



INVESTIGATION OF IMPREGNATED COMMERCIAL RICE HUSKS ACTIVATED CARBON WITH ALKANOLAMINE AS CARBON DIOXIDE (CO₂) ADSORBENT

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ABSTRACT

The adsorption capacity of the activated carbon can be increased by introducing the amine group on the surface of the adsorbent. Modified rice husk activated carbon with different concentration and mixture ratio were prepared using wet impregnation method with alkanolamine. The adsorbents obtained were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). From XRD analysis, the diffraction angles around 21.66° to 22.18° were linked for pyrazole, ethanolamine and diethanolamine which prove the presence of hydrocarbon and amine on the activated carbon surfaces. The presence of amide functional groups in FTIR analysis at 3288 cm⁻¹ and 1651 cm⁻¹ band proved that there was a reaction occurred between carboxyl groups on the activated carbon surfaces with amine bond. For FESEM analysis, it was shown that the morphology of the non-modified activated carbon contains many pores on its surface while the pores on the modified activated carbon were covered with alkanolamines according to the selected concentrations.

Keywords: activated carbon, adsorbent, rice husks, alkanolamine.

INTRODUCTION

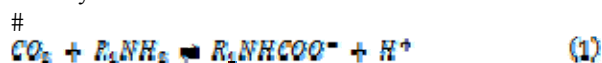
The increasing carbon dioxide (CO₂) emission has been described as the main contributor to global climate change, basically known as the greenhouse effect (Khalil *et al.* 2011). The average temperature of earth's surface has increased by 0.6 °C in 20th Century compared to the past Century (Liu & Lin, 2009). This has become a world concern, where by numbers of approaches have been introduced to significantly reduce and mitigate the release of CO₂ to the atmosphere which is the results of anthropogenic activities.

Adsorption is considered to be one of the most promising methods of mitigating fossil fuel CO₂ emissions and was agreed throughout the world (Snape *et al.* 2004). Activated carbon is one of the sorbent that can be used for adsorption purpose (Hauchhum & Mahanta, 2014). The presence of hydrocarbon such as cellulose and lignin made the rice husk suitable for preparation of activated carbons (Kumar *et al.* 2012). Porous carbon derived from the rice husks has wide availability, fast kinetics and appreciable adsorption capacities (Chen *et al.* 2013). Rice husk that carries a hydrocarbon chain contains many pores with high surface area which perfectly meets the characteristics of a good adsorbent.

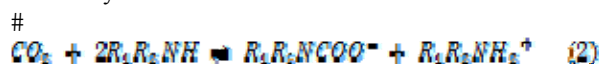
The carbon-based materials sorption capacity can be improved by using amine solution as the impregnator of the porous materials as the amine is characterized by a high absorption capacity in relation to CO₂ (Bukalak *et al.* 2013). Alkanolamine such as primary amine and secondary amine will react with CO₂ which involves

the mass transfer of CO₂ from the gas phase into the aqueous phase of amine in a series of the following reactions:

Primary Amines:



Secondary Amines:



In this research work, surface modification has been made on the rice husk activated carbon with alkanolamine solution for a potential CO₂ adsorbent. The presence of amine on the surface of the adsorbent is expected to enhance the CO₂ adsorption capacity (Boonpoke *et al.* 2012). The research aims to study the characteristics of non-impregnated activated carbon and the impregnated activated carbon with MEA and DEA at different concentration and mixture ratio.

MATERIALS AND METHODS

Materials and Chemicals

The commercial activated carbon made from rice husk ash was supplied by Sin Guan Hup Oil & Rice Mill Sdn Bhd (Penang, Malaysia). Monoethanolamine (MEA) with a molecular weight of 61.08 g/mol and Diethanolamine (DEA) with a molecular weight of 105.14 g/mol were purchased from MERCK with purity of 99%.

Activated Carbon Preparation

The activated carbon particle's size was sifted using 500 nm sieve. The prepared activated carbon particles were rinsed with deionized water followed by heating in a 70°C oven for 6 hours. The sample was then



being kept in a desiccator at room temperature to avoid the moisture effect.

Impregnation Process

The impregnation of activated carbon was done with the presence of MEA and DEA. The concentration of MEA and DEA being used were 2M, 4M, 6M, 8M and 10M. 50 g of activated carbon was used for preparation of one sample. The mixture ratio being used was based on the weight percent of both MEA and DEA mixture to activated carbon. The mixture ratio used was 1:1, 1:3 and 1:5 of activated carbon to MEA mixture and DEA. The activated carbon was impregnated with MEA and DEA based on the concentration and mixture ratio as mentioned above. The mixture was mixed in a beaker and magnetically stirred at 200 rpm for one hour at room temperature. The slurry was then being heated at 70°C at 1 atm for 6 hours to dry completely without any trace of moisture left within its particles and was kept in a desiccator at room temperature.

Activated Carbon Characterization

X-ray Diffraction (XRD)

The Rigaku Miniflex X-Ray Diffractometer of the CuK α radiation filtered by a Ni filter was used in this research with a wavelength of 1.54 Å at 30 kV and 15 mA. The activated carbon samples were initially crushed to a fine powder (< 200 μ m) to minimize inducing extra strain (surface energy) that can offset peak positions, and to randomize orientation. The specimens were placed on the glass specimen holder and pressed using a glass slide. Scanning of samples were performed starting from 3° to 80° at a speed of 1° min⁻¹. The peaks obtained from the analysis were identified using PDLX software.

Fourier Transform Infrared Spectroscopy (FTIR)

The analysis on the non-impregnated activated carbon and impregnated activated carbon were conducted by FTIR (Thermo Scientific) using KBr/Ge mid-infrared optimized technique. The wavelength used was in range 500 – 4000 cm⁻¹.

Field Emission Scanning Electron Microscopy (FESEM)

The activated carbon was analysed by using JEOL field emission scanning electron microscope at the magnifications of 60x and 100,000x. The accelerating voltage was 5.0 kV during image capture using the secondary electron and dark field detectors.

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) was used to reveals information about the crystallographic structure and chemical composition of the non-impregnated activated carbon and impregnated activated carbon with MEA and DEA. Figure-1 shows the difference between diffraction peaks for the non-impregnated activated carbon and impregnated activated carbon with MEA and DEA. The

peaks of pyrazole can be observed at the diffraction angle around 21.66° and 36.25° in Figure-1(A). These results were supported by research performed by (Shafeeyan *et al.* 2010), which proved that pyrazole, pyridine and pyridone were presence on the activated carbon surfaces.

Figure-1(B) shows a lower concentration of MEA used for the impregnation process which is 4M while Figure-1(C) shows a concentration of 10M of MEA impregnated sample. Both figures show the presence of ethanolamine at different diffraction angle. For the lower concentration of MEA, the diffraction angle for ethanolamine can be seen at 22.11° and 36.34° while for higher concentration of MEA, the diffraction angles are around 21.54° and 36.1°. From the results obtained in both figures, it was clearly seen that there are difference in intensity of peaks at different concentration of MEA. Lower peak height indicates that the concentration used is still low and the MEA are not fully covered on the activated carbon surfaces.

Figure-1(D) and 1(E) show the presence of diethanolamine at slightly different diffraction angle. At the concentration of 4M of DEA used, the diffraction angle is around 22.13° while at higher concentration, the diffraction angle is at 22.18°. Based on the previous studies, the alcohol containing amine was able to react with the other amine by nucleophilic reactions (Brotzel & Mayr, 2007). At higher concentration of DEA, the intensity peak height is 20% higher compared to lower concentration of DEA. The intensity peak height of the diffraction does increase at higher MEA and DEA loadings caused by the filling of the mesoporous pores with MEA and DEA (Qi *et al.* 2010). Hence, higher concentration of amines will lead to higher intensity of diffractions of amines (Lee *et al.* 2013).

Based on the FTIR results, the samples have a transmission range from 4000 - 500 cm⁻¹ but the sensitive transmission of the samples were divided into different sensitive transmission regions. The sensitive transmission regions required in this study was the amides regions which include several regions from the range of 3500 - 1500 cm⁻¹. The formation of amides can be explained from the reaction between the carboxylic acid with amine. In this study, the carboxyl functional groups are present on the activated carbon surfaces and the MEA and DEA were introduced to the activated carbon thus, caused the reaction between the carboxyl and amine groups on the activated carbon surfaces. For MEA impregnated activated carbon, the transmittance peaks can be observed at 3287.73 cm⁻¹ and 1651.95 cm⁻¹ which confirmed that there was a presence of amide on the activated carbon structure as shown in Figure-2(A). The modified activated carbon with DEA also shows the presence of amide that can be seen at 3288.44 cm⁻¹ and 1651.60 cm⁻¹ band.

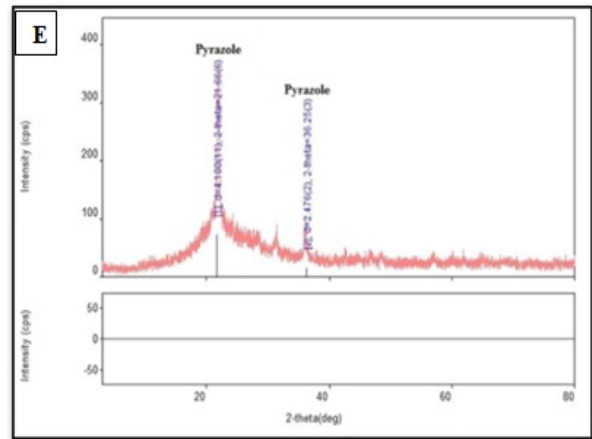
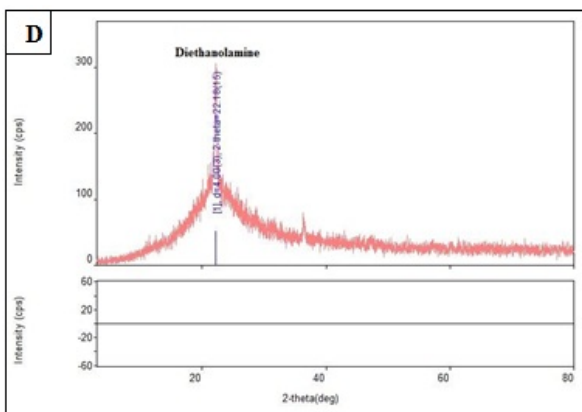
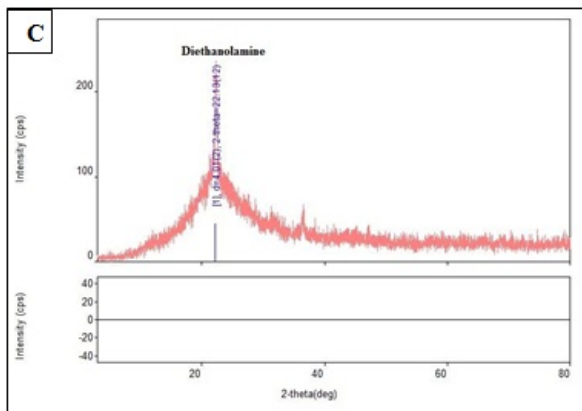
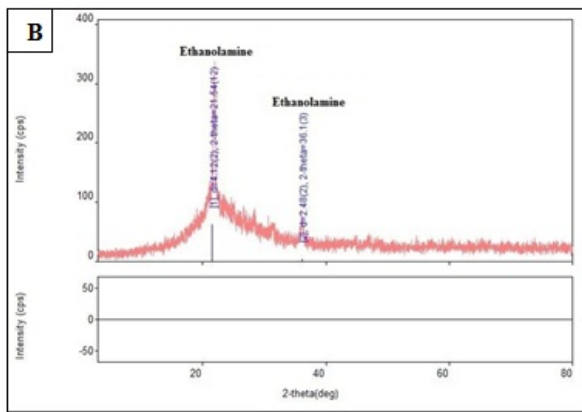
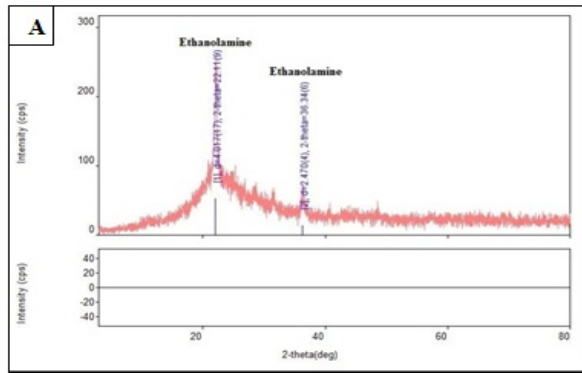
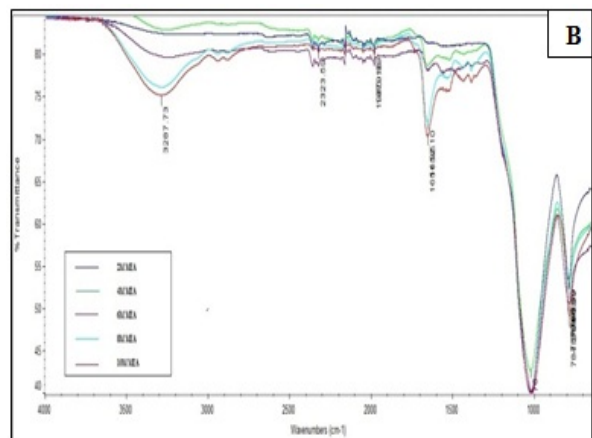
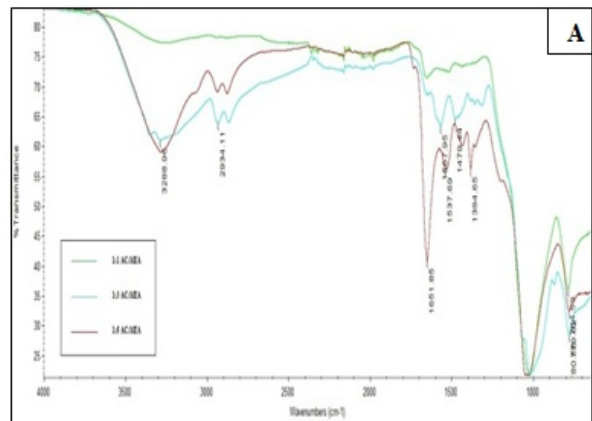


Figure-1. XRD pattern for impregnated activated carbon with (A) 4M of MEA, (B) 10M of MEA, (C) 4M of DEA, (D) 10M of DEA and (E) non-impregnated activated carbon.





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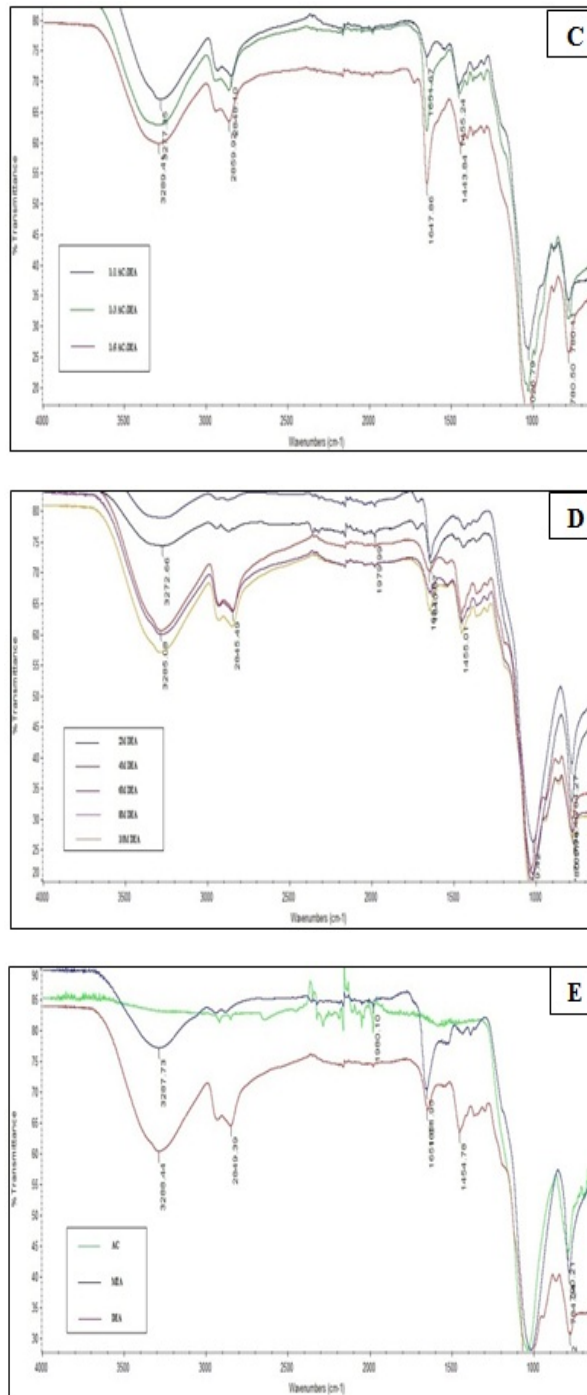


Figure-2. FTIR spectrum of (A) non-impregnated activated carbon and impregnated activated carbon with MEA and DEA, (B) MEA impregnated activated carbon with different concentration, (C) DEA impregnated activated carbon with different concentration, (D) MEA impregnated activated carbon with different mixture ratio, and (E) DEA impregnated activated carbon with different mixture ratio.

The transmittance percentage peaks of DEA are lower than the transmittance percentage peaks of MEA for both amide regions. This can be explained by the presence of amides are more in DEA because DEA have more amine functional groups compared to MEA which have less nitrogen functional groups according to their molecular structure (Kim *et al.* 2013). The transmittance percentage decreased with increasing concentration of MEA used in each samples as the amount of amide formed in higher concentration of amine is larger than the less concentrated amine (Havens, 1989). The patterns for DEA impregnated activated shows similar pattern with MEA impregnated activated carbon. The increasing concentration of DEA resulted in decreasing transmittance percentage as the quantity of amide increasing with the increased DEA concentration. Amine groups were able to condense with carboxyl groups on activated carbon to generate surface consist of amide groups (Houshmand *et al.* 2013). The bands at 3287.73 cm^{-1} and 1656.10 cm^{-1} were formed and indicate the presence of amides in all samples.

The mixture ratio with the same quantity of activated carbon and MEA shows the highest transmittance percentage while the highest mixture ratio of MEA shows the lowest transmittance percentage. The bands formed are parallel with the amide sensitive regions which are 3288.96 cm^{-1} and 1651.85 cm^{-1} . Equal weight of activated carbon and DEA shows the least amide content whereas high mixture ratio of DEA shows a low transmittance percentage. The amide content for the 3 types of mixture ratio is from the range $3289.41 - 3277.35\text{ cm}^{-1}$ and $1647.86 - 1651.67\text{ cm}^{-1}$ band which indicates the amide regions. These results also indicate there are more than one reactions occur between the carboxyl group and the amine group as high amount of amide formed on the surface of the activated carbon (Hayley, 2012).

Figures-3a and 3b show the surface morphology of the non-impregnated activated carbon and impregnated activated carbon with MEA and DEA with the use of FESEM. At magnification of 60 times, a major difference can be seen in the surface structure and pore size of the macropores. The non-impregnated activated carbon has larger pore size compared to the impregnated activated carbon while the impregnated activated carbon with MEA has larger pore size than DEA impregnated activated carbon. The pore sizes for the impregnated activated carbon are also different according to the concentration of MEA and DEA. A higher concentration of MEA and DEA resulted in decrease of pore size. The decrease in pore size indicates that there was some amount of MEA and DEA blocking in the macropores of the activated carbon. Higher concentration of MEA and DEA cause the increased in amount of MEA and DEA loaded in the macropores. (Lin *et al.* 2013), stated that the number of particle covered on top of the sample surface increases when the loading of amine increases.

At magnification of 100,000 times, there is a slight difference in the surface structure and pore size of the mesopores. The impregnated activated carbon shows



that the activated carbon was thickened by the amine coating which indicates there is a blockage of mesopores of the activated carbon (Kangwanwatana *et al.* 2013). A higher concentration of MEA and DEA caused the coating on the activated carbon to be thickened. The highest concentration of MEA and DEA which is 10M shows that all the pores were blocked and the activated carbon was fully covered by MEA and DEA. As in macropores, the mesopores also show that DEA has better attachment and coating on the activated carbon compared to MEA. The coating of DEA is thicker and larger than the coating of MEA on the activated carbon.

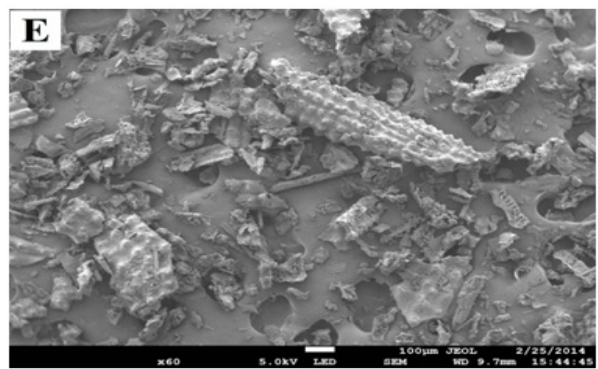
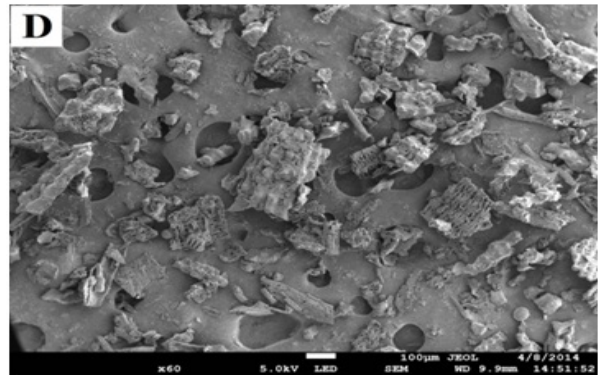
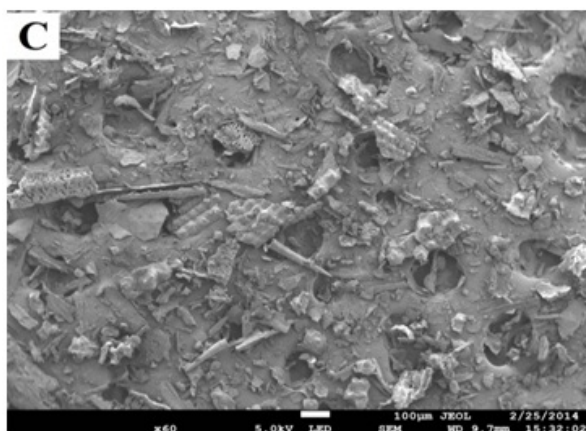
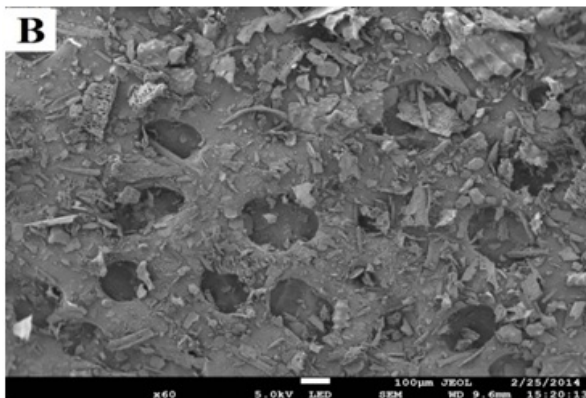
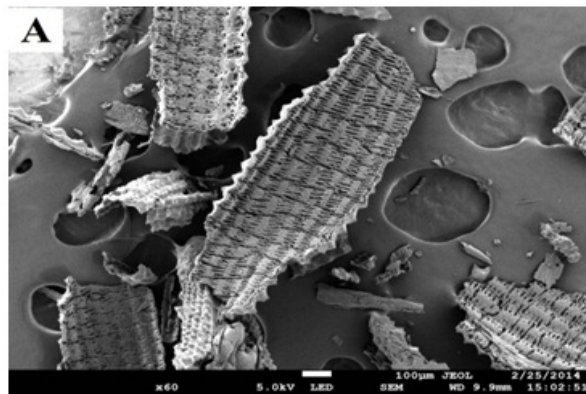
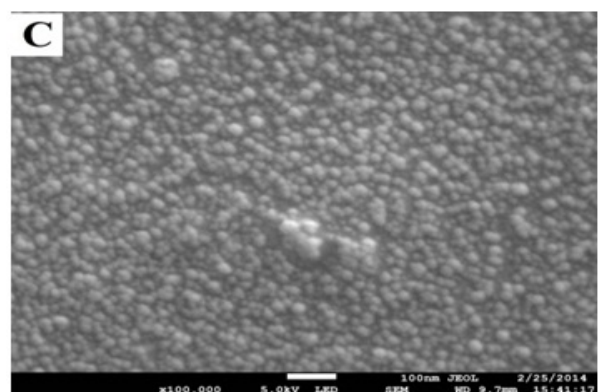
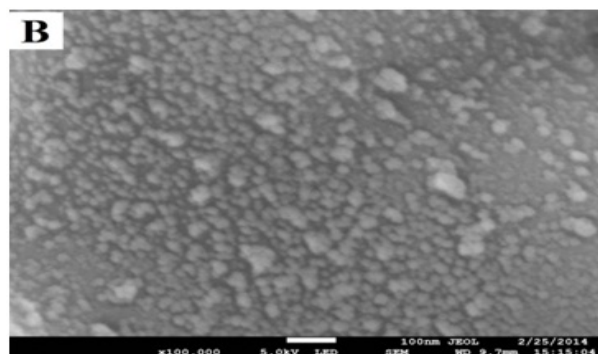


Figure-3a. The FESEM images magnified 60 times of (A) non-impregnated AC, (B) AC impregnated with 4M MEA, (C) AC impregnated with 10M MEA, (D) AC impregnated with 4M DEA and (E) AC impregnated with 10M DEA.



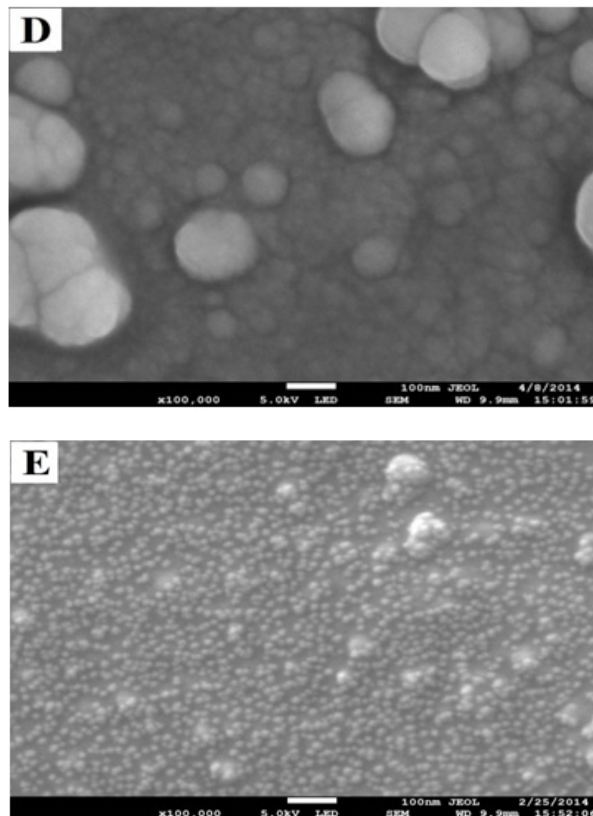


Figure-3b: The FESEM images magnified 100,000 times of (A) non-impregnated AC, (B) AC impregnated with 4M MEA, (C) AC impregnated with 10M MEA, (D) AC impregnated with 4M DEA and (E) AC impregnated with 10M DEA.

CONCLUSIONS

The preparation of non-impregnated activated carbon and impregnated activated carbon with MEA and DEA was successfully carried out in this research. The effect of concentration and mixture ratio on both types of activated carbon was investigated by using various techniques such as XRD, FTIR and FESEM. In XRD pattern analysis, diffraction angle around 21.66° to 22.18° were linked for pyrazole, ethanolamine and diethanolamine. A higher concentration of amine will result in higher intensity of diffraction for the sample. The FTIR analysis of the non-impregnated activated carbon showed that the transmittance percentage of MEA is less than DEA which indicates that DEA contains more amines functional group compared to MEA. The higher concentration and mixture ratio resulted in lower transmittance percentage for both MEA and DEA. In the FESEM analysis, the pores were clearly seen in the non-impregnated activated carbon sample while the impregnated activated carbon with MEA and DEA showed the pores were being filled with amines. The higher concentration of MEA and DEA caused more pores

closure and the distribution of DEA on the activated carbon surface is better compared to MEA.

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