full insight of the hydrogel before it being used in the adsorption column. Table 2 tabulated the degree of swelling for AAc, SPA and AAm in MEA and DEA. As the comparison, the swelling degree of these hydrogels in water was also investigated. The results showed that the AAc hydrogel can swell up to 46 times compared to its original mass in 30 wt% DEA solution. The superabsorbent SPA was able to retain 3,342 % of water but the lower swelling degree were recorded in the MEA and DEA solution. SPA was synthesis using sodium acrylate which resulted from naturalization of acrylic acid using sodium hydroxide. Hence, SPA contain both acrylic and acrylate groups (Ceylan et al., 2019). The acrylic acid group in AAc and SPA has reacted with the bases MEA and DEA solution and enable the hydrogel to retain more amine solution compared to natural pH water. Meanwhile, AAm hydrogel recorded lowest degree of swelling in all solution compared to AAc and SPA. The hydrogels ere immersed three different medium which were distilled water, 30 wt% MEA and 30 wt% DEA solution.

*Table 2: The degree of swelling for AAc, SPA and AAm*

| | Water | MEA | DEA |
|---|---|---|---|
| AAc | 408 % | 1,790 % | 4,634 % |
| SPA | 3,342 % | 729 % | 1,453 % |
| AAm | 851 % | 395 % | 561 % |

### 3.3 $CO_2$ capture analysis

In this section, a comparison of $CO_2$ uptake performance between MEA and DEA infused hydrogels were investigated to better understand which amine solution is best paired with the synthesised hydrogels. The difference in $CO_2$ uptake performance between MEA and DEA infused hydrogels was analysed based on Figure 3(a). In Figure 3(a), the overall results of MEA infused hydrogels were deemed to be better than DEA infused hydrogels. On average, the MEA infused hydrogels has increased more than 50 % performance in $CO_2$ uptake compared to DEA infused hydrogels under the same experimental conditions.

The increased of performance for MEA infused hydrogels can be justified based on few reasons. MEA, being a primary amine, presents less steric hindrance, which eases the reaction with $CO_2$ (de Ávila et al., 2016). The obstruction of a chemical reaction attributed to how the atoms in a molecule are arranged is known as steric hindrance. Less steric obstruction made it possible for faster and more efficient response to occur. The disadvantage of DEA is it exhibits slow kinetics (Warudkar et al., 2013). Therefore, the rate of reaction between DEA and $CO_2$ is slower compared to MEA and $CO_2$. Referring to previous study from de Ávila et al., (2016) and Xu et al., (2018), a similar trend of results was reported regarding MEA and DEA infused hydrogels.

However, it is important to note that the performance of $CO_2$ uptake performance between MEA and DEA infused hydrogels could be observed differently under different experiment conditions. Although MEA infused hydrogels have higher $CO_2$ uptake during its preliminary $CO_2$ capture process, it is known to be more volatile and less stable when comparing to DEA. Hence, under temperature-dependent experiment, DEA may be deemed more suitable due to it being less volatile.

The $CO_2$ capture was further analysed on its dependency to the amine loading, specifically 30 wt% MEA solution. As shown in Table 2, the synthesised AAc, SPA and AAm hydrogel were capable to retain amine up to thousand percent of its weight. The results indicate all the $CO_2$ capture of hydrogels has increased but only AAc hydrogel show a significant increment in $CO_2$ capture after loaded with hydrogel to amine ratio of 1:4. The hydrogel act as the solid support for the MEA and providing larger surface area for the adsorption process of

$CO_2$. Thus, for SPA and AAm hydrogels, obtaining optimum amine loading ratio and larger active site would significantly enhance the $CO_2$ capture compared to increase of amine loading alone.

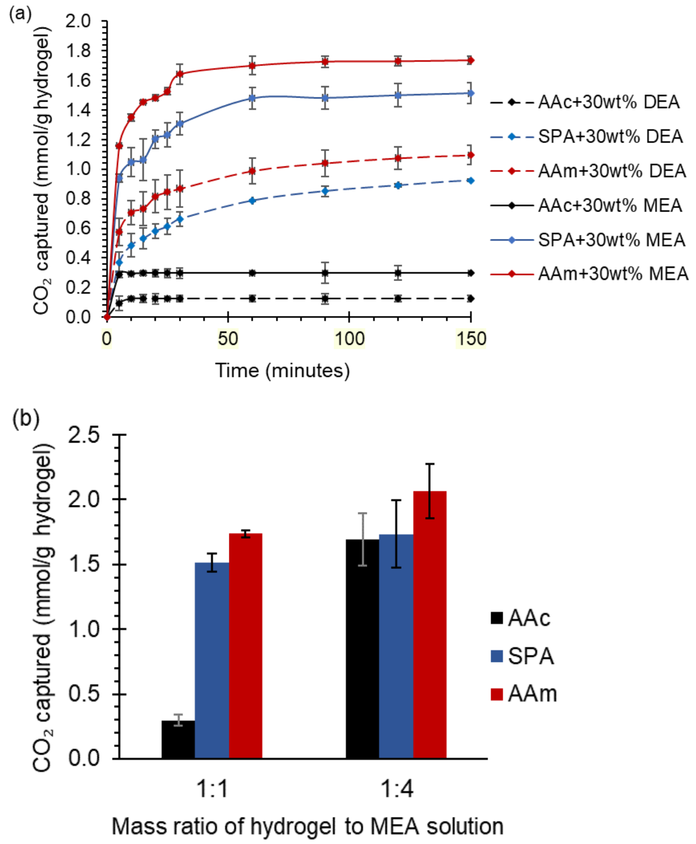


*Figure 3: (a) effect of type amine infused and (b) hydrogel to MEA solution ratio on $CO_2$ captured by the AAc, SPA and AAm hydrogels*

### 3.4 Regeneration of hydrogels

To lower the material costs, adsorbent must be easily regenerated. Thus, the recyclability of amine infused AAc, SPA and AAm hydrogel were accessed using thermal regeneration method in which the saturated amine infused hydrogels were heated in the drying oven at 95 °C for one hour. As shown in Figure 4, generally all the amine infused hydrogels shows an excellent percentage of initial $CO_2$ capture up to third cycle number. However, significant decline was started to show at fourth cycle number. Repetitive heat treatment had caused the amine infused hydrogels to anneal, evaporate the ME A and subsequently reduced the $CO_2$ adsorption capacity.

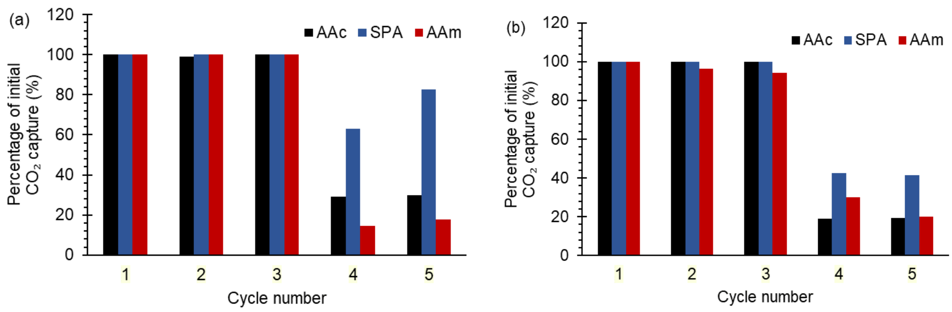


*Figure 4: The recyclability of AAc, SPA and AAm at hydrogel to MEA loading ratio of (a) 1:1; (b) 1:4*

## 4. Conclusions

Three types of hydrogels which were AAc, SPA and AAm have been synthesised and infused with two different amine namely MEA and DEA. The 30 wt% MEA infused AAm hydrogel captured 17 times of $CO_2$ compared to 30 wt% DEA infused AAc hydrogel. Even the SPA is known for its superabsorbent ability in water, but its absorption capacity showed some decrement in bases liquid especially in MEA and DEA. The performance of hydrogel adsorbents depends on its constituents, or the functional group produced by the polymer networks of the gels. The monomer characterization should be carefully selected to produce adsorbent with high $CO_2$ capture ability and high regeneration capacity. Simple $CO_2$ capture analysis was carried out in this work at ambient conditions that restrict the variation of experimental temperature and pressure. Further research using a $CO_2$ adsorption column is required to ensure the effect of condition variation can be determined.

### Abbreviations

AAc – polyacrylic acid
AAm – polyacrylamide
APS – ammonium peroxodisulphate
AR – analytical reagent
CCS – carbon dioxide capture and storage
$CO_2$ – carbon dioxide
DEA – diethanolamine
MBA – N,N'- methylenebis(acrylamide)
MEA – monoethanolamine
SPA – sodium polyacrylate
SPA – sodium polyacrylate

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