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# Effects of $Fe^{2+}$ and $Fe^{3+}$ ratio impregnated onto local commercial activated carbon coconut shell powder on the dye removal efficiency

## *Pengaruh ratio $Fe^{2+}$ and $Fe^{3+}$ di dalam proses impregnasi ke dalam karbon aktif lokal dari tempurung kelapa terhadap efisiensi penyerapan zat warna*

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**ABSTRACT**

The present study reports the performance of magnetic activated carbon impregnated with $Fe^{2+}$ and $Fe^{3+}$ on the removal of dye from a simulated wastewater. The magnetic activated carbon (MAC) as a magnetic absorbent was prepared by co-precipitation method and followed by impregnation process. The activated carbon (AC) was supplied from a local commercial activated carbon coconut shell powder. The objective of this study was to investigate the effects of $Fe^{2+}$ and $Fe^{3+}$ on the quality product of MAC for dye (methylene blue) adsorption. The molar ratios of $Fe^{2+}$ and $Fe^{3+}$ used during the preparation of the MAC were 1:1; 1:2, and 2:1. The MAC products were characterized by using scanning electron microscope (SEM), energy dispersive X-ray (EDX), and Fourier transform infrared spectroscopy (FT-IR) analysis techniques. The results confirmed that the concentration of magnetic particles ($Fe_3O_4$) on the MAC surface increased following the impregnation process. However, this results lowering adsorption properties of the MAC adsorbents, which subsequently affected the dye removal performance. The ratio of $Fe^{2+}$:$Fe^{3+}$ on the MAC preparation did not significantly change the MAC absorbent on the dye removal efficiency. Additionally, MAC derived from local AC possess a prospect as a sustainable alternative for dye pollutant adsorbent.

***Kata kunci:***
*karbon aktif;*
*karbon aktif bermagnet;*
*tempurung kelapa;*
*limbah zat warna;*
*penyerapan zat warna*

***ABSTRAK***

*Penelitian ini melaporkan kinerja karbon aktif bersifat magnet yang di impregnasi dengan $Fe^{2+}$dan $Fe^{3+}$ dalam penyerapan zat warna dari air limbah buatan. Karbon aktif bersifat magnet (MAC) dibuat melalui metode co-presipitasi dan diikuti dengan proses impregnasi. Material karbon aktif (AC) dibuat dari tempurung kelapa yang diperoleh dari pasar lokal. Tujuan dari penelitian ini adalah untuk mengetahui pengaruh ratio dari $Fe^{2+}$ and $Fe^{3+}$ terhadap kualitas produk MAC yang digunakan nantinya di dalam proses penyerapan zat warna (metilen biru). Rasio molar dari $Fe^{2+}$ and $Fe^{3+}$ yang digunakan di dalam penelitian ini untuk menghasilkan MAC adalah 1:1; 1:2, dan 2:1. Produk MAC yang dihasilkan dipelajari karakteristiknya melalui scanning electron microscope (SEM), energy dispersive X-ray (EDX), dan Fourier transform infrared spectroscopy (FT-IR). Dari hasil penelitian yang diperoleh dapat dikonfirmasi bahwa konsentrasi partikel-partikel magnet ($Fe_3O_4$) pada permukaan MAC meningkat setelah proses impregnasi. Walaupun demikian, hal ini menyebabkan turunnya kemampuan adsorbsi dari adsorben MAC. Perbandingan rasio $Fe^{2+}$ and $Fe^{3+}$ tidak secara nyata mempengaruhi efisiensi penyerapan zat warna. Adsorben MAC dari karbon aktif lokal memiliki potensi sebagai bahan alternatif ramah lingkungan untuk penyerap zat warna.*

## 1. Introduction

Environmental pollution due to dye emissions to surface water is inevitable because dyes are greatly employed in textile industries (Robinson et al., 2001). According to (Meyer, 1981) and (Zollinger, 1987), commercial dyes available on market have exceeded 100,000 types and more than 7 x $10^5$ ton of dye substances produced annually. Dyes are visible toxic waste and numerous dyes of industrial effluent wastewater are complicated to remove due to their chemical structure, stable to light and oxidizing agents. Removal of dye from dye-incorporate in industrial effluents can be divided in three groups: chemical, physical, and biological methods. A deep review of these methods has been presented by Robinson et al., 2001). They concluded that mostly removal of dyes from wastewater discharges is conducted by physico-chemical methods, but despite the dyes are eliminated, the methods are generally expensive and generate a disposal concerns due to sludge production.

Activated carbon (AC) produced from biomass waste has been extensively used for sorbent material, for example in water treatment (Orha et al., 2016), soil decontamination (Vasilyeva et al., 2010), purification of air (Nam et al., 2018), remediation of marine sediment (Samuelsson et al., 2015) and sediment management (Ghosh et al., 2011). AC has also been used for the removal of dye wastewaters (Chandra et al., 2007; Regti et al., 2017; Hameed et al., 2017; Kumar et al., 2018). The wide application of AC was due to its high surface area and high pore volume (Iqbal and Ashiq, 2007; Sethia and Sayari, 2016). Moreover, the application of AC produces effluents containing very low of dissolved organic concentrations (Chandra et al., 2007). However, performance of this method depends on the characteristic of the wastewater and the origin of the AC applied (Robinson et al., 2001). Powdered AC has better sorption kinetic properties than that of granular AC (Ghosh et al., 2011). On the other hand, separation of the powdered AC from solution or slurries cannot be easily realized with conventional clarification processes (Han et al., 2015).

In the recent years, several investigators (Oliveira et al., 2002; Zhang et al., 2007; Faulconer et al., 2012) have given attention to magnetic adsorbent applications, particularly because the used magnetic adsorbent is subsequently easily separated from the treated wastewater or slurries with a magnetic field in within a relatively short time (Indira and Lakshmi, 2010). The present study concerned on the modification of local commercial AC coconut shell powder to produce magnetic AC (MAC) for dye removal. The AC was impregnated with iron particles ($Fe_3O_4$) which were prepared from $FeCl_2.4H_2O$ and $FeCl_3.7H_2O$ solutions to produce the MAC prior to the application. The aims of this study were to characterize the MAC absorbents with variation in $FeCl_2.4H_2O$ and $FeCl_3.7H_2O$ and to investigate the adsorbent effectiveness on the dye removal.

## 2. Method

### 2.1. Materials

Chemicals including $FeCl_2.4H_2O$, $FeCl_3.7H_2O$, $NH_4OH$, and dye (methylene blue) of analytical grade were purchased from Merck, Germany. The local commercial AC, nitrogen gas, and neodymium magnet were obtained from a local market. The AC was ground with a ball mill to achieve a 40-mesh size distribution prior to the investigation.

### 2.2. Preparation of the MAC adsorbents

The MAC adsorbents were prepared by two-step processes, i.e. preparation of magnetic particles using a co-precipitation method, and followed by impregnation of the particles onto the AC. In the preparation step, three kinds of solutions containing $Fe^{2+}$ and $Fe^{3+}$ were prepared with a molar ratio of $Fe^{2+}$ and $Fe^{3+}$ of 1:1 (MAC-1), 1:2 (MAC-2), and 2:1 (MAC-3). In order to complete the reaction and precipitation of the particles, the solutions were adjusted under alkaline condition with $NH_4OH$ (25%), heated at temperature of 80°C (Kahani et al., 2010), and strong stirred. Prior to the reaction, the solutions were injected by $N_2$ gas to prevent potential oxidation. After 30 min of the reaction, the respective precipitated products were filtered and repeatedly washed with distilled water before drying in an oven at 105°C.

The impregnation process was conducted by modifying the method reported by Kahani et al., 2007. Two grams of the magnetic particles and 2 g of the AC were prepared in 40 ml distilled water under strong stirring at the ambient condition. The impregnation process was completed within 5 hrs. The reaction of the MAC adsorbent preparation and impregnation involved is given in Eqs. (1) and (2).

$$FeCl_2.4H_2O + 2FeCl_3.6H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 20H_2O \quad (1)$$

$$Fe_3O_4 + AC \rightarrow MAC \quad (2)$$

### 2.3. Characterizations of the AC, the MAC, and the dye removal studies

Characterizations of the AC and the MAC product were observed by SEM (JEOL JSM 6510), XRD (Shimadzu XRD 600), and FTIR (Shimadzu IR Prestige21). For the dye removal studies, a dye solution was prepared by diluting stock solution with concentration of 25% to the final concentration was around of 120 mg/L. The pH solution was not adjusted. The dye solutions (100 ml, 100 mg/L concentration) and 0.2 g of the MAC were used in the respective dye removal studies. The respective study was conducted in a flask and kept in a shaker of 100 rpm at room temperature for until the equilibrium is achieved. Supernatants were taken at different contact time with

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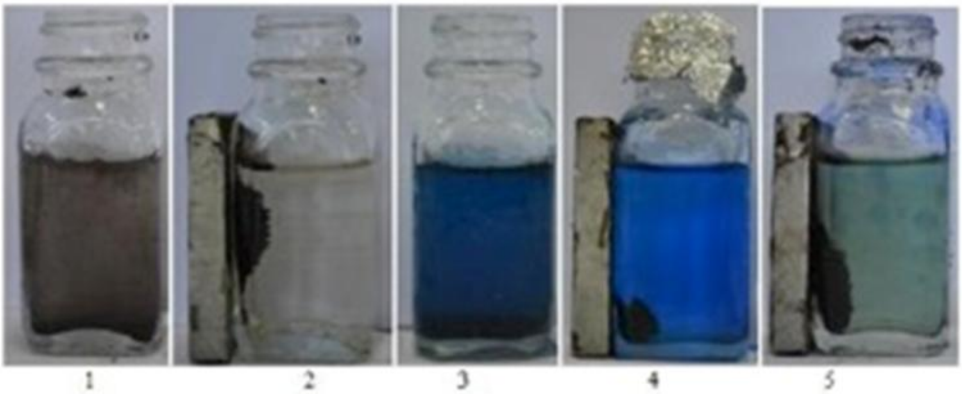


Fig. 1. The MAC adsorbs dye pollutant and responds to magnetic field.

sampling interval of 5 minutes. The supernatants were analyzed by UV-vis spectrophotometer (Shimadzu UV-1700).

The dye removal efficiencies were estimated by equation (3).

$$\textit{Adsorption efficiency (\%)} = \frac{Co-Ce}{Ce} \text{ x } 100\% \qquad (3)$$

where *Co* and *Ce* are the initial and equilibrium supernatant concentrations (mg/L) of dye, respectively.

## 3. Result and Discussions

### 3.1. Characterization results

The aim of magnetic adsorbent approach is to give the magnetic effect to a nonmagnetic material object. Therefore, the object can be quickly and easily withdrawn from the aqueous solution using magnetic field separator. Fig. 1 demonstrates the magnet response of $Fe_3O_4$ which were produced in this study by impregnation of $FeCl_2$ and $FeCl_3$ salt hydrates. Magnetite $Fe_3O_4$ is recognized as ferrimagnetic material (Oliveira et al., 2002). Ferrimagnetic is almost identical to ferromagnetic (Altıntıg et al., 2017). The produced MAC in the present study appeared to be effective on the dye removal.

The morphology of the AC and the MAC absorbent samples are created by SEM. Fig. 2 presents the SEM photographs of the AC and the MAC samples. As can be clearly seen, there are substantial distinctions between the AC (Fig. 2-a) and the MAC (Fig. 2-b to 2-d). The SEM of the AC shows a random porous channel with a different pore sizes. These provided relatively high surface area on the surface of the AC. When magnetite $Fe_3O_4$ was impregnated onto the AC producing the MAC, some non-porous layers were developed on the surface which reduces the MAC sorption capacity. In addition, the SEM/EDX spectra generated for the AC and the typical MAC sample are presented in Fig. 3. In this figure, the peak height shows a strong K peak for carbon and a weak peak for other elements in the AC

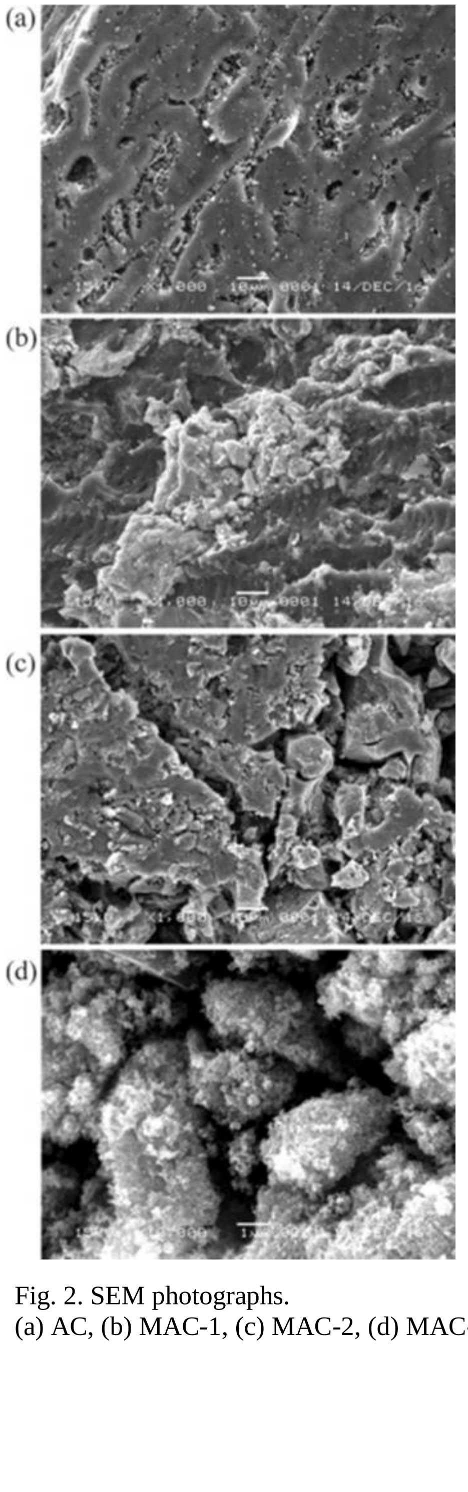


Fig. 2. SEM photographs.
(a) AC, (b) MAC-1, (c) MAC-2, (d) MAC-3.

sample (Fig. 3-a). While in the MAC sample (Fig. 3-b), several iron peaks arose as they considered for the magnetic particles.

The EDX examination verified that concentration of the magnetite $Fe_3O_4$ particles onto the AC sample surface increased following the impregnated process. It was found that the weight percentage of carbon and iron in the AC samples were 94.9% and 0.21%, respectively. The iron was found in significant amount of 55.57% to 97.13% in the MAC samples. Other particles were found in trace amount. Unfortunately, the iron element dispersion onto the surface of the MAC samples are not available in this study. Summary composition of the AC and the MAC samples is presented in Table 1.

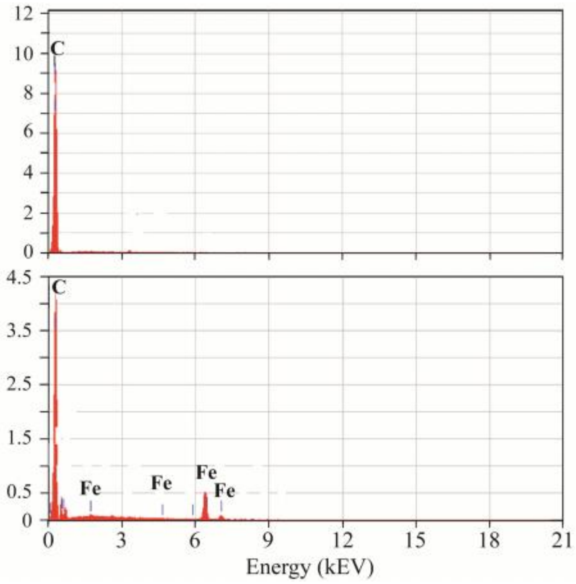


Fig. 3. The EDX spectrum of the AC (a) in the top and the representative MAC (b) in the bottom.

Table 1
Summary compositions of the AC and the MAC.

| Component (%) | AC | MAC-1 | MAC-2 | MAC-3 |
|---|---|---|---|---|
| C | 94.89 | 42.34 | 9.12 | 1.66 |
| FeO | 0.21 | 55.57 | 88.64 | 97.13 |
| Trace | 4.9 | 2.09 | 2.24 | 1.21 |

Fig. 4 presents FTIR spectrum of the AC and the MAC adsorbents. All the samples provided the spectrum which have wide band between 3600 and 3100 $cm^{-1}$. This range corresponds to the stretching vibrations of O−H groups known as fundamental organic groups. The peak of the absorption band obtained between 1500 and 1800 $cm^{-1}$ region is considered with the stretching vibrations of C=C bonds of the aromatic ring (Martínez et al., 2006) (Altıntıg et al., 2017). Several peaks developed between 400 and 600 $cm^{-1}$ regions are due to the iron impregnated to the AC sample.

### 3.2. Effects of Fe ratio on the dye removal efficiency

To determine and compare the AC, MAC-1, MAC-2, and MAC-3 on the dye removal efficiency, dye sorption experiments were conducted at room temperature. As shown in Fig. 5, the percentage of dye removal efficiencies significantly increased around of 70% to 75% for the time intervals being studied starting from to the first 5 min of the experiment for all the samples investigated.

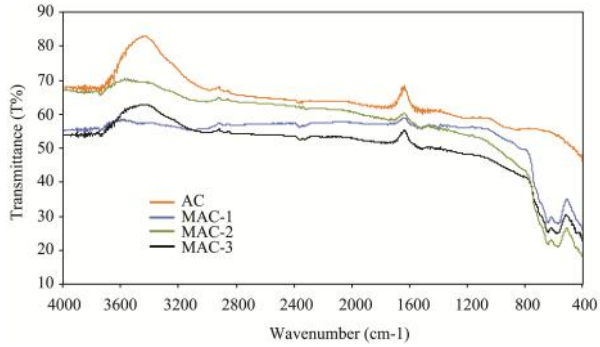


Fig. 4. The FTIR spectrum of the AC and the MAC.

At the next intervals from 5 to 25 min, the efficiencies slightly increased and the trend of the removal were obtained to be consistent. The AC has a performance of 80% removal and gave the higher percentage than MAC-1, MAC-2, or MAC-3. The lower dye adsorption by the MAC-1, MAC-2, or MAC-3 as compared to the AC was probably due to the accumulation of magnetic particles onto the pore surface area of the MAC samples. As apparent from the SEM observation results, the MAC samples have less active site due to iron impregnation which covered the pore surface. However, some researchers reported that the incorporation of Zr into $CeO_2$ increased catalytic activity of a nanocomposite (Li et al., 2012) and iron doping onto activated carbon enhanced active sites (Shah et al., 2014). Moreover, the present study shows that the MAC-1 and MAC-2 have similar performance in the dye removal efficiency and slightly higher than that of the MAC-3. The figure also shows that the percentages of the dye removal efficiency of MAC-1, MAC-2, and MAC-3 are 64%, 63%, and 57%, respectively, in average. These results were in the line with the dye effluent quality of 36 mg/L, 37 mg/L, and 43 mg/L, respectively.

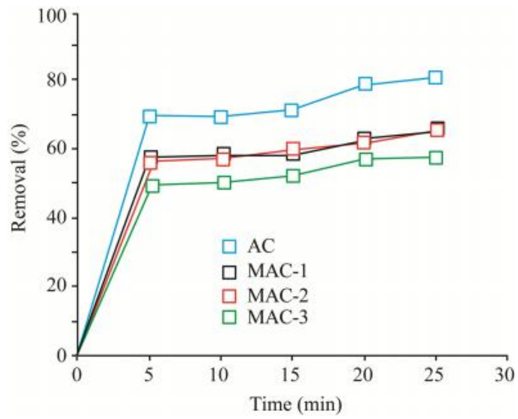


Fig. 5. The effects of the MAC preparation on the dye removal efficiency.

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## 4. Conclusions

In the present study, the MAC adsorbent was produced from the local commercial AC coconut shell. A well-developed iron particle onto the AC surface was successfully prepared by a co-precipitation and impregnation methods. The shifting of peaks in EDX spectrum verified that concentration of the iron on the MAC surface increased following the impregnated process. However, this result decreased adsorption properties of the MAC adsorbent. The ratio of $Fe^{2+}$:$Fe^{3+}$ on the MAC preparation did not significantly alter the dye removal efficiency. However, the performance of the MAC using the ratio of 2:1 presented offered the lowest removal efficiency. Accordingly, this was suspected due to the deposition of iron particles on the pore surface of the MAC.

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