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# Zea mays husk leaf and magnetic zea mays husk leaf as activated carbon used for decolourization of methylene blue dye

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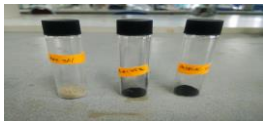
**GRAPHICAL ABSTRACT**



From left: Raw ZHL, ZHLAC 45 and MZHLAC 55

**ABSTRACT**

Zea mays husk leaf (ZHL) and magnetic Zea mays husk leaf (MZHL) as activated carbons were investigated for the removal of methylene blue (MB) dye. The uses of activated carbon ZHL and MZHL are beneficial; it acts as natural adsorbent and will decrease the amount of agricultural waste. The ZHL was treated with different concentration of phosphoric acid, $H_3PO_4$ then calcined at 450℃ to produce activated carbons (ZHLAC45, ZHLAC55, and ZHLAC65). The magnetic activated carbons ZHL (MZHLAC45, MZHLAC55, and MZHLAC65) were prepared by further impregnating the activated carbons with iron oxide. Both ZHLAC and MZHLAC were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis. ZHLAC45 exhibits higher surface area (1035.75 $m^2/g$), while MZHLAC55 has lower surface area (555.70 $m^2/g$) due to impregnation of iron. Nevertheless, the MZHLAC55 exhibits higher adsorption capacity with 79.35% of MB removal.

*Keywords: Zea mayshusk leaf (ZHL), activated carbon ZHL, magnetic activated carbon ZHL, methylene blue.*



## 1. INTRODUCTION

Dyes were made from natural sources, such as plants, minerals, and animals which tend to produce colours that easily washed out. Dyeing is the process of adding colour to textile, cosmetic, or plastic industries like fibers, fabrics, and yarns. Dyes are molecules which absorb and reflect light at specific wavelengths to give human eyes the sense of colour. The dyes physically bound to the fiber by one or more physical forces which including hydrogen bonding, van der Waals, or ionic forces but only in certain cases, it will chemically bound by covalent bonds [1].

Dyeing is normally done in a special solution that contained dyes and particular chemical material. Industries of textile, paper, food, cosmetics and pharmaceutical produced a large amount of wastewater which harmful towards aquatic organisms, mainly due to its organic content. Wastewater pollution will affect domestic water supplies and cause diseases such as cholera, diarrhea, E-coli infections, typhoid fever, and diphtheria [2]. The removal of dyes has become a great concern towards an environmental point of view because some dyes and their degradation products may be toxic and carcinogens [3-5].

Methylene blue (MB) also known as Swiss blue is one of cationic dyes containing heterocyclic aromatic chemical compound [6]. Even though methylene blue is not really hazardous, it was reported that acute exposure of humans causes tachycardia, vomiting, shock, tissue necrosis, quadriplegia, jaundice, and cyanosis [7]. Therefore, the study of removal methylene blue dyes from wastewater is important and need to be treated before being discharge.

Adsorption technique was chosen out of other methods such as biodegradation [8], photochemical degradation [9], electrochemical degradation [10], coagulation or flocculation [11], and membrane filtration [12] because adsorption technique was efficient and also economic process to remove dyes, pigments and other colourants. Attention has been shifted towards the application of magnetic particle technology to solve more problems of environmental in these recent years [13, 14]. These magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after adsorption; they can be separated from the medium by a simple magnetic process [15].

Zea mays husk leaf (ZHL) waste on the farmland are usually used as natural compost material or burned on site, which will lead to air pollution. In this study, zea mays husk leaf activated carbon (ZHLAC) and magnetic zea mays husk leaf activated carbon (MZHLAC) were prepared as an alternative low-cost adsorbents for the removal of methylene blue from aqueous solutions. The adsorbents were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), and Brunauer-Emmett-Teller (BET).

## 2. EXPERIMENTAL

In preparing activated carbon, ZHL was washed with distilled water and dried in an oven at 100℃ for 24 hours. Then, the ZHL was soaked for another 24 hours in 10:1 ratio with 45 wt. %, 55 wt. % and 65 wt. % of $H_3PO_4$ at room temperature. The excess acid was removed and dried in an oven overnight at 80℃. Next, the samples were placed in box furnace and calcined to 450℃ for two hours followed by repeatedly washed with distilled water to remove residual acid until pH of the products near 6.0 and then dried in an oven for 24 hours at 100℃. The activated carbon was grinded manually and sieved to fine powder. These carbons were named as ZHLAC45, ZHLAC55 and ZHLAC65.

Next, all activated carbons prepared were suspended in 20 ml distilled water. A ferric chloride solution ($FeCl_3$) of 0.09 M was freshly prepared by adding 1.46 g of $FeCl_3$ into 60 ml distilled water. Meanwhile, a ferrous sulphate solution, ($FeSO_4$) of 0.88 M was also prepared by adding 1.71 g $FeSO_4$ into 6 ml distilled water. These both solutions were combined and vigorously stirred at 60-70℃. The suspension formed was added into an aqueous solution of ZHLAC at room temperature and stirred slowly for 30 minutes. After mixing these, 10 M NaOH was added dropwise into the suspension until the pH rose to 10.0-11.0 and mixed it for 60 minutes. Then, the suspension was aged at room temperature for 24 hours and repeatedly washed with distilled water followed by ethanol. Finally, the materials were vacuum and dried overnight at 50℃ in an oven to get MZHLAC45, MZHLAC55 and MZHLAC65.

## 3. RESULTS AND DISCUSSION

### 3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Raw ZHL, ZHL45, ZHL55, ZHL65, ZHLAC45, ZHLAC55, ZHLAC65, MZHLAC45, MZHLAC55 and MZHLAC65 were studied by FTIR spectroscopy. Figure 1 - 4, shown the spectra obtained and all wavenumber were tabulated in Table 1 - 4.

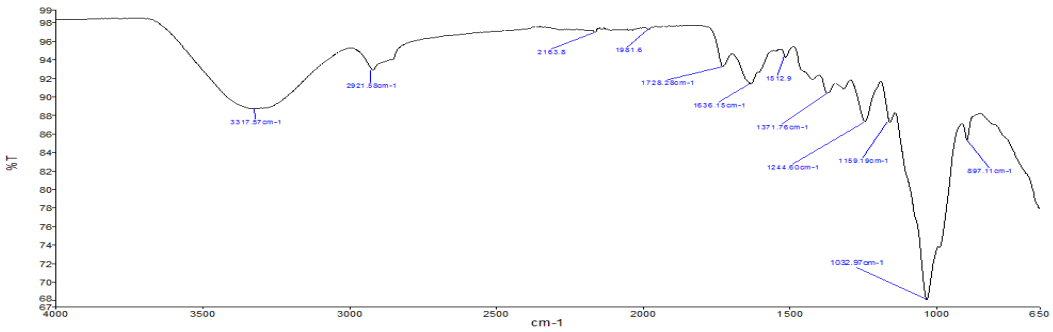



**Figure 1** FTIR spectrum of raw ZHL

**Table 1** FTIR wavenumber of raw ZHL

| Functional group | Raw ZHL ($cm^{-1}$) |
|---|---|
| **O-H (stretching)** | 3317.57 |
| **C-H (stretching)** | 2921.58 |
| **C=O** | 1728.28 |
| **C=C (aromatic)** | 1636.15, 1512.90 |
| **C-C (triple bonds)** | 2163.8 |
| **C-O** | 1244.60, 1159.19 |
| **C-H (Ar-bend)** | 897.11 |

Figure 1 shows the FTIR spectrum for raw ZHL and wavenumbers were tabulated in Table 1. The presence of O-H stretch bonded in the range of 3500-3200 $cm^{-1}$ indicates alcohol, phenol functional group. Strong frequency at 1320-1000 $cm^{-1}$ shows C-O stretch presents alcohol, carboxylic acid, esters or ethers. The stretching band observed at 3000-2850 $cm^{-1}$ was assigned to the aliphatic C-H group. The peak observed at 1728.28 $cm^{-1}$ corresponds to C=O bonds of esters. The peaks present at 1608 to 1636 $cm^{-1}$ and 1510 to 1513 $cm^{-1}$ correspond to C=C aromatic while the peaks present at 1608 to 1629 $cm^{-1}$ correspond to C=C alkene. 2250-2100 $cm^{-1}$ shows the presence of C-C (triple bonds) at medium or weak bands. The one observed at 900-690 $cm^{-1}$ correspond to the C-H aromatic bend. In Table 1 shown many functional groups present in raw ZHL before any treatment.

Figure 2 shows the FTIR spectra for ZHL45, ZHL55 and ZHL65 while the wavenumbers were stated in Table 2. After treatment with phosphoric acid but without calcined, functional groups decrease to only C-H (stretching), C=C (aromatic), C-C (triple bonds) and C-H (Ar-bend). This proves that after $H_3PO_4$ treatments, most of functional groups were removed from raw ZHL as shown in Table 2. Similar pattern were reported for ZHLAC45, ZHLAC55 and ZHLAC65 as in Figure 3 and Table 3.

Last but not least, Figure 4 and Table 4 show the FTIR spectra for MZHLAC45, MZHLAC55 and MZHLAC65. Interestingly, new peak was present due to the iron oxide functional group. These results prove that iron oxide was successfully impregnated onto all activated carbon prepared.

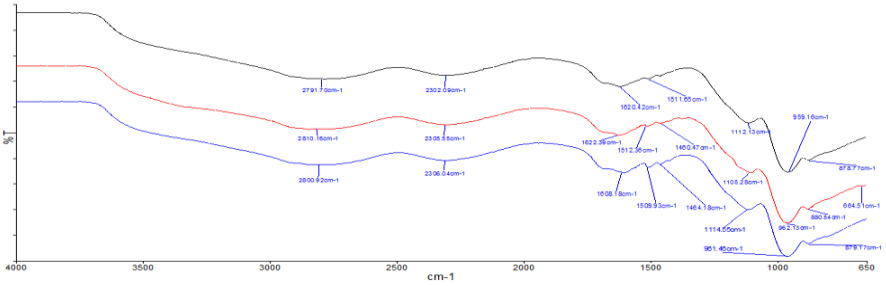



**Figure 2** FTIR spectra of ZHL45, 55 and 65

**Table 2** FTIR wavenumber of ZHL45, 55 and 65

| Functional group | ZHL45 ($cm^{-1}$) | ZHL55 ($cm^{-1}$) | ZHL65 ($cm^{-1}$) |
|---|---|---|---|
| **C-H (stretching)** | 2791.70 | 2810.16 | 2800.92 |
| **C=C (aromatic)** | 1620.42, 1511.65 | 1622.39, 1512.36 | 1608.18, 1509.93 |
| **C-C (triple bonds)** | 2302.09 | 2305.55 | 2306.04 |
| **C-H (Ar-bend)** | 878.77 | 962.13 | 961.46 |

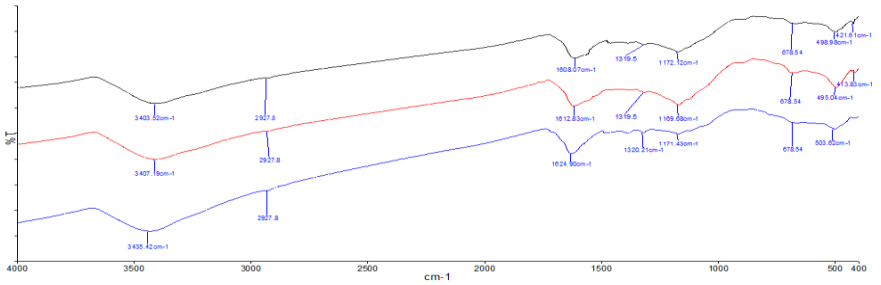



**Figure 3** FTIR spectra of ZHLAC45, 55 and 65

**Table 3** FTIR wavenumber of ZHLAC45, 55 and 65

| Functional group | ZHLAC45 ($cm^{-1}$) | ZHLAC55 ($cm^{-1}$) | ZHLAC65 ($cm^{-1}$) |
|---|---|---|---|
| **O-H (stretching)** | 3403.52 | 3407.19 | 3435.42 |
| **C-H (stretching)** | 2927.8 | 2927.8 | 2927.8 |
| **C=C (alkene)** | 1608.07 | 1612.83 | 1624.9 |
| **C-O** | 1172.12 | 1169.68 | 1171.43 |

**Table 4** FTIR wavenumber of MZHLAC45, 55 and 65

| Functional group | MZHLAC45 ($cm^{-1}$) | MZHLAC55 ($cm^{-1}$) | MZHLAC65 ($cm^{-1}$) |
|---|---|---|---|
| **O-H (stretching)** | 3407.55 | 3418.24 | 3421.26 |
| **C-H (stretching)** | 2954.70 | 2957.70 | 2954.70 |
| **C=C (alkene)** | 1613.23 | 1624.93 | 1629.43 |
| **C-O** | 1099.25 | 1121.80 | 1118.40 |
| **Iron Oxide** | 577.00 | 578.95 | 580.73 |

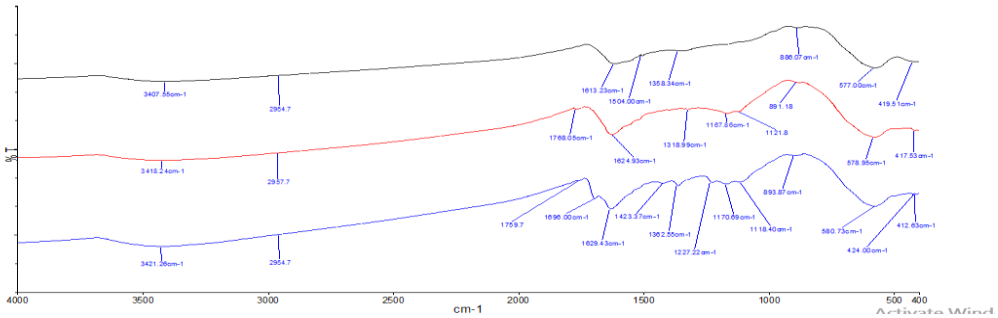



**Figure 4** FTIR spectra of MZHLAC45, 55 and 65

## 3.2. Scanning Electron Microscopy (SEM)

The micrographs of raw ZHL and MZHLAC 55 were obtained by SEM. Figure 5 (A - C) shows the micrographs of raw ZHL taken at magnification of 500 x, 1000 x and 2000 x. It shows a fibrous texture of raw ZHL before impregnation with iron oxide. These micrographs fitted raw ZHL material because of fibrous content and cellulose based structural. It was clearly showing that the surface was agglomerate. Figure 6 (A - C) shows the micrographs of MZHLAC55 at magnification of 500 x, 1000 x and 2000 x. The surface morphology already changed due to impregnation of iron oxide.

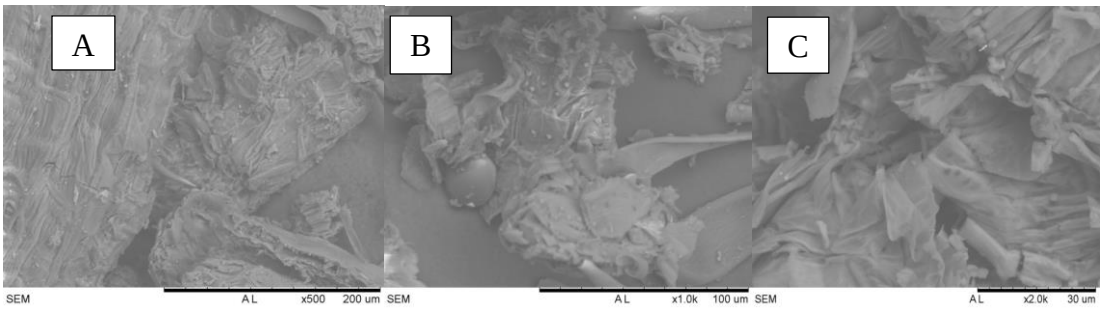



**Figure 5** SEM image of raw ZHL (A) x 500, (B) x 1.0k and (C) x 2.0k

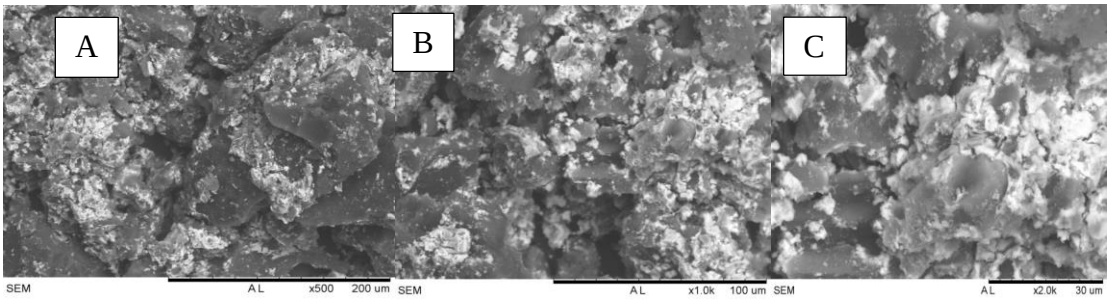



**Figure 6** SEM image of MZHLAC55 (A) x 500, (B) x 1.0k and (C) x 2.0k

## 3.3. Energy Dispersive X-ray (EDX)

The EDX results of ZHLAC45 and MZHLAC55 were presented in Table 5 and Figure 8, which show the amounts of carbon, oxygen, phosphorus and iron in the samples. The rich in carbon content can be an efficient adsorbent for the removal of dyes [19]. Therefore, sample with the highest amount of carbon and the lowest amount of oxygen is expected to be most effective.

ZHLAC45 gave 82.10% of carbon content and 15.64% of oxygen content. Whereas, MZHLAC55 only gave 44.68% of carbon content and 22.44% of oxygen content. MZHLAC55 also give 31.38% of iron content, which proves the impregnation of iron oxide on activated carbon.

However, EDX results only a semi-quantitative analysis. The results did not represent the actual samples since only very small areas of interest were studied during the analysis.

**Table 5** The elemental analysis of ZHLAC45 and MZHLAC55

| Sample | Weight (%) | | | |
|---|---|---|---|---|
| | Carbon (C) | Oxygen (O) | Phosphorus (P) | Iron (Fe) |
| **ZHLAC45** | 82.100 | 15.640 | 2.260 | - |
| **MZHLAC55** | 44.681 | 22.442 | 1.196 | 31.382 |

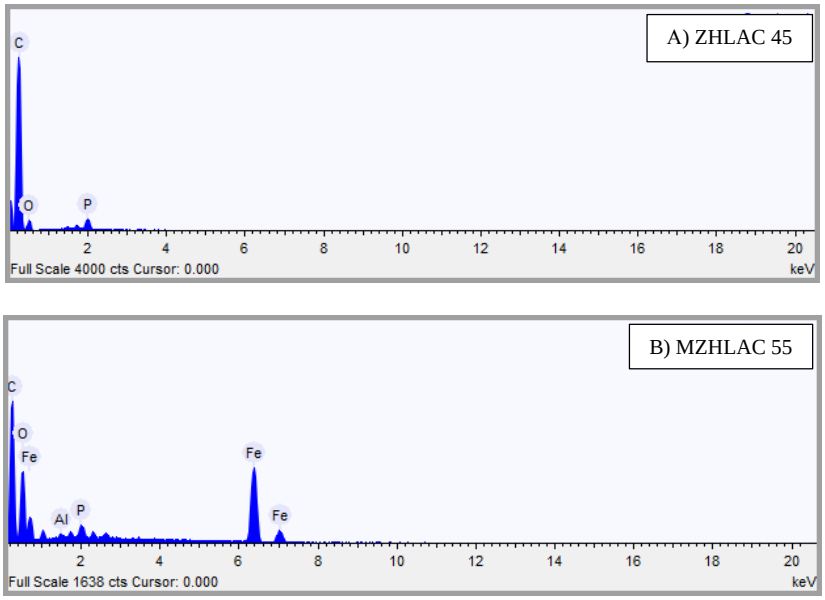



**Figure 8** EDX spectra (A) ZHLAC45 and (B) MZHLAC55

## 3.4. Brunauer-Emmett-Teller (BET)

Raw ZHL only gave 53.37 $m^2/g$ surface areas. After chemical treatment and activation process, the surface area of ZHLAC45 was elevated to 1035.75 $m^2/g$. This shows that activation process successfully enhanced the surface area which might be useful of adsorption process. After magnetically modified, the surface area of MZHLAC55 reduced to 555.70 $m^2/g$. The surface becomes substantially smaller due to the impregnation of iron oxide on the surface of activated carbon. Table 6 showed the total surface area for raw ZHL, ZHLAC45 and MZHLAC55. Activated carbon will increase the surface area of adsorbent. From the analysis, it was observed that surface area of ZHLAC45 was very high as compared to raw ZHL and MZHLAC55, which results in better adsorbent for adsorption purpose. The surface area of ZHLAC45 was 1035.75 $m^2/g$. Based on Table 6 raw ZHL has the lowest surface area with 53.37 $m^2/g$. After magnetically modified in the form of MZHLAC55, surface area becomes substantially smaller than ZHLAC45 with 555.7 $m^2/g$. This was due to less carbon per unit weight present in MZHLAC55 than ZHLAC45 because 31.382% of the weight of MZHLAC55 was iron oxides present in its structure.

## 3.5. Adsorption capacity of Methylene Blue dye on ZHL and MZHL

Figure 9 shows the adsorption capacities of MB on raw ZHL. At 10 minutes, the raw ZHL manage to remove 11.35% of MB with increasing of time. After 40 minutes, the MB removal start plateau with highest MB removal was 50.01%.

Figure 10 shows the adsorption capacities of MB removal onto ZHLAC45, ZHLAC55 and ZHLAC65. ZHLAC45 gave the highest MB removal (65.35%) from 10 minutes whereas ZHLAC65 gave the lowest MB removal (16.67%). From BET analysis, the surface areas of ZHLAC were greatly improved compared to raw ZHL. It proves here that surface area plays important roles during adsorption process.

Finally, Figure 11 shows the adsorption capacity of MB onto MZHLAC45, MZHLAC55 and MZHLAC65. MZHLAC55 gave the highest MB removal (79.35%) meanwhile MZHLAC65 gave the lowest MB removal (46.10%). From BET analysis, surface area of MZHLAC was lower compares to ZHLAC. These results proof that, aside from surface area, magnetically modified surface also plays important role during adsorption process. This might be due to positive charge of MB was interacted to magnetic field charge from MZHLAC.

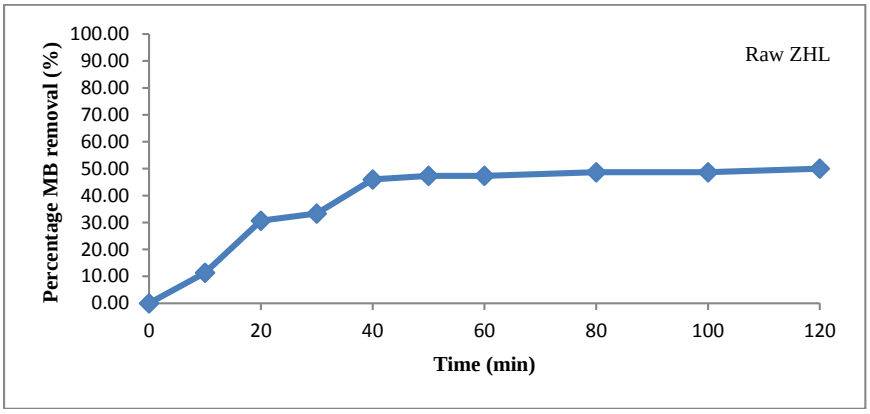



**Figure 9** Effect of adsorption capacity of MB onto raw ZHL

**Table 6** Surface area of raw ZHL, ZHLAC45 and MZHLAC55

| Sample | Surface Area ($m^2/g$) |
|---|---|
| **Raw ZHL** | 53.37 |
| **ZHLAC 45** | 1035.75 |
| **MZHLAC 55** | 555.70 |

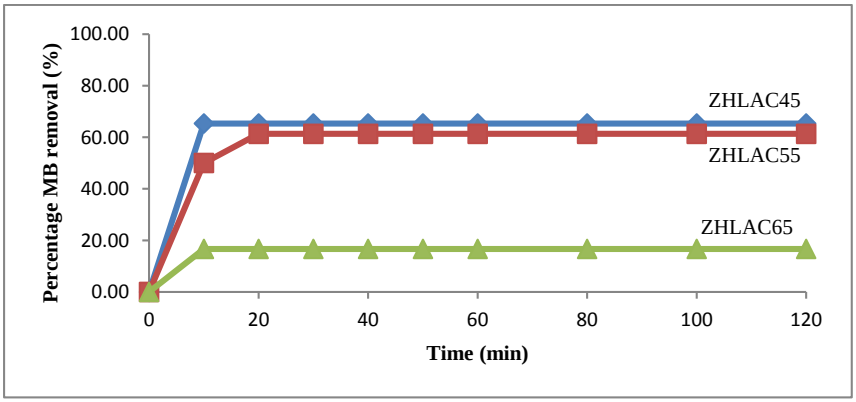



**Figure 10** Effect of adsorption capacity of MB onto ZHLAC 45, 55, and 65

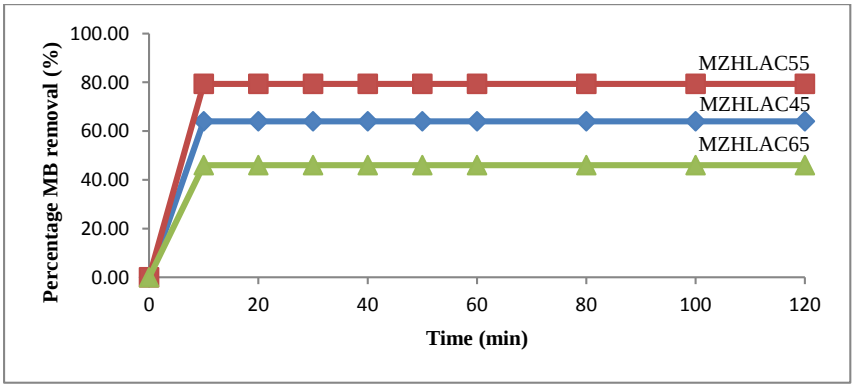



**Figure 11** Effect of adsorption capacity of MB onto MZHLAC45, 55, and 65

## 4. CONCLUSION

In this study, activated carbons and magnetic activated carbons were successfully prepared from raw ZHL which is low-cost material and environmental friendly. Characterization of raw ZHL, ZHLAC and MZHLAC were conducted using FTIR, TGA, SEM, EDX and BET. The ZHLAC 45 gave highest surface area (1035.75 $m^2/g$) while MZHLAC 55 gave low surface area (555.7 $m^2/g$) due to impregnation of iron oxide. Nevertheless, MZHLAC 55 exhibits the best adsorption capacity with 79.35% of MB removal. As a conclusion, surface area and magnetically modified surface play important role during decolourization of MB.

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