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Research Article

Optimization and Characterization of Adsorbent from Palm Kernel Shell Waste Using H_3PO_4 Activator

Optimasi dan Karakterisasi Adsorben dari Limbah Cangkang Kelapa Sawit Menggunakan Aktivator H_3PO_4

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Abstract

Palm kernel shell is solid waste produced from the processing of crude palm oil (CPO). In this context, phosphoric acid (H_3PO_4) serves as an essential activator for producing an adsorbent with maximum micropore under operating conditions at a temperature of <450°C. Therefore, this study aimed to determine the optimal adsorbent condition of the palm kernel shell using H_3PO_4 activator. The production process was optimized using Response Surface Methodology (RSM) and Central Composite Design (CCD) methods with activator concentration variations of 4%, 5%, and 6%, at activation times of 23 hours, 24 hours, and 25 hours, respectively. The quality of the adsorbent produced fulfilled SNI standard 06-3730-1995, characterized by water content of 1.001%, ash content of 5.767%, missing substance level of 18.932%, and fixed carbon content of 75.301%. Furthermore, this work effectively optimized the RSM and CCD adsorbent production process, achieving 4.785% variation in activator concentration and 24.679 hours activation time.

Keywords: adsorbent; fixed carbon; H_3PO_4 activator; iodine charcoal power; palm kernel shell

Abstrak

Cangkang kelapa sawit adalah salah satu limbah padat yang dihasilkan dari proses pengolahan minyak kelapa sawit. Aktivator H_3PO_4 dapat menghasilkan adsorben yang memiliki mikropori maksimum pada kondisi operasi suhu <450 °C. Tujuan penelitian ini adalah untuk menentukan kondisi optimum adsorben dari cangkang kelapa sawit dengan menggunakan aktivator H_3PO_4. Proses pembuatan adsorben dioptimasi menggunakan metode Response Surface Methodology (RSM) khususnya Central Composite Design (CCD) dengan variasi konsentrasi aktivator yaitu 4%, 5%, dan 6% serta dengan variasi waktu aktivasi yaitu 23 jam, 24 jam, dan 25 jam. Kualitas adsorben dari cangkang kelapa sawit telah sesuai dengan standar SNI 06-3730-1995 pada karakteristik kadar air 1,001%, kadar abu 5,767%, kadar zat yang hilang 18,932%, fixed carbon 75,301%. Selain itu, penelitian ini juga berhasil mengoptimalkan proses pembuatan adsorben menggunakan metode RSM dan CCD dengan variasi konsentrasi aktivator 4,785% dan waktu aktivasi selama 24,679 jam.

***Kata kunci**: adsorben; aktivator H_3PO_4; cangkang kelapa sawit; daya jerap iod; fixed carbon*

1. Introduction

In Indonesia, the palm oil mill industry is experiencing significant growth, with an annual production of two million tons [1]. This phenomenon has led to the generation of a substantial amount of waste, requiring the adoption of net zero waste and the development of treatment initiatives to prevent greenhouse gas emissions. According to the 2020 data from the National Statistical Agency, Indonesia has 14,858,000 hectares of palm plantations, with 196,000 hectares located in Lampung Province [2].

The primary products of palm industry are liquid and solid waste, as well as crude palm oil (CPO). This solid waste comprises the palm kernel shell, the empty bunch, and the sludge from the decanter's output. Meanwhile, liquid waste consists of the exhaust waste from the sterilization and clarifier stations. Solid waste is considered suitable for processing into valuable products such as plant fertilizer made from sludge and empty palm [3]. However, palm kernel shell waste has not been fully exploited for large-scale use due to its harder texture, and application as fuel for boilers. In industry settings, the exploitation is against the existing rules, causing damage to boiler pipes.

Palm kernel shell constitutes approximately 60% of waste generated in the production of palm oil. Furthermore, it consists of hemicellulose, cellulose, lignin, and ashes, with a proportion of 33.52%, 38.52%, 20.36%, and 3.92%, respectively [4]. To mitigate the environmental impact of this waste, using palm kernel shell as an adsorbent offers a promising solution. The resultant adsorbent produced in this method can be used to remove hazardous chemicals or heavy metals from wastewater, contributing to the reduction of air and water pollution.

Adsorbent technique uses chemical processes to remove heavy metals, while aeration and biosorbent cellulose xanthate demand more energy [6,7]. Therefore, to address heavy metals related to water and air pollution, absorbent method is a cost-effective and environmentally responsible substitute.

A previous study conducted by Hendra reported that the highest quality absorbent could be made from palm kernel shell at a temperature of 850^oC [8]. In order to increase the adsorbent's adsorption capacities and efficiency, chemicals including phosphate acid (H_3PO_4) [9], chloric acid (HCl) [10], sodium hydroxide (NaOH), and potassium hydrogen oxide (KOH) [11] have also been used in the activation process. Specifically, H_3PO_4 activator has shown the ability to effectively produce chemical reactions in the synthesis of organic compounds [12], increasing final product yield to ensure better adsorption with enhanced physical and chemical stability. This makes adsorbent suitable for use in gas filters, water purification, catalyst supports, and the treatment of industrial waste [13-15]. Therefore, this study aimed to determine the optimal conditions for converting palm kernel shell into adsorbent using H_3PO_4 activator.

2. Research Methods

This study was conducted at the Analysis and Chemical Industry Laboratory of the Politeknik Negeri Lampung on March 29th and October 31st, 2022. The ingredients used included palm kernel shell, H_3PO_4 solution (Merck), iodine (Merck), starch 1%, KIO_3 (Merck), sodium thiosulfate 0.1 N, and aquadest.

Furthermore, the tools used included laboratory pyrolysis, a drying oven (UN 110, Memmert, German), an analytical balance (Shimadzu, Japan), a pH meter, a furnace, thermometer, and a grinder.

2.1 Collection, preparation, and activation using H_3PO_4

Palm kernel shell was collected from PT Anaktuha Sawit Mandiri, Wates, Lampung Tengah, Indonesia. A pyrolysis process, as shown in Figure 1 was used to burn 500 g palm kernel shell at a temperature of 400 ^oC for 4 hours [16-18]. Subsequently, a pyrolysis coal was put into the grinder machine to reduce the size to 100 mesh. Charcoal powder was stored at room temperature of 25 ^oC, preventing water absorption. The activation with H_3PO_4 was carried out as an adsorbent to enhance adsorption capabilities. Response Surface Methodology (RSM) was used for the combination of adsorbent production from palm kernel shell, as shown in Table 1.

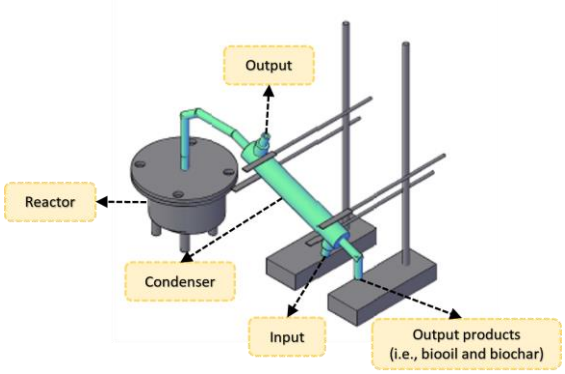

Figure 1. Pyrolysis laboratory-scale for burning kernel shell.

Each 100 g of charcoal powder was activated using three different concentrations: 4%, 5%, and 6% [19]. The activation was carried out at different times, including 23, 24, and 25 hours. After activation, distilled water was used to filter and neutralize adsorbent to a pH of 7, which was placed into the oven to dry at 110°C for 3 hours. Product adsorbent was carried out to determine optimum conditions during activation using H_3PO_4 and activation time.

Tabel 1. Experimental design of adsorbent production

Run-n	Concentration activator (%)	Activation time (Hours)
1.	4	23
2.	4	24
3.	4	25
4.	5	23
5.	5	24
6.	5	24
7.	5	24
8.	5	24
9.	5	24
10.	5	25
11.	6	23
12.	6	24
13.	6	25

2.2 Adsorbent Characterization

The characterization of adsorbent was based on SNI 06-3730-1995, such as water, ash, and lost substance content, including fixed carbon, and iodine adsorption capacity. These parameters were measured to determine the quality and effectiveness of adsorbent. Subsequently, the optimum conditions were determined using RSM with Central Composite Design (CCD) model in the Design Expert version 13 software [20].

2.2.1 Quantification of water content

An adsorbent weighing 0.5 g was inserted into the cup, and it was baked for 3 hours at 115 ^oC. Subsequently, the cup was inserted in the desiccator for 10 minutes, weighed using an analytical balance, and counted with Equation 1 to

determine the final weight. Where, a, b, and c (gram) indicated empty cup, empty cup and initial sample, as well as weight cup and sample after the oven, respectively.

$$Water\ content\ (\%) = \frac{(b-c)}{(b-a)} \times 100\% \quad \textbf{.....(1)}$$

2.2.2 Quantification of ash content

Weighed at 1 g, the adsorbent was placed in an empty cup and heated to 900 ^oC for two hours in a furnace. The cup was inserted in the desiccator for 10 minutes, weighed using an analytical balance, and counted with Equation 2 to determine the final weight. Where, a, b, and c (gram) indicated empty cup, empty cup and initial sample, as well as weight cup and sample after the furnace, respectively.

$$Ash\ content\ (\%) = \frac{(c-a)}{(b-a)} \times 100\% \quad \textbf{.....(2)}$$

2.2.3 Quantification of lost substance content

Approximately 1 g of adsorbent was weighed, put into an empty cup, placed into a furnace at a temperature of 950^oC for 15 minutes, and inserted into the desiccator for 10 minutes. Subsequently, the cup was weighed using an analytical balance and counted with Equation 3 to determine the final weight. Where, a and b (g) indicated empty cup and initial sample as well as weight cup and sample after the furnace, respectively.

$$Weight\ loss\ (\%) = \frac{(a-b)}{a} \times 100\% \quad \textbf{.....(3)}$$

2.4.4 Quantification of fixed carbon (FC)

FC was determined using Equation 4 following adsorbent removal of water, ash, and lost substance content. Where A, B, and C presented water content, ash content, and weight loss, respectively.

$$FC\ (\%) = 100\% - \big(A + B + (A - C)\big) \quad \textbf{.....(4)}$$

2.4.5 Quantification of iodine adsorption

A 0.5 g adsorbent was added to 5 mL of 0.1 N Iodine solution and infused for 15 minutes. The solution was added to 25 mL of aquadest, and 5 mL filtrate was irrigated with a 0.1 N sodium thiosulfate solution until the yellow disappeared. This was followed by the addition of 1% amino solution and titration again until the blue color became uncolored. Subsequently, the power of iodine adsorption was calculated using Equation 5. Where, W, V_1, V_2, N_1, and N_2 represent of mass of adsorbent, filtrate volume, titrate volume, concentration of $Na_2S_2O_3$, and Iodium, respectively.

$$Iod\ (mg/g) = \frac{(V_1 - V_2) \times N_1 \times N_2}{W} \times 126.93 \quad \textbf{.(5)}$$

3. Results and Discussion

Table 2 shows the characterization results of adsorbent generated, including the quantities of water, ash, substance loss, fixed carbon, and iodine resin capacity.

3.1 Water content of adsorbent

Table 2 shows the highest water content of 1.0037%, with a combination of activator concentrations and activation times of 4% and 25 hours, respectively. The lowest water content of 1.000% was found at activator concentration of 4% and an activation time of 23 hours. Another study stated that water content obtained

from palm kernel shells with the H_3PO_4 activator was 5.30% [21]. In this context, palm kernel shell adsorbent performed better compared to cocoa shell. An excessive amount of water in the adsorbent would disrupt the adsorption process, as the molecule or particle dissolved in water and became ineffective at interacting with the surface [22]. This disruption can reduce the efficiency of the absorption process and desired final result.

The airborne residue yield that was obtained complied with SNI 06-3730-1995, at approximately 15%. This suggested that the resulting adsorbent had a longer shelf life. Furthermore, the similarity of the free variables employed in the experiment may have contributed to the low water content, which averaged 1%.

3.2 Ash content of adsorbent

In the treatment with a 4% activator concentration over 23 hours of activation, the maximum adsorbent ash level was found to be 8.32%. Furthermore, there was a low ash level of 3.22% at a 6% activator concentration for 25 hours. The resulting palm kernel shell adsorbent had an ash content of less than 10%, based on SNI 06-3730-1995.

A previous study conducted by Syamsudin reported that an increase in ash levels could occur due to the formation of mineral salts during the carbonization process [23]. When the carbonization process was excessively long at a higher temperature, a significant increase would be anticipated in the ash level on the adsorbent.

Table 2. Results of characterizing adsorbent from palm kernel shell with H_3PO_4 activator

Run-n	Water content (%)	Ash content (%)	Substance loss (%)	Fixed carbon (%)	Iodine Adsorption ($mg.g^{-1}$)
1.	1.0002	8.32	20.82	70.86	603.10
2.	1.0005	7.93	20.56	71.50	610.56
3.	1.0037	6.33	19.88	73.79	595.89
4.	1.0002	5.72	18.84	75.44	620.34
5.	1.0006	5.75	18.51	75.74	636.92
6.	1.0007	5.77	18.53	75.70	626.66
7.	1.0005	5.79	18.54	75.67	625.53
8.	1.0006	5.78	18.44	75.78	646.91
9.	1.0008	5.73	18.52	75.75	640.19
10.	1.0032	5.36	18.45	76.19	640.09
11.	1.0004	4.16	17.32	78.52	707.14
12.	1.0006	3.91	17.10	78.99	709.25
13.	1.0007	3.22	17.04	79.74	703.62
SNI 06-3730-1995	Max. 15	Max. 10	Max. 25	Min. 65	Min. 750

3.3 Lost substances in palm kernel shell

The most lost substance test results were obtained at a 23-hour activation time of 20.82% and a 4% activator concentration. With an activator concentration of 6% and an activation time of 25 hours, 17.04% of adsorbent had the lowest amount of lost substances. This showed that the adsorbent level of lost substance at 950^{o}C heating was less than 25%, in compliance with SNI 06-3730-1995, allowing its use as an adsorbing agent. In this study, pyrolysis was used to carbonize palm kernel shell, at a

temperature of 400°C for 4 hours [24,25]. This investigation also showed that the amount of lost substance increased when carbonization was carried out at low temperatures for a short period of time.

3.4 Fixed carbon

The highest fixed carbon result of 78.99% was obtained at 6% activator concentration and a 24-hour activation time. Meanwhile, the lowest fixed carbon result at 4% concentration was obtained at 23 hours of activation, with 70.86%. Activator concentration and activation time had an impact on the value of the fixed carbon rate generated. In adsorption process, high fixed carbon levels are preferable to low, as adsorbents perform better when the pore surfaces are larger [24]. Fixed carbon from adsorbent produced complied with SNI 06-3730-1995, which was at least 65%. This compliance enables fixed carbon to be used as an adsorbent to remove water-soluble substances such as heavy metals and organic materials. Additionally, high capacity of adsorbent facilitated the effective absorption of substances.

3.4 Iodine adsorption power

The highest-performing iodine cranes of 709.25 mg/g were generated at a 24-hour activation time and activator concentration of 6%. The lowest iodine potency was found at a 4% activator concentration and a 23 hours activation time of 603.10 mg/g. However, the SNI 06-3730-1995 requirement for technical activated carbon of 750 mg/g was not met by adsorbent made using iodine cranes. This phenomenon occurred due to the prolonged exposure of iodine solution to sunlight during the titration procedure, causing variation in concentration. Moreover, the ability of the adsorbent to adsorb iodine indicates deactivation, due to an increase in adsorption power [26].

3.5 Optimization of adsorbent production

In this study, Design Expert Version 13 software was used in the optimization to determine the ideal threshold for activator consistency and activation time during the adhesive manufacturing process. The ideal activator coefficient and activation time of 4.785% and 24.679 minutes, respectively, were used to determine the desirability coefficient of 1, as shown in Figure 2.

Figure 2 shows optimization results using desirability values, considering the activator concentration and activation time simultaneously. The selection of desirability values in the optimization process is essential, as a lower value (<1) results in reduced accuracy.

4. Conclusion

In conclusion, this study showed that the ideal conditions for producing adsorbent were 4.785% concentration and 24.679 hours activation time in H_3PO_4 activator. The amount of iodine charcoal produced increased with the concentration of activator used. The Water content of adsorbent obtained under ideal conditions was 1.001%, followed by ash, lost substance, and fixed carbon content of 5.767%, 18.932%, and 75.301%, respectively, according to SNI 06-3730-1995. However, the iodine resin capacity that was produced did not meet the 619.866 mg/g SNI standard.

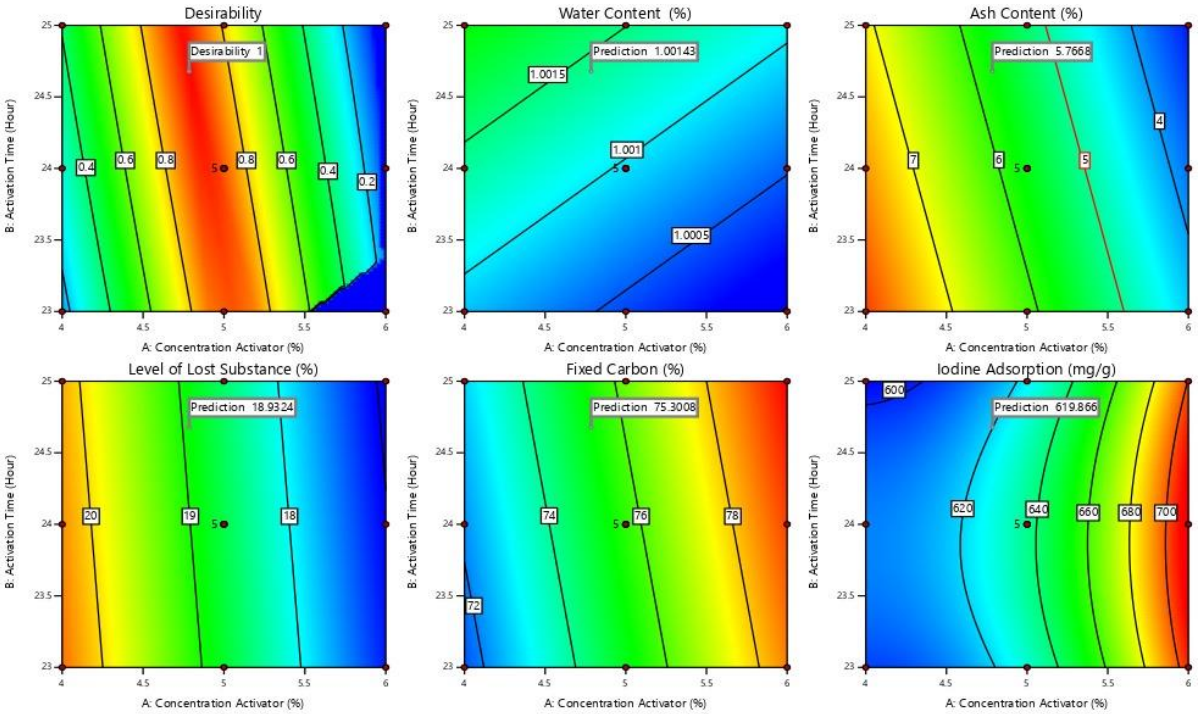

Figure 2. Design Expert for optimizing palm kernel shell adsorbent

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