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Characterization of Egg Shell Waste As Adsorbent for Cooking Oil Waste Purification

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ABSTRACT

Eggshell has a shaft and a high surface area, so it has the potential to become an adsorbent. The adsorbent is an adsorbent in the filtration process. Waste cooking oil can be reused as raw material with economic value. So far, the waste bank that accommodates used waste has not gone through the filtration process, so the selling price is low. Waste cooking can be filtered using various adsorbent media, including activated carbon, commercial silica, and local adsorbents such as eggshells. A filtration process on waste cooking oil is expected to increase income for waste banks. The objective of this study was to investigate formulations adsorbent from eggshells for purification waste cooking oil. The variables used were a variety of particle size adsorbents (60, 80 mesh) and adsorbent weight (10, 15 g). The optimal result for the decreased acidic number was obtained at 60 mesh particle size, weight 15 grams.

1. Introduction

In 2020, the number of egg production in Indonesia was 8,871,721 tons, while in Yogyakarta, it was 66,692 tons [1]. If eggshells weigh 9-12% of the total weight, then there are around 871 thousand tons of eggshell waste produced annually in Indonesia, and Yogyakarta contributes about 6.7 thousand tons annually. Until now, eggshell waste has not been appropriately managed, so it is feared that it will cause pollution to the environment, namely by the presence of an unpleasant odor and can cause disease [2].

In addition to eggshells, the waste studied in this study is used cooking oil. In 2019, Indonesian households consumed 16.2 billion liters of cooking oil, with a potential production of 3 billion liters of used cooking oil per year [2]. The potential of this large amount of used cooking oil needs to be handled seriously not to harm the environment and the surrounding community. Cooking oil that has been used contains carcinogens, so it can cause disease when consumed. However, if the used cooking oil is disposed of without proper treatment, it can cause damage to soil and water. Public knowledge about the processing and utilization of used cooking oil is still minimal [3], so if it is not appropriately managed, it is feared that it will cause harm to the community and the environment.

Used cooking oil can be reused after the purification stage, namely to be processed into dish soap [4], candles [5], floor cleaners [6], even to alternative fuels [7,8]. This means that the purified used cooking oil can increase the economic value, although the purification of used cooking oil in the waste bank is still simple [3]. The purification of used cooking oil in the waste bank needs to be optimized so that income for waste can increase and support its members' economy.

One of the stages of filtering used cooking oil to be processed into raw materials requires a catalyst media that can utilize basic or acidic raw materials [9]. The utilization of eggshells as a filter is an effort to use eggshell waste that has been only thrown away. Eggshells have high $CaCO_3$ (calcium) levels, which is 87%-97%, and have natural pores, so they can absorb substances that are not useful [10, 11]. The research results by Niju et al. [7] and Ur Rahman et al. [8] provide empirical evidence that eggshell waste can be an efficient catalyst for the transesterification of used cooking oil. This study aims to find the best eggshell adsorbent formulation to purify used cooking oil.

2. Method

2.1. Materials

The materials used in this study were an eggshell waste, aquadest, strong acid H_2SO_4 for activation of eggshell surface area, cooking oil, activated carbon for comparison, and other supporting chemicals for acid number analysis and saponification. The chemicals were obtained from the Universitas Ahmad Dahlan Laboratory (UAD). Eggshell waste was received from donations from the UAD academic community, traders/residents around the UAD campus, and bakery entrepreneurs in Semanu, Gunung Kidul.

2.2. Equipment

The main tools used in this research are a furnace for ashing eggshells, screen for sifting. The supporting tools used are a blender, mortar and porcelain cup, filter paper. The analytical tools XRD analyzer (Bruker D2 Phaser), Scanning Electron Microscopy (SEM) (Phenom Pro X) to see the morphology of the eggshell. The analytical tool for acid numbers is a series of titration tools.

3. Procedure

3.1. Material Preparation

The eggshell is cleaned from the egg membrane, then washed thoroughly. The sample was washed twice with distilled water. The clean eggshells were dried at room temperature.

3.2. Adsorbent Formation

The prepared eggshells were ground and sieved with a size of 80 mesh. Then the sample was dried at 105 °C for 24 hours using an oven [7]. After drying, the following process is CaO calcination in eggshells. The sample was divided into two experimental groups. The first group did not use calcination/activation, and the second group used calcination. The calcination method is carried out by ashing the sample using a furnace at a temperature of 700 °C for 2 hours [11].

3.3. Analysis of Adsorbent Characterization

Analysis of adsorbent characterization includes analysis of specific surface area using X-Ray Diffraction (XRD) to determine the size of crystalline particles of adsorbent and surface morphology analysis of adsorbent shaft using Scanning Electron Microscopy (SEM). This analysis aims to evaluate the effectiveness of the adsorption capacity of the adsorbent. The characterization analysis was carried out at the UII Integrated Laboratory.

X-ray powder diffraction analysis was performed with a Bruker D2 Phaser. X-ray powder diffractometer on finely powdered samples using Cu Ka radiation (40 kV and 30 mA) and a Ni filter with a scanning speed of $0.005° \, 2\theta \, s^{-1}$. The time constant was set at 2 s [12].

Scanning Electron Microscopy (SEM) analysis procedure was analysis A sample of 1 mg was attached to an aluminum specimen stub with double-sided tape, then coated with 20 nm gold. After that, the attached samples were checked and photographed. Layers, films, samples were cut into strips, frozen in liquid nitrogen, and then cracked. The cracked surface is sprinkled with a layer of gold [13].

3.4. Wasted Cooking Analysis

100 mL of used cooking oil was soaked using eggshell adsorbent as 10, 15 grams, size variations of 60 and 80 mesh for 30 minutes of immersion. Then the oil is filtered using filter paper. Do the same for activated carbon adsorbents. After the test, the acid number was analyzed using the titration method with 0.1 N NaOH. The acid number was calculated using Equations 1 and 2 [10].

$$\%\ \text{Free Fatty Acid (FFA)} = \frac{\text{V NaOH x N NaOH x MR Fatty Acid}}{\text{Sample Weight (g)}} \text{ x } 100\% \qquad (1)$$

$$\text{Acid Number} = \frac{\%\ \text{FFA x MR KOH}}{\text{MR Fatty Acid/10}} \qquad (2)$$

4. Result and Disscussion

4.1. X-Ray Diffraction (XRD) Analysis

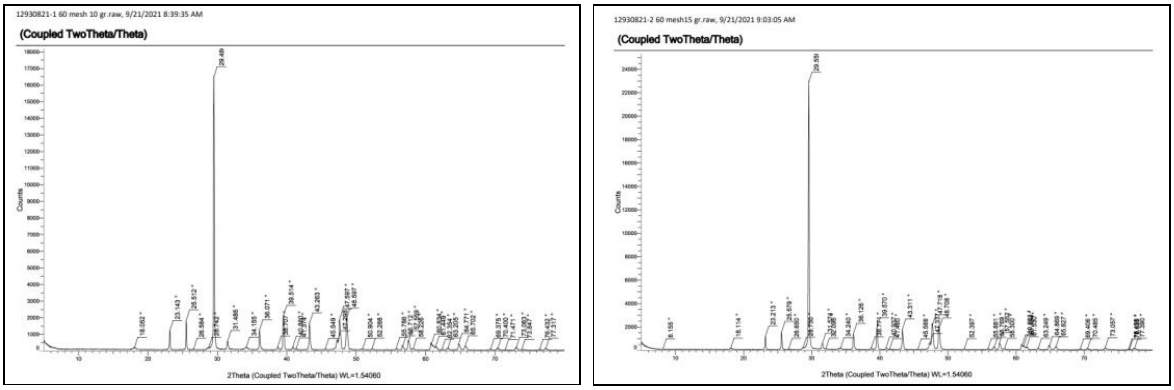
X-Ray Diffraction (XRD) test determines the shape and size of adsorbent particles [14]. The crystal size is shown based on the XRD data presented in Table 1. The formula obtains the crystal size:

$$n\lambda = 2d \sin\theta \qquad (3)$$

The XRD chart data is shown in Fig.1-3. Fig.1a shows the XRD results of an eggshell adsorbent with a particle size of 60 mesh and a weight of 10 grams. The peak of the eggshell adsorbent with 60 mesh was 29.44°. The highest peak of eggshell adsorbent with a size of 60 mesh and a weight of 15 grams was 29.55° (Fig. 1b). Fig. 2a shows the highest peak in the 80 mesh size 10 gram adsorbent is 80 mesh 29.47°. The highest peak in the 80 mesh size adsorbent weighing 15 grams shown in Fig.3b is 29.52°. Fig. 3 shows the highest peak at the adsorbent size of 80 mesh weighing 10 grams without activation at 29.47°. The CaO phase in the eggshell is $Ca(OH)_2$, which corresponds to the Joint Committee on Powder Diffraction Standards (JCPDS) database. The peak of the results corresponds to the $Ca(OH)_2$ phase in the Gago and Ngapa [15] study of 28.699°. There is a difference in the highest peak obtained, although it is insignificant. The highest peak was received at the adsorbent size of 60 mesh with a weight of 15 grams at 29.55°. The weight of the adsorbent affects the amount of $Ca(OH)_2$ on the adsorbent, and this is evident from the higher the weight of the adsorbent, the higher the XRD peak produced. The highest crystal size produced on the 60 mesh adsorbent weighing 10 grams was 0.075 Å.

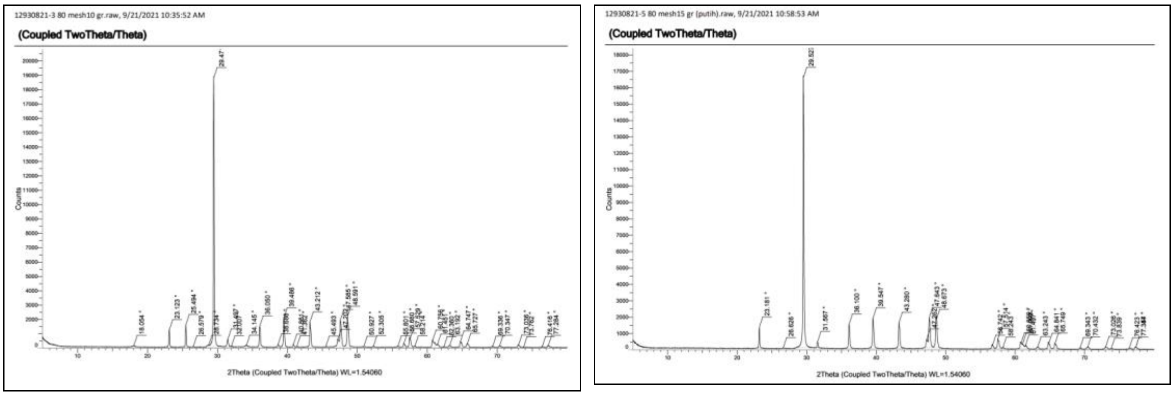
Table 1. Adsorbent Crystal Size

Sample	Variable		Crystal Size (Å)
	Particle size (mesh)	*Adsorbent weight (g)*	
Activation H_2SO_4	60	10	0.075316249
		15	0.055044809
	80	10	0.052091708
		15	0.052300224
Non Activation H_2SO_4	80	15	0.054007768



(a) (b)

Fig. 1.XRD analysis results from adsorbent 60 mesh (a)10 grams; (b) 15 grams



(a) (b)

Fig. 2.XRD analysis results from adsorbent 80 mesh (a)10 grams; (b) 15 grams

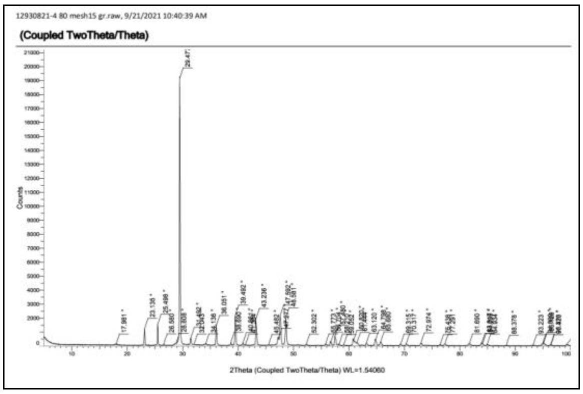
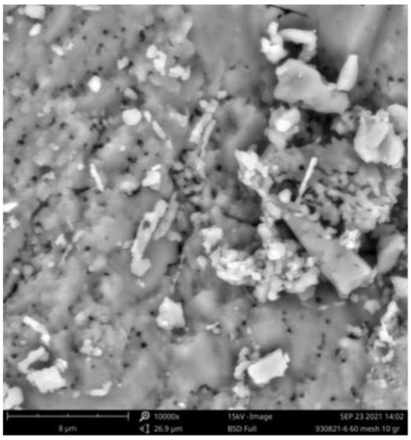


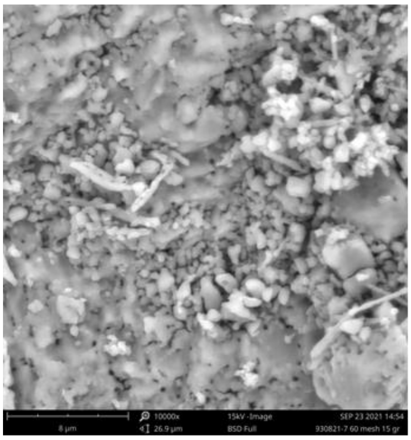
Fig. 3.XRD analysis results from adsorbent noncalcination 80 mesh, 15 grams

4.2. Scan Electron Microscopy (SEM) Analysis

Scan Electron Microscopy (SEM) analysis to determine the surface shape of the adsorbent. SEM analysis on eggshell adsorbent with almost the same size at a magnification of 10,000x shows that the visible shape is very tight and irregular. Still, the shape is different for 80 mesh size 15 grams. The adsorbent 80 mesh 15 grams is like large granules (Fig. 4). The surface shape of the 60 mesh adsorbent is almost the same between the weight of 10 and 15 grams as a small needle. The surface of the eggshell adsorbent for 80 mesh size differs between 10 grams and 15 grams. Weighing 10 grams, the shape is flat and fused, while 15 grams is shaped like a granule. There is a difference between the size of 80 mesh 15 grams of activated and inactivated. The form of the unactivated adsorbent is still fused and flat as in 80 mesh 10 grams. The surface is visible at a particle size of 8 m. Research by Njju et al. [7] reported that the shape of the CaO shaft as a result of calcination and hydration of eggshells was like a honeycomb at 2 m in size. Differences that occur may be due to differences in calcination treatment. The shaft that is close to the form of CaO [7] is an adsorbent with a size of 80 mesh 15 grams.



(a)



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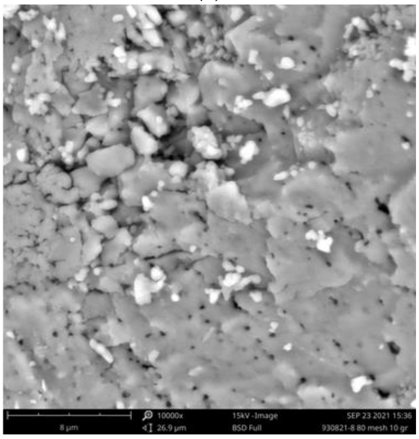
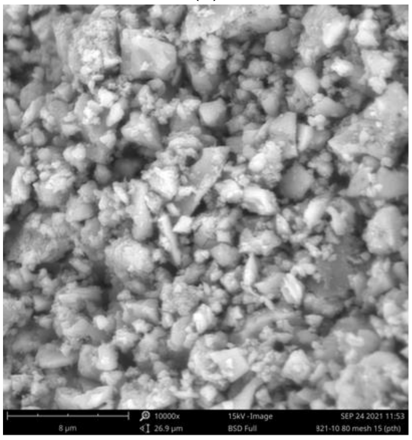
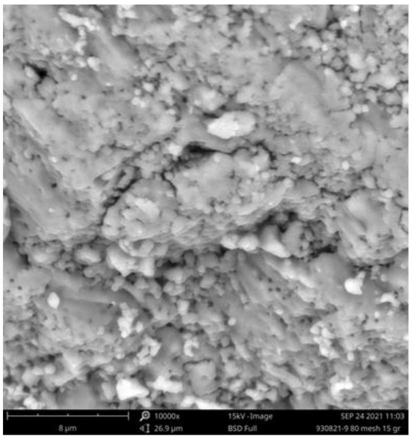


(c)



(d)



(e)

Fig. 4.SEM analysis results of eggshell adsorbent (a) 60 mesh 10 grams; (b) 60 mesh 15 grams; (c) 80 mesh, 10 grams; (d) 80 mesh 15 grams; (e) without activation 80 mesh 15 grams

From the results of the analysis above, it can be seen that the recommended optimal crystal size and shape of the shaft is a particle size of 80 mesh with a weight of 15 grams. The more shafts of an adsorbent, the better the adsorption capacity. This is because more shafts will increase the surface area [7].

4.3. Acid Number

The results of the analysis of acid numbers are shown in Table 2.

Table 2. Analysis of Acid Numbers

Sample	Variable		%FFA	Acid Number (mg KOH/g)
	Particle Size (mesh)	*Adsorbent Weight (g)*		
Control	-	-	3.0770	4.8000
Activation	60	10	0.3419	0.5333
		15	1.8804	2.9333
	80	10	1.4530	2.2667
		15	3.4189	5.3333
Non Activation	60	15	2.6497	4.1333
Carbon active	60	15	2.6497	4.1333

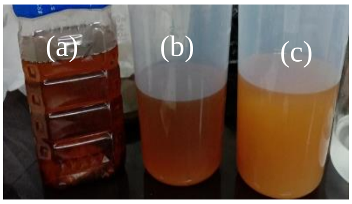


Fig. 5. The result of soaking used cooking oil with adsorbent (a) control, (b) activated charcoal adsorbent, (c) eggshell adsorbent

The acid number is one of the quality parameters of cooking oil. The acid number indicates the free fatty acid content of the oil. In used cooking oil, the acid number is very high. This is due to the oxidation process in the oil during the frying process. The acid number in cooking oil allowed by SNI 01-3741-2002 is a maximum of 0.6 [10]. The results obtained showed that the adsorbent activated using strong acid H_2SO_4 had a lower acid number than that which was not activated except for the size of 80 mesh 15 grams. The weight of the best adsorbent to reduce the acid number of used cooking oil is 10 grams with a particle size of 60 mesh. This may be due to the largest crystal size of the adsorbent 60 mesh 10 grams compared to the others. Fitriyana and Safitri [10] reported that for the adsorption of used cooking oil with eggshells without activation, the stirring time was 45 minutes with an adsorbent weight of 10 with an acid number of 0.777 mgKOH/g from an acid number of blank used cooking oil 4.3707 mg KOH/g. In Fitriyana and Safitri's research, how many particle sizes were used was not explained. The study was conducted to obtain more optimal results at the adsorption time of 30 minutes with the same weight as the adsorbent. This may be due to the small particle size of 60 mesh and strong acid activation.

The results in Table 2 show that the acid number of the activated adsorbent is lower than that of the unactivated adsorbent. This study also compared commercial activated charcoal adsorbents with activated eggshell adsorbents. The results of the acid number in Table 2 show that the activated eggshell adsorbent has a lower acid number and color clearer (Fig. 5) than activated charcoal. This proves that eggshells can compete with commercial adsorbents and can be recommended as an adsorbent to purify used cooking oil. This can be a solution to reduce egg waste. This may be due to the higher adsorption capacity of CaO compared to carbon [16]. Based on the acid number analysis that has been carried out, the optimal results on the eggshell adsorbent with a size of 60 mesh and a weight of 10 grams are 0.5333 mg KOH/g.

5. Conclusion

Based on the research and discussion results, it can be concluded that the recommended eggshell adsorbent formula is 60 mesh 10 grams because it has the largest crystal size, high CaO peaks, and can reduce the acid number in used cooking oil.

Notation

V NaOH = volume NaOH (mL)
N NaOH = normality NaOH (N)

MR = Mass Molar Relative Fatty Acid (g/gmol)
% FFA = percentage of free fatty acid
MR KOH = Mass Molar Relative KOH (g/gmol)
λ= X-ray wavelength (Å)
d = distance between grids (Å)

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