**Adsorption Study of Carbon-Spent Bleaching Earth for Methylene Blue as a Preliminary Assessment for Sensor**

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**Abstract****.** The performance of electrochemical sensors is strongly influenced by the adsorption of target molecules or ions at the sensing surface. In this study, carbonized spent bleaching earth (C-SBE) was explored as a low-cost and sustainable material for wastewater sensing applications, with methylene blue (MB) employed as a probe molecule. C-SBE was prepared via pyrolysis of spent bleaching earth (SBE) and demonstrated a high adsorption efficiency of 92.99% at pH 8 within 40 minutes. This performance is attributed to the presence of active functional groups and the enhanced surface area generated by carbon deposition during pyrolysis. The results highlight the potential of waste-derived C-SBE as a novel adsorptive material for environmental sensing, offering both functional advantages and added value to an industrial by-product.

**Keywords**: spent bleaching earth, sensor, adsorption, methylene blue

1. **INTRODUCTION**

The processing of crude palm oil (CPO) into cooking oil requires several refining steps, one of which is bleaching. This process aims to lighten the color of CPO from brown to a clear yellowish hue while removing residual impurities, gums, and free fatty acid (FFA) residues. Typically, bleaching is carried out using activated clay or bleaching earth. In addition to produce oil with relatively low impurity content, the bleaching step also generates spent bleaching earth (SBE), a by-product that retains a certain amount of oil on its surface [1–3]. According to Government Regulation No. 22 of 2021, SBE with an oil content of less than 3% is classified as non-hazardous and non-toxic waste. Consequently, SBE has been explored for various applications, including as a raw material for briquette production and as an adsorbent for wastewater treatment [4–7].

SBE can also be considered as a potential precursor for sensor materials due to its porous surface and the presence of conductive silica-based functional groups. During sensing processes, both Faradaic and non-Faradaic mechanisms occur. The Faradaic process involves redox (reduction-oxidation) reactions of target molecules or ions at the electrode surface, while the non-Faradaic process refers to their adsorption on electrode materials [8]. However, untreated SBE has limited adsorption capacity. To enhance its performance, activation is often required, either through chemical routes (e.g., acid treatment) or physical methods such as thermal processing [9]. Thermal activation, in particular, is practical because residual oil and organic impurities decompose into carbon, thereby increasing porosity and surface area [4]. Such improvements in surface properties may enhance the adsorption of target molecules and provide insight into the suitability of SBE-derived materials for sensor applications.

Recent advances in carbon-based materials have significantly improved electrochemical sensor design and performance. Graphene and its derivatives (e.g., reduced or chemically modified graphene) as well as carbon nanotubes (CNTs) are widely employed as electrode materials or modifiers owing to their high conductivity, large surface area, and strong interactions with analytes. Activated carbon and biochar derived from local biomass also show great promise, particularly after chemical or thermal activation that enhances porosity and surface chemistry. Despite this progress, research on activated carbon electrodes derived specifically from SBE remains limited, especially in terms of elucidating the relationship between structural/surface properties (surface area, functional groups, porosity) and sensor performance [10–13]. This gap highlights the potential of converting SBE into carbonized material (C-SBE) as a cost-effective candidate for electrochemical sensors.

The adsorption capacity of C-SBE further supports its application as a pre-concentration or sensing layer in electrochemical devices. In particular, its ability to adsorb methylene blue (MB) serves as a useful indicator of interaction with cationic probe molecules and, by extension, with other pollutants such as heavy metal ions and organic contaminants. MB is widely employed as a model probe because its cationic nature makes it readily analyzable by spectroscopic methods, thereby providing a direct measure of adsorption performance [14,15]. If such adsorption behavior can be effectively translated into enhanced electrochemical signals, C-SBE offers strong potential as a low-cost yet competitive alternative for sensor materials.

1. **METHODOLOGY**

**2.1 Materials**

The materials used in this research were SBE from PT. Jhonlin Agro Raya Tbk. Tanah Bumbu, South Kalimantan, methylene blue (Merck), HCl (37%, Merck), NaOH pellet (99.9%, Merck), Whatman filter paper no. 1, commercial deionized water (amidis brand) and alminium foil. The equipment used in this research was a set of glassware, a pyrolysis reactor, 180 mesh electric sieve shaker, Fujitsu FSR-A Analytical Balance, Memmert UI M 400 Oven, UV-Vis Spectrophotometer (Genesys 10uv), Scanning Electron Microscope equipped with Energy Dispersion X-ray (SEM-EDX) Seiss EVO-MA 10 and a Thermogravimetric Analysis (TGA) instrument..

**2.2 Preparation of C-SBE**

SBE samples were pyrolyzed at 700ºC for 2 hours using a pyrolysis reactor. The result of this pyrolysis is carbon-SBE (C-SBE). The obtained C-SBE was sieved using a 180-mesh electric sieve shaker.

Thermogravimetric (TGA) analysis was performed on C-SBE to indicate the presence of carbon on the surface of SBE. SEM-EDX analysis was performed to observe the particle morphology and elemental distribution. The surface area was measured using the MB adsorption method [16]

**2.3 Adsorption Experiments**

In the batch adsorption experiment, the adsorption capacity of MB on C-SBE was investigated by examining the effect of various experimental variables, including pH (2–12) and contact time (10-100 minutes). Using a pH meter, the initial pH of the solution was adjusted using 0.1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution. 0.1 g C-SBE was added to a 250 mL conical flask containing 100 mL of 100 ppm MB solution. The mixture was then stirred with a magnetic stirrer at a speed of 140 rpm. Subsequently, the solution was filtered using filter paper. The filtrate was used for the determination MB concentration. The absorbance of dyes remaining in the solutions was determined using a UV–visible spectrophotometer at 664 nm. All experiments were conducted in triplicate to ensure reproducibility.

The isothermal adsorption was determined based on the fitting of the adsorption data to Langmuir and Freundlich equation (Equation 1 and equation 2, respectively).

………….. (equation 1)

………….. (equation 2)

where *ce* (mg/L) is the equilibrium concentration of MB, *qe* (mg/g) is the MB amount adsorbed at equilibrium, *qm* (mg/g) and *KL* (L/mg) are Langmuir constants related to the adsorption capacity and adsorption energy, *Kf* and 1/*n* are Freundlich constants related to the adsorption capacity and adsorption energy. The adsorption data used for the fitting was obtained from the experiment using C-SBE dosage of 0.1 g, MB dosage 100 – 300 ppm, pH=8, and contact time of 40 minutes.

1. **RESULT AND DISCUSSION**

**3.1 Physical properties and elemental distribution of C-SBE**

*3.1.1 SEM-EDX Analysis*

SEM observation was performed to observe the surface morphology of the C-SBE. Figure 1 shows the SEM image while Figure 2 shows the elemental mapping of the C-SBE. SEM image shows irregular C-SBE particles with rough surface, which can be attributed to the formation of carbon induced by the pyrolysis process of the SBE. During 700 oC pyrolysis process, the adsorbed oil and possible organic matter on the surface of SBE were decomposed, leaving the carbon on the surface of SBE. The remaining carbon particles make the surface of SBE to be rough.

A close-up of a rock

Description automatically generated

Figure 1. SEM image of C-SBE

To confirm the dispersion of carbon on the surface of SBE, the elemental mapping using EDX was performed. As presented in Figure 2a-c, Si and Al elements, can be observed homogeneously in all particles. Si and Al are two major elements in montmorillonite, which is the main phase of SBE [3] In addition to Si and Al, the C element (Figure d) is also homogeneously observed on the surface of C-SBE particles. The homogeneous mapping of the C element indicates that the carbon is also dispersed homogeneously on the surface of SBE.

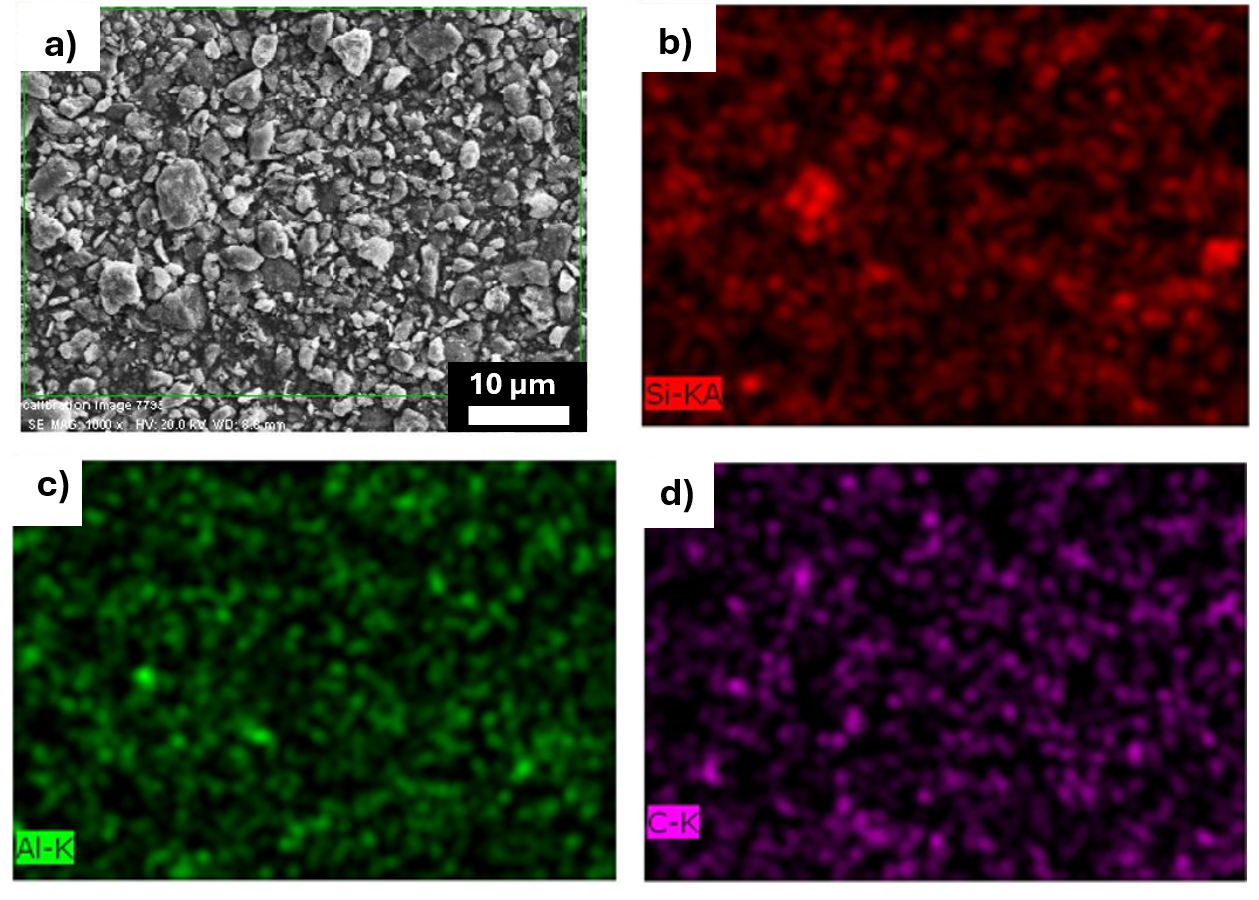


Figure 2. a) SEM image with the corresponding elemental mapping of b) Si, c), Al, and d) C elements.

3.1.2 *TGA Analysis*

TGA analysis was performed to investigate the changes in the mass of a material over time. The changes in weight of C-SBE samples can be seen in Figure 3. Based on Figure 3, at a temperature ˂ 200°C (area I) a mass loss of C-SBE is around 11.34%. The mass loss below 200 oC can be associated with the evaporation of physically adsorbed water molecules. The amount of adsorbed water (11.34% relative to the total materials) is relatively high, indicating that the C-SBE can adsorb more water. In this regard, after the pyrolysis process, the surface area of C-SBE can be more open. As a consequence, the C-SBE has the ability to bind more water on the surface. In the temperature range of 200-700°C (area II), a weight loss of around 22.39% is observed. The mass loss occurs steadily over the temperature increase up to 700 oC, which can be attributed to the decomposition of the carbon materials from the SBE surface. We note that the TGA analysis was performed under air atmosphere, and therefore, the carbon materials can be decomposed into CO2. At a temperature of ˃ 700°C, the mass tends to be constant, indicating that the decomposition process of carbon compounds has ended, leaving the SBE. The mass loss in TGA indicates the decomposition of C on the SBE, which verifies the presence of carbonaceous materials on the surface of the SBE.

A graph of a temperature

Description automatically generated

Figure 3. TGA curve of C-SBE

*3.1.3. Surface Area of C-SBE*

One of the important factors in the adsorption process is the surface area. The larger the surface area of ​​the adsorbent, the greater its ability to adsorb the adsorbates. The surface area of C-SBE was measured based on the adsorption of MB method. For reference, the surface area of SBE was also evaluated. Table 1 depicts the surface area of SBE and C-SBE. Table 1 shows that C-SBE has a higher surface area than SBE. During the pyrolysis process at 700 oC, the adsorbed oil and organic matter are oxidized partially. Besides forming carbon, it also produces gas-phase molecules, which are released from the body of SBE creating the pores. Due to the pore formation, the surface area of C-SBE becomes higher compared to the bare SBE.

Table 1. The surface area of SBE and C-SBE

|  |  |  |
| --- | --- | --- |
| **Sample** | **Maximum adsorption of MB (mg/g)** | **Surface area**  **(m2/g)** |
| SBE | 86.35 | 319.52 |
| C-SBE | 92.93 | 343.85 |

**3.2 Adsorption study of C-SBE over MB**

*3.2.1 The Effect of pH initial and Contact Time on MB Adsorption*

pH is an important parameter for adsorption. Figure 4 shows the effect of initial pH solution on the adsorption ability (% adsorption) of MB. MB adsorption increases at increasing pH but leveling off at pH 8, above which, no increase in adsorption at further increase of pH.

Figure 4. The influence of pH Methylene Blue

This phenomenon can be explained based on the interaction between the MB ions and the charge of the C-SBE surface. MB is a cationic dye with a positive charge. When MB ions approach the C-SBE, there will be an electrostatic interaction between the MB ions with the surface of C-SBE. Previous reports mentioned that the carbon materials made by the pyrolysis process have surface functional groups such us C=O (carbonyl groups) or COOH (carboxylic groups), which tend to interact with the positively charged molecules of ions by electrostatic attraction [15]. Because of the high amount of H+ ions in the solution, which disrupts the bonding between MB ions and C-SBE, the %adsorption tends to decrease at low pH. It also suggests that there is a competitive adsorption between H+ and the MB ions with C-SBE. Conversely, at the high pH, OH- in the solution does not influence the interaction between the MB ions and the surface of C-SBE, resulting in an increase in the adsorption. However, upon the higher pH (pH > 8), the adsorbent is saturated and can no longer adsorb MB.

The effect of the contact time of MB adsorption is presented in Figure 5. Figure 5 shows the %adsorption of MB reaching 94-96% at various contact times from 40-100 minutes. The longer the contact time, the more adsorbate is adsorbed. More adsorption occurs because there are more opportunities for adsorbent particles to contact the adsorbate (MB), therefore, more adsorbate is adsorbed, and %adsorption increases. After the adsorption reaches equilibrium at the optimum contact time, the prolonged contact time does not have a significant effect on the absorption of MB.

Figure 5. The influence of contact time

*3.2.2 Adsorption Isotherm*

An adsorption isotherm study is conducted on two isotherms, Langmuir and the Freundlich. The fitting of the isotherm equation is compared by considering the correlation coefficients (R2). The adsorption isotherm shows how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes. This fitting was performed based on the adsorption data obtained with the C-SBE dosage of 0.1 g, MB dosage of 100 – 300 ppm, pH=8, and contact time of 40 minutes. The adsorption data obtained are subjected to the Langmuir equation model (Ce.qe-1-Ce plot) and the Freundlich equation model (log qe-log Ce plot) for linear fitting, the fitting results are shown in Figure 6. The Freundlich isotherm adsorption model has a correlation coefficient r2 of 0.909, which is higher than the Langmuir isotherm adsorption model (R2 = 0.867). This result implies that the adsorption of MB on the surface C-SBE follows the Freundlich model, in which the MB molecules are adsorbed physically on the surface. This suggests that sorption of MB occurs at multilayer on the C-SBE with non-uniform distribution of sorption heat and affinities over the heterogeneous surface[17]. While Table 2 summarizes the reported maximum adsorption capacities (qm) of MB onto waste-derived carbonized adsorbents.

A graph of a function

Description automatically generated with medium confidence

Figure 6. Fitting of a) Langmuir and b) Freundlich isothermal adsorption

Table 2. Maximum adsorption capacities (qm) of MB onto waste-derived carbonized adsorbents

|  |  |  |
| --- | --- | --- |
| **Material** | **qm** | **References** |
| SBE | 82.64 | [18] |
| SBE | 94.52 | [19] |
| SBE | 53.91 | [14] |
| Cashew nut shell | 22.88 | [20] |
| C-SBE | 94.89 | This work |

Table 2 shows t that the result of this work presents satisfactory adsorption ability among other carbonized adsorbents. The enhanced performance is attributed to the active functional groups in C-SBE and surface area enlargement induced by the presence of carbon in the surface of SBE. These findings highlight the novelty of utilizing waste-derived C-SBE as a promising adsorptive material for environmental sensing.

**CONCLUSION**

In summary, it can be concluded that the pyrolysis process of SBE successfully produced C-SBE, which has the potential to be applied as a low-cost and sustainable electrochemical sensing material. C-SBE showed a high adsorption capacity toward MB reaching up to 92.99% at pH 8 within 40 minutes, thereby demonstrating competitive performance compared to other carbonized materials. These findings highlight the novelty of utilizing waste-derived C-SBE as a promising adsorptive material for environmental sensing applications. Moreover, this study contributes to the advancement of waste-based electrochemical sensing materials while simultaneously supporting more sustainable industrial waste management.

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