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Manufacture and Characterization of Adsorbers Utilizing Pahae Natural Zeolite-Chicken Eggshell for Purifying Used Cooking Oil

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ABSTRACT

This research investigates the synthesis and characterization of Pahae natural zeolite-chicken eggshell adsorber to refine used cooking oil. The primary objective is to develop effective adsorbents for enhancing the quality of used cooking oil through refining. The methodology involves sieving the zeolite through a 74 µm sieve, chemically activating it using a 10% KOH solution for 1 hour and drying it at 100°C. The eggshells are also sieved through a 74 µm sieve, followed by washing and drying at 105°C for 12 hours. Various combinations of natural zeolite and chicken eggshell compositions (100% : 0%, 0%: 100%, 95%: 5%, 90%: 10%, 85%: 15%, 80%: 20%) are then prepared and pressed using a hydraulic press under a load mass of 6 tons for 10 minutes. The resultant samples are further activated by heat treatment at 600°C for 2 hours. The adsorbents undergo a comprehensive characterization process, encompassing physical properties (porosity and water absorption), mechanical properties (hardness), surface morphology (SEM), elemental composition (XRF), X-ray diffraction (XRD) analysis, and practical applications assessment (density, viscosity, moisture content, color, and odor). The optimal adsorbent configuration is identified as 80% natural zeolite and 20% chicken eggshell composition, activated at 600°C, exhibiting a porosity of 81.54% and an oil absorption of 46.86%. The highest hardness value of 119.64 MPa is achieved with 100% natural zeolite composition at 600°C. SEM analysis indicates an average pore diameter of 1.232 µm, while XRF results highlight calcium (Ca) as the predominant element at 49.64%. XRD analysis confirms the formation of a rhombohedral crystal structure.

Keywords: Adsorber, Chicken Eggshell, Natural Zeolite Pahae, Purification of Used Cooking Oil

ABSTRAK

Penelitian ini mengkaji sintesis dan karakterisasi adsorber zeolit alam-cangkang ayam Pahae untuk memurnikan minyak jelantah. Tujuan utamanya adalah untuk mengembangkan adsorben yang efektif untuk meningkatkan kualitas minyak jelantah melalui penyulingan. Metodologinya melibatkan pengayakan zeolit melalui saringan 74 µm, mengaktifkannya secara kimia menggunakan larutan KOH 10% selama 1 jam dan mengeringkannya pada suhu 100°C. Cangkang telur juga diayak dengan saringan 74 µm, dilanjutkan dengan pencucian dan pengeringan pada suhu 105°C selama 12 jam. Berbagai kombinasi komposisi zeolit alam dan cangkang telur ayam (100% : 0%, 0%: 100%, 95%: 5%, 90%: 10%, 85%: 15%, 80%: 20%) kemudian disiapkan dan dipress menggunakan hydraulic press dengan massa beban 6 ton selama 10 menit. Sampel yang dihasilkan selanjutnya diaktifkan dengan perlakuan panas pada suhu 600°C selama 2 jam. Adsorben menjalani proses karakterisasi yang komprehensif, meliputi sifat fisik (porositas dan penyerapan air), sifat mekanik (kekerasan), morfologi permukaan (SEM), komposisi unsur (XRF), analisis difraksi sinar-X (XRD), dan penilaian aplikasi praktis (densitas, viskositas, kadar air, warna, dan bau). Konfigurasi adsorben yang optimal adalah komposisi zeolit alam 80% dan cangkang telur ayam 20%, yang diaktifkan pada suhu 600°C dengan porositas 81,54% dan penyerapan minyak

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46,86%. Nilai kekerasan tertinggi sebesar 119,64 MPa dicapai dengan komposisi zeolit alam 100% pada suhu 600°C. Analisis SEM menunjukkan diameter pori rata-rata 1,232 µm, sedangkan hasil XRF menyoroti kalsium (Ca) sebagai elemen dominan sebesar 49,64%. Analisis XRD mengkonfirmasi pembentukan struktur kristal rombohedral.

Keywords: Adsorber, Cangkang Telur Ayam, Pemurnian Minyak Jelantah, Zeolit Alam Pahae

1. Introduction

Cooking oil is an indispensable ingredient for many, serving as a medium for heat transfer and enhancing the flavor and appearance of dishes through its distinctive brownish-yellow hue during frying [1]. However, the high heat involved in cooking leads to the formation of undesirable compounds, including free fatty acids, carbonyl compounds, and peroxides, which can potentially pose chronic health risks [1].

Used cooking oil contaminated with these compounds becomes unsuitable for further use and poses environmental hazards if improperly disposed of. Nevertheless, by improving its quality, the used cooking oil can be repurposed to produce soap, cosmetics, and even biodiesel [2]. The term "used cooking oil" refers to oil subjected to frying on multiple occasions, typically exceeding 3-4 cycles. In response, researchers have explored methods to purify used cooking oil, and using adsorbents is a promising approach.

Adsorbents are substances or minerals capable of absorbing and retaining liquids or gases within their structure [3]. Porous adsorbents facilitate adsorption within their internal structures or specific sites. These adsorbents can be categorized into non-porous and porous types, with commercially recognized options including activated carbon, zeolite, silica gel, activated alumina, and eggshells [4]. Among these, natural zeolite and eggshells stand out as promising candidates.

Zeolites comprise hydrated alumina silicate crystals incorporating alkaline or alkaline earth cations within a three-dimensional framework. These minerals, found around volcanic areas or in hot spring locales, feature interconnected cavities, making them ideal for adsorption due to their extensive surface area [5,6]. Due to their remarkable physical and chemical properties, zeolites have the potential to serve as ion exchangers, molecular filters, adsorbents, and catalysts. Natural zeolites find extensive use in various applications, such as filtration, hydrogen purification through steam filtration, ethanol refinement, fuel cell membranes, and desalination processes [7–14].

Eggshells, byproducts of the food and baking industries, comprise distinct layers, including the outer ceramic cuticle, rubbery calcareous layer, and inner flat layer [15]. In this study, chicken eggshells heated to 600°C are utilized, containing approximately 94% $CaCO_3$ and trace amounts of CaO, rendering them suitable as adsorbents. Each eggshell boasts a significant number of pores, ranging from 7,000 to 17,000 [16].

Previous research efforts have explored the refinement of used cooking oil using various adsorbents, including zeolites and eggshell-based materials. These studies have explored parameters such as temperature, particle size, and reaction time to achieve desirable results [17,18]. Despite these efforts, investigations specifically involving natural zeolite-based adsorbents from thighs and chicken eggshells for used cooking oil purification have yet to be conducted. In response to this research gap, the current study explores the development and characterization of adsorbents based on natural zeolite and chicken eggshells.

2. Methods

2.1. Processing of Pahae Natural Zeolite

The zeolite utilized in this study was sourced from Indonesia and is initially present as sizable chunks. The chunked zeolite was first subjected to crushing, either manually using a mortar or hammer, resulting in a finely crushed state. Then the finely crushed zeolite was then sifted through a 200 mesh (74 µm) sieve for size refinement. Subsequently, the sieved zeolite powder was activated by immersion in a 10% KOH activator solution. The activated zeolite was then separated from the solution using filter paper and rinsed with distilled water until achieving a neutral pH. Finally, the treated zeolite was dried in an oven at 100°C for 1 hour to achieve desiccation. This preparation process ensures the transformation of the original zeolite chunks into a processed, activated, and dried zeolite powder suitable for further study.

2.2. Chicken Eggshell Processing Process

In order to be employed for the absorber, the chicken eggshell underwent the processing procedure. Firstly, the chicken egg shells were cleaned by washing and separated from the membrane layer. Then, the chicken eggshells were dried in an oven at 105°C for 12 hours. After that, the sample was crushed using a mortar and sieved using a 200 mesh (74 μm) sieve.

2.3. Process for Making Pahae Natural Zeolite-Chicken Eggshell Adsorber

The Pahae natural zeolite- chicken eggshell adsorbers were carried out for 5 minutes using a sieve shaker with variations in the composition of the ingredients of 100%:0% (ZA), 0%:100% (CT), 95%:5% (A1), 90%:10% (A2), 85%:15% (A3), and 80%:20% (A4). The results of mixing the composition are put into a mold with a thickness of 1 cm, length 3 cm, and width 3 cm with a mold volume of 10 grams. Then printing was done with a hydraulic press for 10 minutes with a mass of 6 tons. The results of the hydraulic press sample are in the form of solids, which are left in an open space for one week to prevent the sample from cracking during the heating prayer. Samples left for one week were then physically activated at 600°C for 2 hours. The activated sample was left for one day in the oven in the off condition. The adsorber was produced from this activation, which was ready to be tested for physical properties (porosity and water absorption), mechanical properties (hardness), SEM, XRF, and XRD.

2.4. Used Cooking Oil Refining Process

The used cooking oil in this study was characterized (density, viscosity, moisture content, color, and odor test) before it was refined. Then the adsorber whose weight had been measured was placed in the beaker glass. As much as 100 mL of used cooking oil was poured into a beaker glass. The adsorber and the used cooking oil were added to the Erlenmeyer and then stirred using a hot plate magnetic stirrer at 8 rpm at 60°C for 1 hour. Then the refined used cooking oil was characterized (test density, viscosity, flow rate, color, and smell).

3. Results and Discussion

3.1. Porosity Test Results

Results of the porosity test of Pahae natural zeolite-chicken eggshell absorbers were conducted according to ASTM C 642-90.

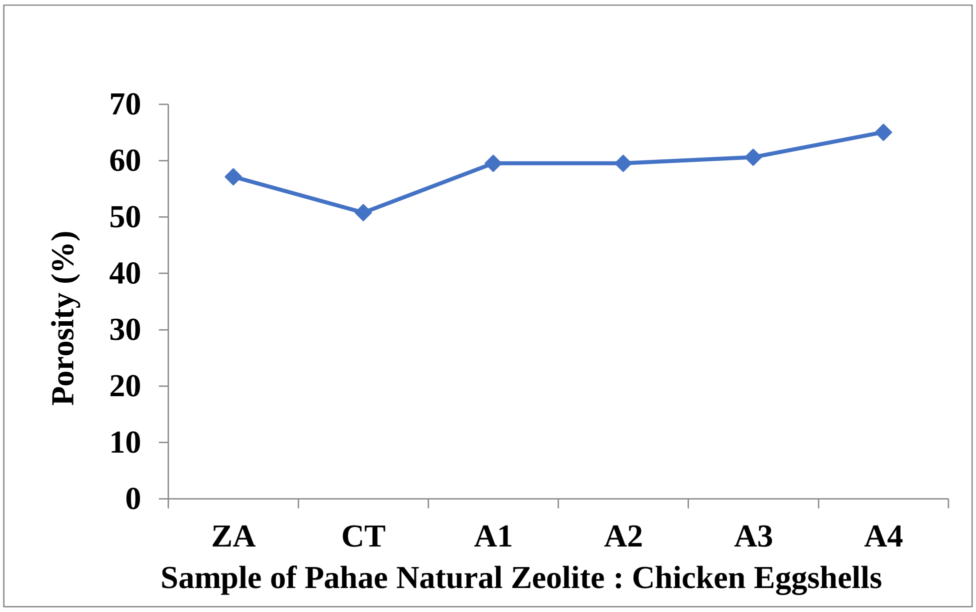

Figure 1. Graph of adsorber porosity test results.

Figure 1 illustrates that the maximum porosity measurement of 65.07% is observed in sample A4, consisting of an 80%:20% ratio. Conversely, the minimum porosity measurement of 49.52% is evident in the CT samples, comprising a 0%:100% ratio. Consequently, incorporating chicken eggshell filler into zeolite leads to an elevation in porosity levels. This phenomenon can be attributed to the presence of pores with significant surface area in the chicken eggshell, heated to 600°C, and its content of $CaCO_3$, which plays a pivotal role in enhancing the purification of used cooking oil.

3.2. Water Absorption Test Results

The results of the water absorption test Pahae natural zeolite-chicken eggshell absorbers were obtained based on SNI No. 03 – 0349.

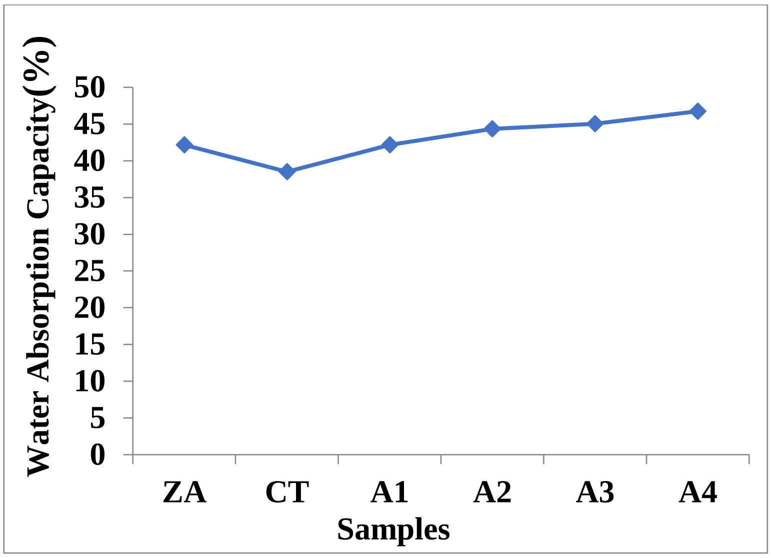

Figure 2. Graph of water absorption capacity result.

Figure 2 depicts the peak water absorption measurement of 46.75% observed in sample A4, composed of an 80%:20% ratio. In contrast, the least water absorption measurement, amounting to 38.51%, is noted in the CT sample with a composition of 0%:100%. Hence, the introduction of chicken eggshell filler to zeolite yields an enhancement in water absorption capabilities. The attained water absorption capacity directly correlates with the porosity value, indicating that greater pore or cavity dimensions within an adsorbent correspond to elevated water absorption readings.

3.3. Hardness Test Data Results

Hardness test results of Pahae natural zeolite-chicken eggshell absorbers were conducted using the Vickers hardness test.

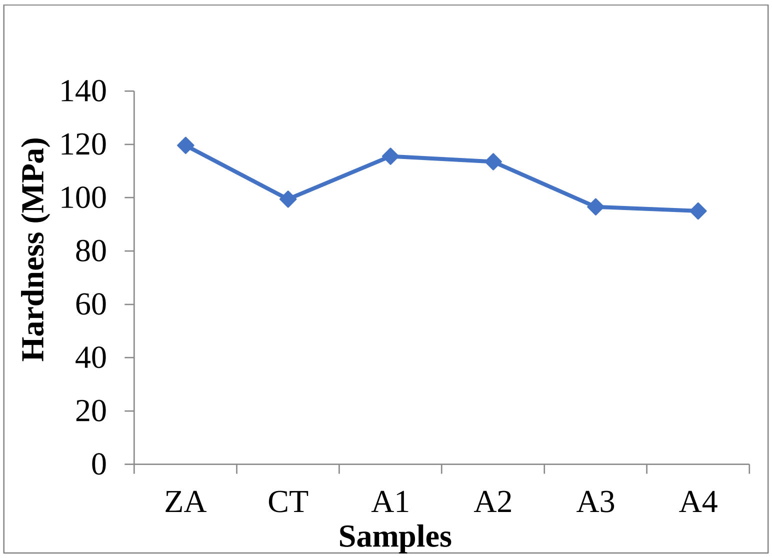

Figure 3. Graph of hardness test results.

Figure 3 shows a graph of the hardness test results of Pahae natural zeolite-chicken eggshell absorbers. It can be seen that the highest hardness value is 119.64 MPa in the ZA (composition of 100%:0%), while the lowest hardness value is 95.60 MPa in the A4 (composition of 80%:20%). The results of the non-linear hardness test with the physical properties test proved that adding chicken eggshell filler to the adsorber could not increase the hardness value. This phenomenon arises due to the chicken eggshell, subjected to a temperature of 600°C, developing numerous pores with a substantial surface area, thereby influencing the hardness value through the variation in pore count.

3.4. Morphological Analysis Using SEM

SEM testing was conducted to analyze the sample's surface morphology and determine the pore diameter's size. Figure 4 shows the SEM results on sample A4 (composition of 80%:20%). This composition was selected due to the optimum composition of the previous physical tests.

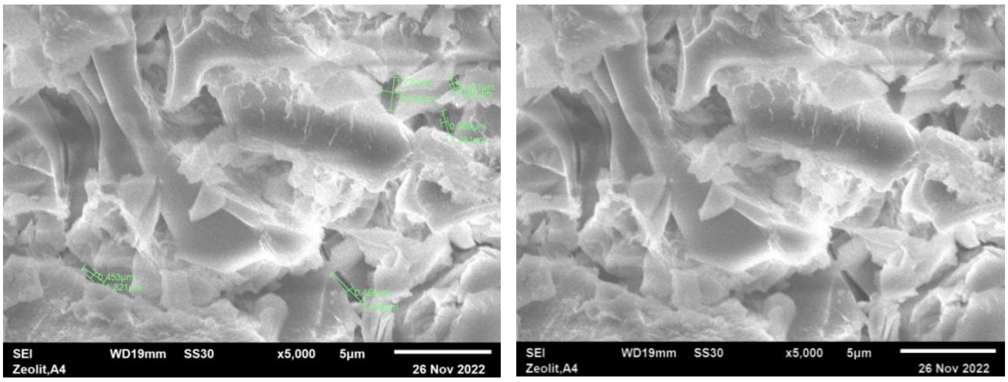

Figure 4. SEM images of Pahae natural zeolite-chicken eggshell absorbers with the composition of 80%: 20% (5000-time magnification).

Figure 4 shows the results of the adsorber SEM test at 600°C with a composition of 800%:20%; it was found that the material was not mixed evenly; this can be seen from the pore diameters on the adsorber surface. The average pore diameter was 1.232 µm, which was obtained from each pore size, namely 2.036 µm, 1.321 µm, 1.281 µm, 0.894 µm, and 0.632 µm.

3.5. Test Results For Elemental Content Using XRF

XRF testing was carried out to determine the elemental content in the sample. Table 1 shows the XRF results with the highest elemental values in sample A4 (composition of 80%:20%). The sample selection was based on the optimum composition of the physical tests.

Table 1. XRF test results.

Element	% Weight
Si	17.21
Al	5.51
Fe	9.94
K	11.04
Ca	49.65
P	1.74
Mn	0.15

Table 1 shows some elements in sample A4 (composition of 80%:20%). The most dominant element content in zeolite is Si and Al; this is because zeolite is an alumina-silica mineral structure bound by oxygen atoms, forming pores in the zeolite structure. According to Warsy et al. [19], who has tested elemental levels in chicken egg shells, there are several constituent elements, namely Ca as the most dominant element, K, P, and Mn. This is because the chicken eggshell has many pores and a large surface.

3.6. Crystal Structure Analysis Using XRD

XRD testing was carried out to determine the crystal structure of the sample. Figure 5 shows the diffraction pattern on sample A4 (composition of 80%:20%). Selection of the sample was based on the optimum composition of the physical tests. Figure 5 shows the diffraction pattern of the adsorber in sample A4 (composition of 80%:20%) at 600°C; the highest intensity peak obtained from the adsorbent is the compound calcium carbonate ($CaCO_3$) with the crystal structure formed on the adsorber being rhombohedral. This proves that the addition of chicken eggshells which have calcium carbonate compound ($CaCO_3$) as a filler can change the crystal structure of the amorphous natural zeolite.

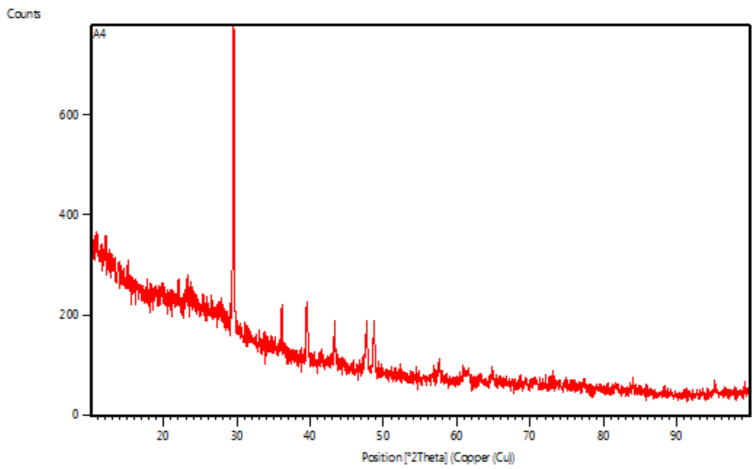

Figure 5. XRD Pattern of Pahae natural zeolite-chicken eggshell absorbers with a composition of 80%:20%.

3.7. Test Results on Used cooking oil Applications

Tests on the application were carried out to determine the potential of the adsorber for refining Used cooking oil and to meet the Indonesian National Standard 3741-2013 Quality of Cooking Oil. The sample used is A4 (composition of 80%:20%). Selection of the sample was based on the optimum composition of the physical test.

Table 2. Test results on used cooking oil applications.

Number	Test Criteria	Testing of Used cooking oil		Quality Standards	Information
		Before	After		
1	Density	0.8655 g/mL	0.8061 g/mL	Max. 0.80 g/mL	Fulfill
2	Viscosity (thickness)	0.0500 P	0.0345 P	Max. 0.0391 P	Fulfill
3	Water content	3.74%	0.29%	0.1 – 0.30 %	Fulfill
4	Color	Tanned	Yellow	Pale Yellow - Yellow	Fulfill
5	Smell	Smell rancid and slightly rancid	Normal	Normal	Fulfill

Table 2 shows the test results of Pahae natural zeolite-chicken eggshell absorbers for refining Used cooking oil. The table shows that all test parameters have met the Quality of Cooking Oil [20] with a purification percentage of 68% of density, 31% of viscosity, and 92% of water content.

4. Conclusion

In summary, the utilization of natural zeolite-based adsorbers infused with chicken eggshells has shown promising results for enhancing the purification of used cooking oil. The optimized composition, exemplified by sample A4 (80%:20%), exhibited favorable physical and mechanical attributes, including a porosity of 81.54%, oil absorption of 46.86%, and hardness of 119.639 MPa, all achieved through a 600°C treatment. This composition demonstrated a notable decrease in density (68%), improved viscosity (31%), and reduced water content (92%), along with color enhancement to yellow and the restoration of typical smell. The study's exploration of composition variations indicated a direct relationship between chicken eggshell filler and higher porosity and water absorption. Additionally, while the hardness test did not display a linear correlation with physical properties, the SEM analysis revealed an average particle size of d = 1.232 µm. The XRF and XRD analyses highlighted dominant elements (Si, Al, and Ca) and revealed the formation of a rhombohedral crystal structure. These findings collectively underscore the potential of this innovative adsorber configuration for effective used cooking oil refinement. Further research and practical applications are warranted to harness these advancements fully.

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