

IMPREGNATION OF COMMERCIAL PALM SHELL ACTIVATED CARBON WITH MONOETHANOLAMINE FOR ADSORBING CO₂ FROM GAS MIXTURE

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Abstract. Impregnated activated carbon beds used in this research to adsorb and separate CO₂ gas from gas mixture stream. The results showed that impregnation of 500 µm particle's size activated carbon with monoethanolamine (MEA) enhanced more than other amine based-chemicals the adsorption separation of CO₂. Impregnation with MEA led to the blockage of the activated carbon particle's pores by MEA molecules, which reduced the surface area of the impregnated activated carbon samples by about 13 times. On the other hand impregnation with MEA achieved an adsorption bed capacity improvement by 172 and 94 % for particle's size of 500 µm and 710 µm activated carbon beds respectively comparing to non-impregnated activated carbon beds of the same particle's size. Activated carbon particle's size also plays role in the enhancement of the CO₂ adsorption. Operating temperature and feed gas flow rate affects on breakthrough time were investigated in this study.

Keywords: Activated carbon; CO₂; Adsorption; Impregnation; MEA.

1. INTRODUCTION

In the transition towards a more sustainable energy economy, fossil fuels are likely to remain the main source of global energy supply for the foreseeable future. Forecasts of global energy use in the 21st century suggest an increasing dependence on fossil fuels, such as coal, oil and natural gas [1], [2] and [3]. However, related CO₂ emissions are a major concern as increasing CO₂ emissions has been identified as a contributor to global climate change, commonly known as the greenhouse effect, [1]. The continuous use of fossil fuels is dependent on the reduction of CO₂ emissions, [1]. Malaysia is the world's top producer of palm oil and this sector generates huge amounts of solid wastes such as empty fruit bunches (EFB) and palm shell, [4]. Activated carbons are sorbents with a highly developed porosity, especially micropores and mesopores, that are used in a wide range of household, medical, industrial, military and scientific applications, including gas-phase and liquid-phase processes, [5]. It has been shown that the CO₂ capture capacity can be increased by introducing nitrogen functional groups on the surface either by NH₃ heat treatment or chemical impregnation,[6], [7] and [8].

The objective of this research is to study the affect of impregnating activated carbon particles with amine-based chemicals to enhance the adsorption separation of CO₂ from simulated flue gas stream and then to find out the best among them to produce the activated carbon basket (ACB).

2. EXPERIMENTAL

2.1. Materials

The commercial activated carbon made from palm shell charcoal produced by physical activation process with steam as the activating agent. It purchased from Bravo Green SDN. BHD (Sarawak, Malaysia). Monoethanolamine (MEA) from UNILAB 97.

The apparatuses employed in this study are shown in Figure 1:

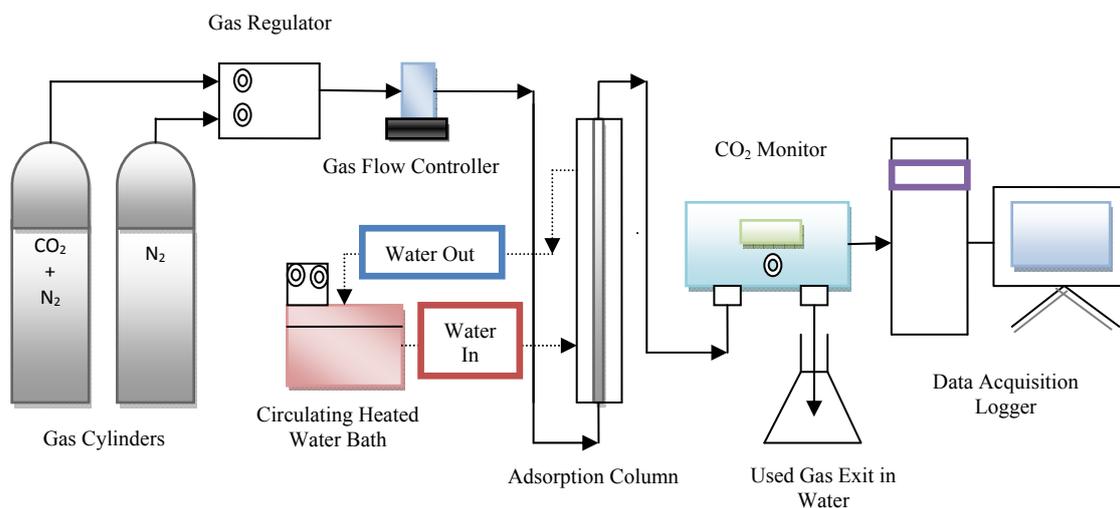


Figure 1 Experimental Setup

2.2. Surface treatment of activated carbon samples

2.2.1. Activated carbon particle's size characterization

Activated carbon particle's size was characterized using 850, 710 and 500 μm sieves. Household coffee blender made by PHILLIPS was used to crush the activated carbon particles. Two sizes were acquired.

1. Particles passing 850 μm and stopping on 710 μm (710 μm).
2. Particles passing 710 μm and stopping on 500 μm (500 μm).

2.2.2. Impregnation process

Impregnation process was carried out [9] by weighting activated carbon particles to 5 g each in a beaker. 2 g of MEA added (0.4 w/w, MEA/activated carbon) to the beaker with 10 g of deionized water (0.2 w/w, MEA/deionized water). The obtained slurry magnetically stirred at 500 rpm for one hour at room temperature. The final slurry then dried in Heraeus Instrument Vacuthermo oven. The slurry heated to 70 $^{\circ}\text{C}$ under 1000 mbar vacuum for 6 hours to dry completely without any trace of moisture left within its particles.

2.2.4. Evaluation method of activated carbon bed

In this research breakthrough time used as practical approach to evaluate the performance of impregnated and non-impregnated activated carbon beds. Breakthrough time could be defined as the time spanning from the beginning of the adsorption experiment until the CO_2 molecules start to breaking through as the adsorption bed is in the process to be saturated. Guardian Plus CO_2 monitor was used to measure the percentage (%) of CO_2 gas exiting the adsorption column. Data Acquisition Logger was used to measure the breakthrough time in minutes.

3. RESULTS AND DISCUSSIONS

3.1. Effect of different amine-based chemicals on breakthrough time

Different breakthrough times obtained from activated carbon beds impregnated with different amine based chemicals. The results in Figure 2 below are showing that there is declining in the breakthrough time mainly due to the steric hindrance influence. Steric hindrance influence defined as the prevention or retardation of a chemical reaction, caused by the arrangement of atoms in a molecule. Steric hindrance or steric resistance occurs when the size of groups within a molecule prevents chemical reactions that observed in related smaller molecules. For bigger size molecules of the amine-based chemicals used in this study the reactive nitrogen atom is surrounded by many other atoms of hydrogen, carbon and oxygen. Steric hindrance would hamper CO_2 molecules to be close enough to react with the reactive nitrogen atom, which will lead to reduction in the breakthrough time as less CO_2 molecules would be adsorbed and more CO_2 molecules would be leaving the adsorption bed.

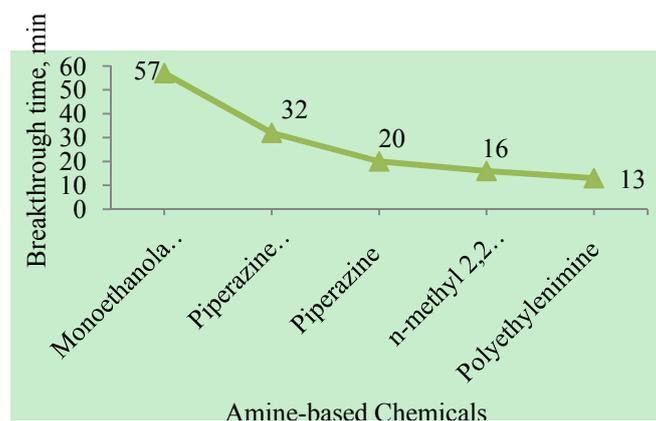


Figure 2 Breakthrough time in minutes for the amine based chemical used in this study

3.2 Effect of impregnation with MEA on the adsorption performance of activated carbon beds

Table 5 is showing that breakthrough time of MEA-impregnated activated carbon bed has improved significantly comparing to non-impregnated activated carbon bed of the same particle's size. This improvement is due to that the impregnated bed has more probability to adsorb CO₂ molecules as the impregnation with MEA would develop many active sites on the surface and inside the pores of the activated carbon particles where more CO₂ molecules would be chemisorbed. MEA impregnated beds would adsorb CO₂ molecules in more efficient and selective manner as physisorption is the method of adsorbing in non-impregnated activated carbon beds with limited adsorbing active sites. The effect of the particle's size of the activated carbon particles also clear in Table 5. Smaller activated carbon particles (500 μm) tend to have more surface area per unit weight, which means more MEA to be loaded and more efficient adsorbing. On the other hand small smaller size activated carbon particles provide quicker rate of adsorption which reduces the amount of contact time required for the adsorbing process to be accomplished

Table 5 Effect of impregnation with MEA and activated carbon particle's size on the improvement of activated carbon beds breakthrough time

Type of adsorption bed	Break through time	Breakthrough time improvement, %
Non-impregnated bed710 μm	30	90
MEA-impregnated bed 710μm	57	
Non-impregnated bed500 μm	34	165
MEA-impregnated bed 500μm	90	

3.3 Adsorption isotherm of impregnated and non-impregnated activated carbon

The adsorption isotherm of impregnated and non-impregnated activated carbon was measured using ASAP 2020. ASAP 2020 would introduce controlled dosages of inert gas, nitrogen, to the impregnated and non-impregnated activated carbon previously degassed samples. In Figure 3, the adsorption isotherm of 500 μm activated carbon sample impregnated with MEA is corresponding to class II isotherm. This class of isotherm is characteristic with weak adsorbate-adsorbent interactions or adsorption on non-porous particles

and macropore particles, which is the case here as large amount of the activated carbon particles pores blocked by the impregnated amine. The quantity of N_2 gas adsorbed in Figure 3 is little at low partial pressure of N_2 . The situation continue until the partial pressure of N_2 reached the value of atmospheric pressure, at this point the quantity adsorbed of N_2 sharply raised due to the high pressure exerted on the impregnated activated carbon sample. The BET surface area is found to be $65 \text{ m}^2/\text{g}$. Figure 4 is showing adsorption isotherm of non-impregnated activated carbon of particle's size of $500 \mu\text{m}$, the Figure is corresponding to class I isotherm, which is for adsorbents with a predominantly micropore particles (< 2 nanometer).. In micropore, the potential of both sides of the pore walls overlap, which would enhance the adsorption potential. With smaller pore width the potential becomes deeper resulting in enhancing the adsorption energy and adsorption occur at very low pressures, which make adsorption process starting almost instantly when the N_2 molecules contact the activated carbon particles as shown in Figure 4, [10]. BET surface area of non-impregnated activated carbon sample was found to be $838 \text{ m}^2/\text{g}$. Comparing the BET surface area of the two samples, MEA-impregnated surface area is 13 times less than BET surface area of non-impregnated activated carbon sample. The significant reduction in the surface area is suggesting that MEA molecules blocked the pores of the impregnated activated carbon particles, but at the same time creating many active sites for CO_2 adsorption and that the adsorption process was chemisorptions in nature, which explains the surge in the breakthrough time of the impregnated activated carbon beds comparing to the non-impregnated beds, as many active sites had been installed on the MEA-impregnated activated carbon particles and inside its micropores.

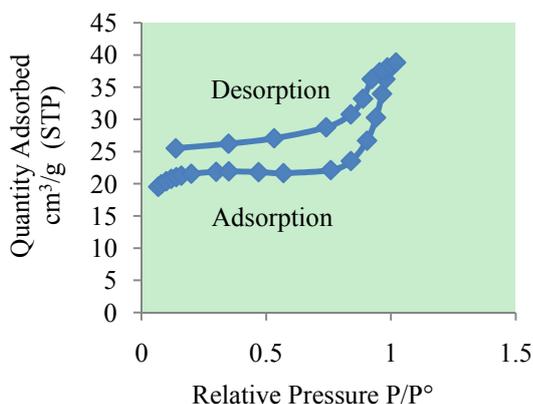


Figure 3 N_2 adsorbed onto $500 \mu\text{m}$, activated carbon particles impregnated with MEA at 77 K

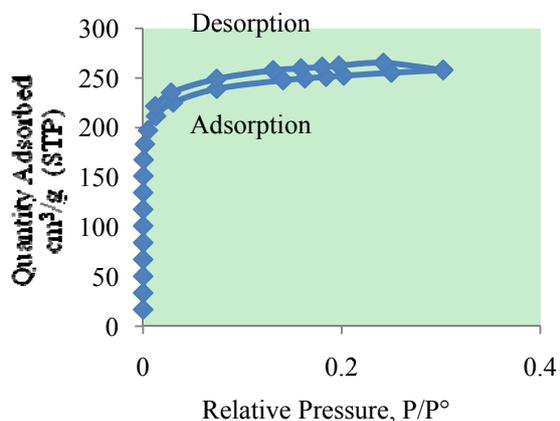


Figure 4 N_2 adsorbed onto $500 \mu\text{m}$, non-impregnated activated carbon particles at 77 K

3.4. Affect of feed gas flow rate on the adsorption of CO_2 for non-impregnated and MEA-impregnated activated carbon beds

Figure 7 is showing the effect of operating temperature on the breakthrough time of non-impregnated and MEA-impregnated activated carbon beds at feed gas flow rate of $10 \text{ ml}/\text{min}$. In Figure 7 the breakthrough time drop for MEA-impregnated activated carbon bed was higher than the drop of breakthrough time for non-impregnated activated carbon bed. The mechanism of how the two beds adsorb CO_2 is different, while in the case of non-impregnated activated carbon bed the method of adsorbing is physical with no chemical reaction involved, and the CO_2 molecules would be bonded to the activated carbon particles by the weak Van der Waals attraction forces. Although the adsorption process is to some extent exothermic by nature, the increase in temperature due to the exothermic affect would be in the order of one or fraction of one degree Celsius, which would not affect much the adsorption of CO_2 . The method of adsorbing CO_2 molecules in the MEA-impregnated beds is mostly chemical as the CO_2 molecules would be reacted chemically with the MEA-impregnated onto the activated carbon particles. CO_2 molecules would be bonded to the MEA-impregnated activated carbon particles by strong chemical bond. The nature of this reaction is exothermic and it would not favor increasing in the surrounding temperature where the reaction would be shifted to the negative side where less CO_2 molecules would be adsorbed and more would leave the adsorbing bed. An experiment was conducted to measure the increase in temperature during the adsorption

process. For non-impregnated activated carbon, the temperature increase was between 0.5-1 °C and for MEA-impregnated activated carbon bed was 5 °C.

3.5. Affect of feed gas flow rate and operating temperature on the adsorption of CO₂ for non-impregnated and MEA-impregnated activated carbon beds

Results in Figure 7 are showing the effect of feed gas flow rate at room temperature on the breakthrough time of MEA-impregnated and non-impregnated activated carbon beds. At low feed gas flow rate of 10 ml/min, there is sufficient time for the chemical reaction to occur between CO₂ molecules and the impregnated activated carbon beds. When the feed gas flow rate increased to 30 ml/min, the residence time available for the chemical reaction would decrease significantly and more CO₂ molecules would leave the adsorption column without having the chance to react and to be captured by the impregnated activated carbon bed, which cut down the breakthrough time. The increase in feed gas flow rate would have less affect on the physical attraction between CO₂ molecules and the non-impregnated activated carbon beds as there is no chemical reaction. The same trend noticed on the increase of the operating temperature at fixed feed gas flow rate of 10 ml/min, as seen in Figure 8.

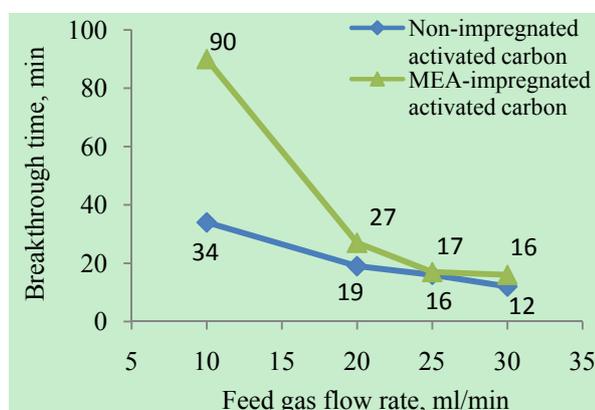


Figure 7 Breakthrough time of non-impregnated and MEA-impregnated 500 µm activated carbon beds at different feed gas flow rates

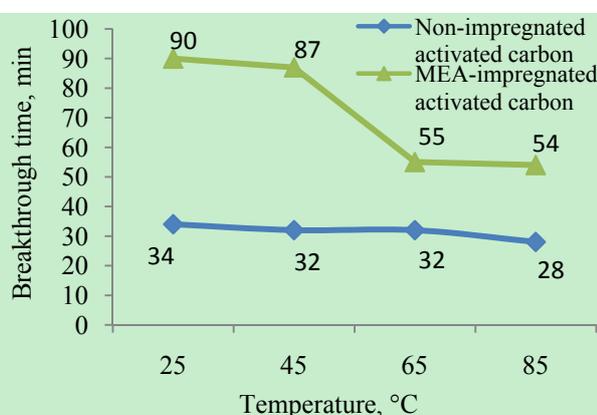


Figure 8 Breakthrough time of non-impregnated and MEA-impregnated 500 µm activated carbon beds at different operating temperatures

4. CONCLUSIONS

The results in this research had showed that the adsorption of CO₂ by activated carbon can be enhanced considerably by impregnation with Monoethanolamine (MEA). Activated carbon particle's size also playing a role in the adsorption process, as smaller particles would result in longer breakthrough time, due to that more surface area would be available to adsorb CO₂. An increase in breakthrough time by about 172 and 94% for 500 µm and 710 µm particle's size impregnated activated carbon beds respectively, comparing to non-impregnated activated carbon beds of the same particle's sizes. Significant reduction in the surface area of the impregnated activated carbon particles by 13 times was due to the particle's pores blockage by MEA molecules, which created many active sites for CO₂ adsorption. Results showed that feed gas flow rate affected the breakthrough time more adversely than operating temperature.

5. ACKNOWLEDGMENT

The authors would like to thank University of Malay for offering the necessary fund for this research through the Institute of Research Management and Monitoring (PPP) fund system.

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