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SYNTHESIS AND CHARACTERIZATION OF Fe_3O_4-COCONUT SHELL ACTIVATED CARBON COMPOSITES

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ABSTRACT

Synthesis and characterization of Fe_3O_4-coconut shell activated carbon composites has been carried out to create a magnetic adsorbents. Composites were synthesized using the coprecipitation reflux method by mixing a solution of Fe^{3+}/Fe^{2+} iron salt (mol ratio 2:1) and suspension of activated carbon in water followed by the addition of NaOH solution. The structure, functional groups, morphology and surface area of the composites were characterized using FTIR, XRD, SEM and GSA. The magnetic properties of composites are tested by response to magnetic fields. The characterization results showed that the embedment of Fe_3O_4 on coconut shell activated carbon was successfully carried out through the interaction of hydroxyl groups at wave numbers 601.79 and 416.62 cm^{-1}. Diffraction peaks at 2θ 30.12° [220], 35.58° [311], 43.14° [400], 53.57° [422], 57.18° [511] and 62.83° [440] indicate the existence magnetite sized of 11.72 nm. Activated carbon has an average pore size of micropores with an average pore of 1.46 nm. Magnetite embedment reduced the surface area of activated carbon from 91.16 m^2/g to 12.04 m^2/g. The response of sample to the magnetic field indicates that composite has magnetic properties.

***Keywords**: Magnetic adsorbent, activated carbon, pyrolysis, coconut shell, Fe_3O_4, coprecipitation*

INTRODUCTION

Industrial development can create a wide variety of products, and also sometimes produces byproducts in the form of waste, especially wastewater. Wastewater is residual disposal resulting from a process that is no longer used [1]. Wastewater potentially generated from industrial activities such as metal and textile industries which may contain a spread of heavy metal waste. The handling of heavy metal wastewater is a very important issue because the occurrence and accumulation in the environment can cause environmental pollution problems that must be processed in a certain way [2].

Several technologies were developed to reduce heavy metal content from waste-water. The methods commonly used are chemical reduction and precipitation, ion exchange and adsorption [3, 4, 5]. The draw-back of the method of reduction and precipitation is contaminated sludge forma-tion in large quantities [6]. In addition, this method resulted in changes in the chemical structure of the waste substance. The advantage of using the adsorption method is that it does not change the chemical structure

of the waste substance and can be separated after the adsorption process [7].

The adsorbent that is widely used in the adsorption process is activated carbon. Activated carbon is used because it is easily created and customized structures, physical and chemical properties [8]. The large surface area, micro-sized pores, and surface chemical properties of activated carbon have the potential as an adsorbent in the handling of heavy metal waste [9, 10]. The relatively expensive cost of activated carbon preparation can be reduced by using carbon-containing materials such as lignite, peat, coal, and various biomass such as wood, sawdust, bagasse, and coconut shell [11]. Coconut shell contains 33.6% cellulose, 36.5% lignin, 29.27% pentosan and 0.61% ash [12]. In addition, the composition of the constituent elements of coconut shell consisting of 74.3% carbon, 21.9% oxygen, 0.2% silica, 1.4% potassium, 0.5% sulfur and 1.7% phosphorus, potentially as activated carbon [13].

Carbon from biomass contains a lot of lignin, so it needs to go through a chemical activation process to reduce the lignin structure in lignocellulose [14]. Several research on the manufacture of activated carbon from lignocellulosic materials that derived from the mango seeds [10] and Indian palm seeds (*Ziziphus jujuba*) [9] to adsorb chromium metal waste. Both of them perform chemical activation of carbon from lignocellulosic materials. The results of both studies showed that activated carbon from lignocellulose can be used as an adsorbent of heavy metal waste. However, after adsorption it takes a long time to separate the adsorbent [9, 10].

Several studies have shown that activated carbon can be composited with magnetite and produce adsorbents which have magnetic properties [15, 16, 17]. The combination of activated carbon and iron oxide can be use to adsorb contaminants in the water. The results showed that the composites were able to absorb organic compounds and dyes without any reduction process. The addition of iron oxide on activated carbon showed a reduction in the surface area of activated carbon [15]. Another study show that magnetic adsorbents which synthesized from activated carbon and magnetite are used to absorb thorium. The results showed that the addition of magnetite particles hardly reduced the adsorption capacity [16]. Moreover, the adsorbents from iron oxide / activated carbon composites reported can remove boron and organic compounds from water. The magnetic properties of the adsorbent can reduce waste generation by separating using external magnets. The addition of iron oxide on activated carbon showed a reduction in the surface area of activated carbon [17].

Based on this review, this research will carry out the synthesis and characterization of Fe_3O_4 composites based on activated carbon from coconut shells to produce adsorbents with magnetic properties. Characteristics of functional groups, crystal phase, surface area, and surface morphology were analyzed using FTIR, XRD, GSA, and SEM. Magnetic properties are tested using an external magnetic field.

METHODS

1. Materials and Tools

The materials needed in this research is the coconut shell carbon, KOH (pro analysis, Merck), NaOH (pro analysis., Merck), $FeCl_3.6H_2O$ (pro analysis, Merck), $FeCl_2.4H_2O$ (pro analysis, Merck), HCL solution 1 N (mediss), aquades, and aquabides.

The equipment used in this research is FTIR Thermo Nicolet Avatar 360, XRD Shimazu 6000, and Quantachrome NOVAtouch Lx4, SEM Phenom Desktop ProXL and other laboratory equipment.

2. Carbon Preparation

The coconut shells are dried for approximately 6-7 days. The dried coconut shell is then pyrolyzed at a temperature of 650 °C for 4 hours. The coconut shell charcoal that has been formed is then washed and cleaned with distilled water and dried using the oven. After passing through the drying process, the next process in the puree that are uniform in size.

3. Carbon Activation

Several grams of carbon sample was added to 50% KOH solution for 24 hours. The samples were then washed with distilled water and dried at 110 °C for 3 hours. Physical activation is carried out using a furnace at 500 °C for 1 hour. The coconut shell activated carbon is then stored in a desiccator.

4. Synthesis of Fe_3O_4-CSAC Composite

Composite manufacturing method refers to previous research [11]. Several grams of solid $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ (2: 1 mole ratio) were dissolved in 1 N HCl solution. The mixture was stirred until clear and diluted to 25 mL with aquabidestilla. In another container, activated carbon is suspended in 200 mL of aquabidestilla. The composite are made based on the weight ratio of Activated Carbon:Fe_3O_4 (2:1). The mixture was then heated and 2.5 M NaOH solution was added dropwise. The solution temperature is maintained at 70 °C while stirring for 3 hours.

Composites are then separated using an external magnetic field and washed with aquadestilla until neutral. The solids are dried at 70 °C until dry and continued at 120 °C for 2 hours. The magnetic adsorbent Fe_3O_4-activated carbon is crushed and stored in a bottle.

5. Composite Characterization

The composites are characterized using various instruments, including; FTIR to determine the functional groups of chemical compounds at wave numbers 4000-300 cm^{-1}. The Crystalline phase were identified using XRD instrument with a source of Cu-Kα radiation (λ = 1.54 Å) at 2θ 0° to 90°. SEM was used to see surface morphology with a voltage rate of 15 Kv at various magnifications. Analysis of the total surface area, pore volume and mean pore radius was known using the Quantachrome NOVAtouch LX4 instrument with the Branaur-Emmett-Teller (BET) method. Samples were degassed at 90 °C for 1 hour.

6. Magnetic Properties Test

The magnetic properties of the sample are known based on their influence on the

external magnetic field. Each sample was placed in a container made of glass. Neodymium magnets were then held close to each sample to determine the magnetic properties of the sample response.

RESULT AND DISCUSSION

1. Characterization Results

FTIR spectra of carbon, activated carbon and composite samples are presented in Figure 1.

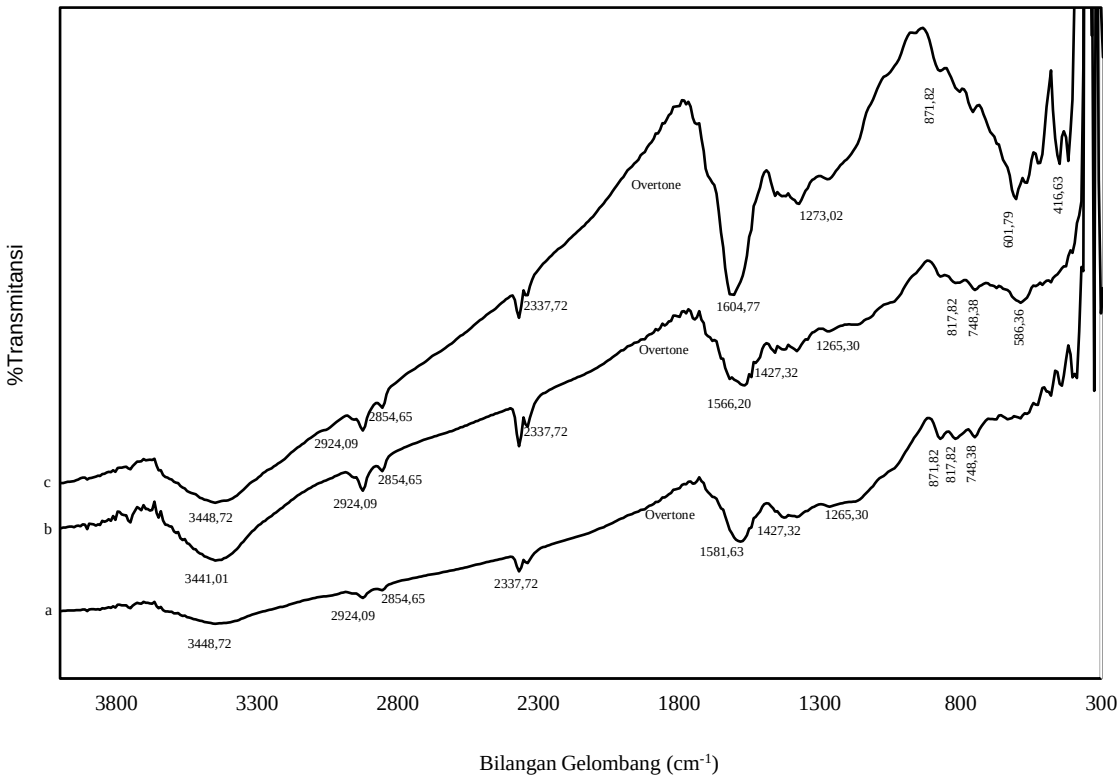

Figure 1. FTIR Spectra of a. Carbon, b. Activated Carbon and c. Composite

Shown in Figure 1.a. the carbon sample has an -OH group at wave number 3448.72 cm^{-1}. The presence of stretched CH is shown at wave numbers 2924.09 and 2854.65 cm^{-1} which causes asymmetric vibrations of CH_2 and symmetry of CH_3. The presence of absorption at 2337.72 cm^{-1} indicates that carbon, activated carbon and composite samples have interacted with CO_2 molecules from the atmosphere [18]. Overtone uptake in the region 2000-1700 cm^{-1} and absorption at 1581.63 cm^{-1} indicate the presence of aromatic C = C groups. The absorption at the wave number 1265.30 cm^{-1} shows the -C-O-C stretching vibration [19]. The presence of aromatic structures reinforced with uptake aromatic C-H bending (out-of-plane) at wave numbers 900-690 cm^{-1}. The presence of absorption other than carbon is assumed to arise from the structure of lignin and cellulose in coconut shells [19].

FTIR results for activated carbon in Figure 1.b. showed that the activation carried out succeeded in breaking down the structure

of lignin and cellulose as evidenced by the reduced intensity of infrared absorption. Figure 1.c. presents absorption at wave numbers 601.79 cm^{-1} and 416.62 cm^{-1}, which are tetrahedral Fe-O bonds and octahedral Fe-O bonds indicate the presence of iron oxide in the composite [20, 21].

The results of the FTIR spectra confirmed using XRD diffractogram presented in Figure 2. Figure 2.a. and 2.b. displays the diffraction patterns of carbon and activated carbon. Two peaks are visible at an angle of 2θ 24.48° [002] and 43.96° [110] and 2θ 24.17° [002] and 43.55° [110] which indicates that the carbon from the coconut shell has an amorphous phase structure [22, 23]. The presence of iron oxide was confirmed by diffraction peaks of 2θ 30.12° [220], 35.58° [311], 43.14° [400], 53.57° [422], 57.18° [511] and 62, 83° [440] which corresponds to JCPDS database no. 19-0629.

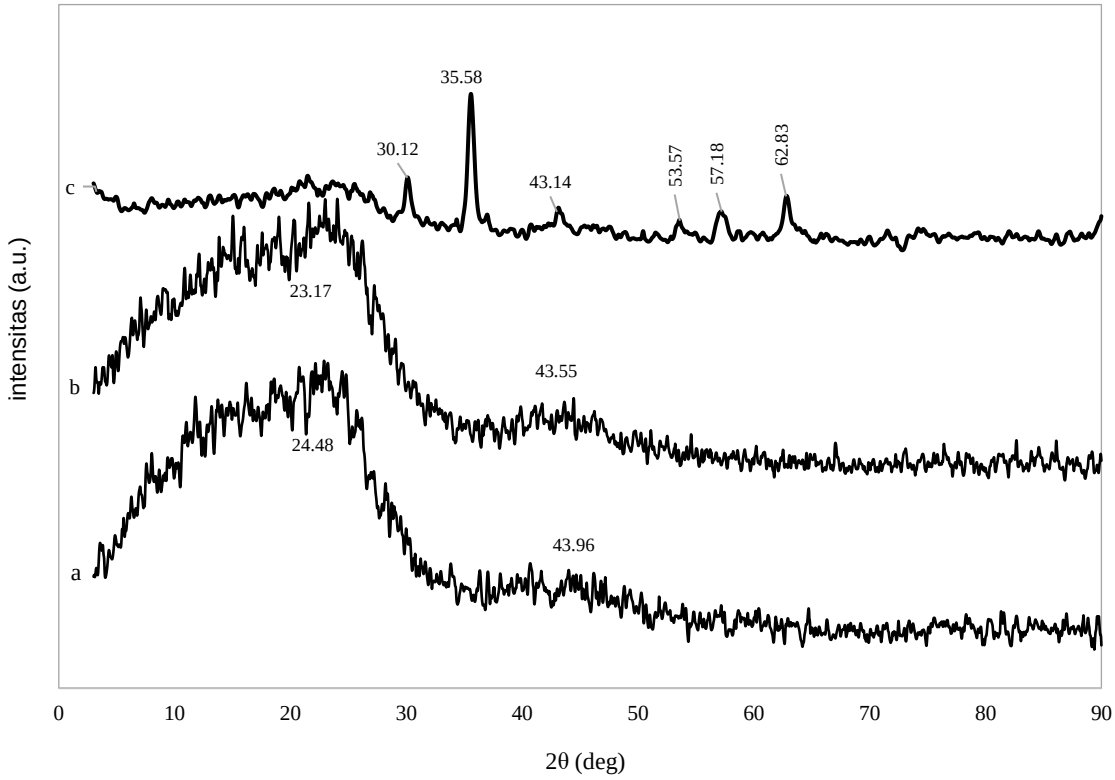

Figure 2. XRD Diffractogram of a. Carbon, b. Activated Carbon, and c. Composite

The calculation of the lattice parameter value shows that the iron oxide in the composite has a lattice parameter of a = 0.838 nm. The results of the calculation of the diffracting plane distance from the composite, ie d = 2.96, 2.52, 2.09, 1.71, 1.61 and 1.48 Å, confirm that the composite contains magnetite [15]. Based on the calculation results, the composite particles have an average size of 11.72 nm with the smallest size reaching 8.03 nm. This indicates that Fe_3O_4 has nano-magnetite size.

The information obtained from the GSA measurement results includes the total surface area, pore volume and pore size. The results showed the carbon has a total surface

area of 91.16 m^2/g, with a pore volume 5,24x10^{-2} cc/g for pore size below 17.46 nm and having an average pore size of 1.15 nm. The analysis shows activated carbon has a pore size that is included in the size of the microporous because it has a smaller pore size of 2 nm [24].

The addition of magnetite on the surface of activated carbon causes a decrease in surface area 12.04 m^2/g. The surface area is reduced due to the presence of magnetite on the surface and pore activated carbon that causes micro-sized pore covered. This is confirmed by the ratio of the pore distribution shown in Figure 3.

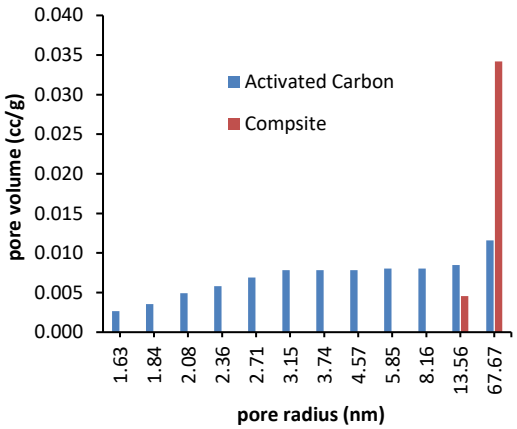

Figure 3. Pore Distribution Ratio of Activated Carbon and Composite

The results of the FTIR, XRD, and GSA analysis confirmed using SEM micrograph presented in Figure 4. In Figure 4. a and b, it appears that activated carbon has a porous surface morphology and there are visible impurities covering the surface and pores. The activated carbon micrograph Figure. 4. c and d shows that the impurities on the surface and the pores of the carbon have been reduced which causes micro-sized pores to exist.

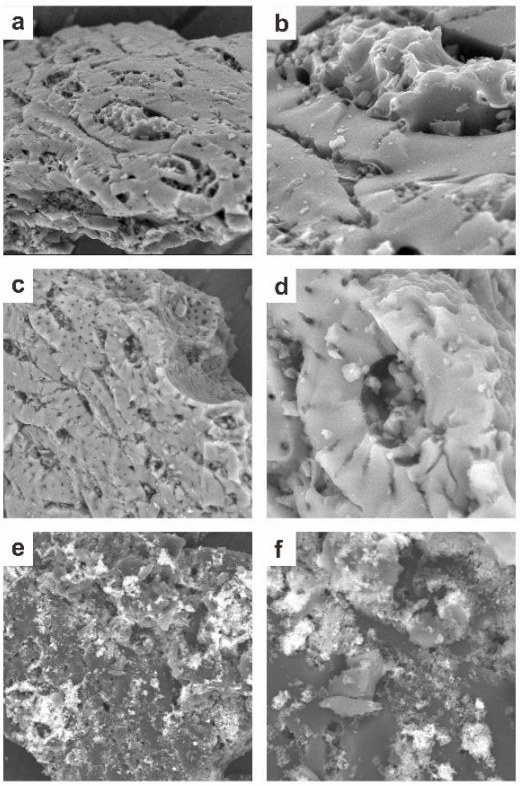

Figure 4. 3000x and 10000x Magnification Micrograph of; a-b. Carbon, c-d. Activated Carbon, and e-f. Composite

Carbon activation needs to be done to reduce impurities, one of which is by breaking down the lignin structure contained in coconut shells. In addition, the activation is done so that the carbon has a pore and a larger surface area [14]. Activation will produce more pores because KOH is a strong reagent, so the surface area will increase. KOH can interact with the carbon atom thus accelerating dehydrogenation and oxidation which causes an increase in porosity and changes in tar [25].

Composite micrographs show that there are pores on the composite surface indicated by dark color and composite particles which are indicated by lighter color [15]. Composite micrograph strengthens the results of the surface area analysis of the pore distribution which shows the micropore-

sized pores are covered by nanometer-sized magnetite particles that confirmed by the ratio of the pore distribution shown in Figure 3.

2. Magnetic Properties Test Results

The magnetic properties of the samples were known based on the magnetic properties test using magnetic field. The results of the magnetic properties test are summarized in Table 1.

Table 1. Magnetic Properties Test

	Magnetic Fields	
	Affected	Non Affected
Carbon	-	**V**
Activated Carbon	-	**v**
Composite	**v**	-

* tested using neodymium magnetic field

Both carbon samples and activated carbon do not respond to a given magnetic field, while the composite responds to a magnetic field by sticking in the direction of a given magnetic field. It shows carbon and activated carbon does not have magnetic properties, while the composite samples have magnetic properties. The magnetic properties contained in the composites indicate that magnetite has been successfully embedded in activated carbon. This is confirmed by the FTIR spectras, XRD diffractograms and SEM micrographs that indicate the existence of magnetite [15, 20, 21].

CONCLUSION

Coconut shell activated carbon-embodied Fe_3O_4 composites have been successfully prepared. The characterization results showed that Fe_3O_4 in coconut shell activated carbon was successfully carried out through the interaction of hydroxyl groups at wave numbers 601.79 and 416.62 cm^{-1}. The peaks of 2θ 30.12° [220], 35.58° [311], 43.14° [400], 53.57° [422], 57.18° [511] and 62.83° [440] indicate the presence of magnetite phase measuring 11.72 nm. Coconut shell activated carbon has microporous character with an average pore size of 1.46 nm. The presence of magnetite in the composites reduced the surface area of activated carbon from 91.16 m^2/g to 12.04 m^2/g. The response of the sample to the magnetic field shows that the composite has magnetic properties.

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