Optimization of regeneration process of spent bleaching earth

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Abstract. The bleaching process is critical to improving the colour, flavour, taste, and stability of the final oil products of palm oil. The bleaching process uses bleaching earth (BE), which after several cycles, becomes a waste called Spent Bleaching Earth (SBE). Impurities cover the surface of SBE from the purification process. Regeneration by utilizing acid can increase the absorption capacity of SBE. The purpose of this research is to obtain the optimal combination of nitric acid concentration and heating temperature in the regeneration process of SBE. Response Surface Method (RSM) with Central Composite Design (CCD) was employed, using two factors of concentration of nitric acid and the heating temperature. The responses analysed in this research include colour, absorption efficiency, and yield. The obtained optimum condition in the treatment was found in the concentration of nitric acid (0.75 M) and a heating temperature of 430.8°C. The results of this research indicated colour absorption efficiency of 95.7557%, the yield of 52.4846%. The verified optimal solution obtained was 94.68% of absorption efficiency and 51.43% of yield. The Regenerated Spent Bleaching Earth (RSBE) optimum conditions compared to BE. The colour absorption efficiency utilizing BE was 96.77%, 2% higher than that of RSBE at 94.68%. The value of RSBE colour absorption efficiency in optimum conditions similar to that of the BE.

1. Introduction
Indonesia regarded as one of the largest producers of palm oil worldwide. The refining process of Crude Palm Oil (CPO) consists of several stages, including degumming, neutralizing (removal of free fatty acids), bleaching, and deodorizing [1]. Among these stages, the bleaching process becomes essential to improve the colour, aroma, taste, and stability of the final product (palm oil). The bleaching process on CPO utilizes bleaching earths [2].

Bleaching earth is a term used in the world of commerce for a type of clay that has a montmorillonite structure, such as bentonite. The mineral content in bentonite dominated by 85% of the chemical formula [(OH) 4Si₈Al₄ • nH₂O] consisting of aluminium silicate crystals (SiO₂, Al₂O₃), water-bound, alkali metals (calcium oxide (CaO) and magnesium oxide (MgO) and other transition metals such as iron oxide (Fe₂O₃) [4]. Bentonite can swell due to the interlayer, which accommodates the hydrated ions or molecules of a specific size. Bentonite is used as adsorbent or catalyst due to its interchangeable cations and a large surface area [4].

The waste of the CPO bleaching process is Spent Bleaching Earth (SBE). Impurities cover the surface of the SBE, including phosphatides, gums, metals, fatty acids, and dyes [5]. SBE is
toxic and hazardous material waste (B3 waste) because of its high oil content causing pollution and flammability. The current handling of SBE is landfill dumping or stacked on vacant land, which potentially leads to fire and environmental pollution at a large scale.

SBE can be regenerated to restore the absorption ability close to the original bleaching earth by using ion exchange. The force of physical adsorption is the Van der Waals force, a weak hydrogen bond that can easily broke down. The materials adsorbed are reversible, so they are relatively easy to be released from the surface of the adsorbent [6].

SBE regeneration for biodiesel and CPO purification with the addition of 5% of HNO₃ by comparison (1:2) was the most effective to purify CPO with bleaching efficiency of 77.92% [7]. Parts of bentonites such as the surface area and acidic properties can be optimized by controlling activation conditions (such as type and amount of acid, temperature, and time of activation) [8].

2. Materials and Method

The SBE was purchased from Sinar Mas Resources and Technology Tbk., and the nitric acid (HNO₃), aquadest, and clothing dyes (Wantex) were obtained from the local chemical store.

This study employed the Response Surface Method with a Central Composite Design using two factors: 1) Nitric acid concentration (0.4 M; 0.7 M; and 1 M) and 2) Heating temperature (100°C, 300°C, and 500°C). A total of 13 experiments were conducted, 5 of which were replications at the midpoint.

Characterisation of the SBE was carried out, including water content [9], ash content [10], and pH [11]. The regeneration processes were as follows: A 30 g of SBE samples was weighted and mashed by using mortar. Then the samples were sieved at 100 mesh. Next, nitric acid (HNO₃) was added with a ratio of SBE and nitric acid (w/v) 1:10. SBE mixture and nitric acid was stirred using a magnetic stirrer for 1 hour at 70°C. The SBE was then separated from the oil using filter paper. The solid residue was washed several times by using distilled water and dried at 105°C for 24 hours. Regenerated SBE was then heated for 2 hours at temperature variations according to the experimental design [12].

Absorption efficiency testing carried out to determine the absorbance ability of RSBE. RSBE absorption efficiency was tested by using a Wantex solution. Following are the steps in testing the efficiency of RSBE absorption [12]:
1. A 0.2 g of RSBE sample was weighed then put into 20 mL of 500 ppm dye solution.
2. The solution was then separated by gravity for 1 hour at 70°C, and then the solution was separated from the sample.
3. The filtrate from the absorption was analysed by using a UV-Vis spectrophotometer at a wavelength of 560 nm.
4. The absorption efficiency was calculated by using Equation 1 [11]:

\[
\text{Ep} = \frac{(A_0 - A)}{A_0} \times 100\%
\]

Where,
\(\text{Ep}\) = absorption efficiency
\(A_0\) = initial concentration (ppm)
\(A\) = residual concentration (ppm)

The yield of the RSBE sample was calculated by using Equation 2 [13].

\[
\%R = \frac{\text{weight (pre regeneration)}}{\text{weight (post regeneration)}} \times 100\%
\]

The characteristics of RSBE and BE were then compared, including the efficiency of colour absorption, water content, ash content and pH.
3. Results and Discussion

3.1. Characteristics of SBE

Table 1 shows that the SBE’s water content was 3.63%. The water content of SBE was low because SBE contains oil absorbed during the bleaching process, thereby reducing the ability of SBE to absorb water molecules [7]. The ash content indicates the amount of non-organic material contained in the ingredients. The ash content in the SBE was 64%. That is due to the presence of phosphate mineral residues carried away from the CPO degumming process [14]. The pH value of the SBE was 4.6, which possibly due to the addition of acid during the degumming process.

| Parameter          | Result |
|--------------------|--------|
| Water content (%)  | 3.63   |
| Ash content (%)    | 64     |
| pH                 | 4.6    |

3.2. Regeneration of Spent Bleaching Earth (RSBE)

SBE regeneration carried out to restore SBE absorption ability. Physical analysis of RSBE includes the colour of RSBE as seen in Figure 1. Visually, RSBE colours are brown, black, and grey-ish, depending on the heating temperature of the regeneration. Regenerated at 100°C, RSBE colour was brown, because the heat can only remove the water content from RSBE. At 300°C, the RSBE colour turned black, and when heated at 500°C, the RSBE colour becomes grey-ish. The black colour found in RSBE caused by organic compounds that are absorbed in the SBE structure turned into char. After the acid extraction and heating, RSBE colour tends to be grey-ish, indicating that the organic compounds found in the SBE structure were released, and ash was produced [15]. In the acid activation, a cation exchange of mineral salts (Ca$^{2+}$ and Mg$^{2+}$) in the interlayer of bleaching earth with H$^+$ ions from acid, followed by the dissolution of Al$^{3+}$ ions and other metal ions such as Fe$^{3+}$ from the pale soil lattice layer. As a result of the dissolution of Al$^{3+}$ ions, the pale soil became negatively charged, thereby increasing absorption capacity and surface area.

![Figure 1. The colour of RSBE a) Heated at 100°C; b) Heated at 300°C; c) Heated at 500°C](image)

3.3. Colour absorption efficiency

The lowest colour absorption efficiency was on the treatment of average nitric acid concentration and low heating value with a value of 12.32%. The highest efficiency of colour absorption was in the treatment of 0.7 M nitric acid concentration and heating temperature of 300°C with an amount of 96.77%. The results of this study indicated that the decrease in the efficiency of colour absorption when nitric acid concentrations are less than 0.7 M and more than 1 M, this is because SBE contains oil and impurities that cover the pores; therefore, an extraction process is required to remove the oil and the dirt. A low nitric acid concentration is not effective in the extraction process as it cannot extract oil and impurities that cover the pores of the SBE. Meanwhile, the high level of nitric acid damaged the surface structure. The higher
the concentration of acid, the more $\text{H}^+$ ions exchanged to the lattice bleaching earth layer; thus, more $\text{Al}^{3+}$ ions dissolve, resulting in decreasing both the surface area and absorption capacity [15].

The colour absorption efficiency increased with increasing temperature. At temperatures below 200°C, oil polymer attached to the SBE. The polymerization reaction is expected to form hydrocarbon compounds that have a complex chemical structure with a high molecular weight. At temperature above 200°C, a preheating stage occurred where the hydrocarbon compounds change into char. Char, with the help of acid and high temperature, became an active surface. This process ends when it approaches 700°C [4].

The polynomial equation of the Quadratic model of response $Y$ (colour absorption efficiency) was influenced by factors such as nitric acid concentration ($X_1$) and heating temperature ($X_2$) as follows:

$$Y = -54.81296 + 148.69656 X_1 + 0.52914 X_2 + 0.016667 X_1 X_2 - 106.35833 X_1^2 - 7.34556E-004 X_2^2$$

Based on this equation, it is apparent that the constant value or its determination is -54.81296. Factor $X_1$ (nitric acid concentration) is worth of 148.6965, which means that every increase in 1 point will have an effect of 148.6965. Factor $X_2$ (heating temperature) is deserving of 0.52914, which means that every increase in 1 point will have an impact of 0.52914.

3.4. Yield

The lowest yield was at the treatment of 0.7 M nitric acid concentration at high heating temperature. This result is due to higher acid concentration, and more oil is extracted. The higher the heating temperature, the more components such as water vapour and organic compounds will be evaporated, lowering the yield. Loss of adsorbed water or hydration ($\text{H}_2\text{O}$) occurs at temperatures of 100-200°C [16]. Loss of water molecules occupied interlamellar or intercalation ($\text{H}_2\text{O}^+$) spaces was at temperatures of 475-525°C. At temperatures of 600-700°C, dehydroxylation montmorillonite minerals occurs, consisting of the release of OH- groups in the framework of the structure of montmorillonite minerals, including those from H-OH. At temperatures of 875-950°C, there is a change in the structure of montmorillonite minerals, where these structural changes can come from the melting of old crystals into new crystals or switches in amorphous substances to crystals.

The polynomial equation of the Linear model from the $Y$ response (yield), which is influenced by nitric acid concentration ($X_1$) and heating temperature ($X_2$) is as follows:

$$Y = 82.57520 - 2.66421 X_1 - 0.065214 X_2$$

Based on this equation, it is apparent that the constant value or its determination is 82.57520. Factor such as $X_1$ (nitric acid concentration) has a value of -2.66421, which means that a 1-point decrease will have an effect of 2.66421. Factor $X_2$ (heating temperature), which shows -0.065214 indicates that every decline in 1 point will have an impact of 0.065214.

3.5 Optimum solution and verification

The optimum solution selected was at the concentration of 0.75 M nitric acid and heating temperature of 430.82°C, resulting in a prediction of the response in colour absorption efficiency of 95.7557% and yield of 52.4846%. The choice of an optimal solution based on the desirability value was equal to 0.923. The value of desirability ranges from 0-1; the closer it is to number 1, the ability of the program to produce the desired product [17].

The results of the optimum conditions are verified using the response variable values predicted by RSM. The optimum results verification is performed to prove that the optimum variable solution provided by the Design Expert presents the results of the response by the predetermined response.
Table 2 shows that the verification response of colour absorption and yield was 94.68% and 51.43%. There are 1.128%, and 2.016% difference to that of the predicted value, respectively. The comparison indicated that the difference in predictions with the verification results was less than 5%; thus, the verification value was acceptable.

**Table 2. Comparison of optimization results and verification results**

| Variable          | Prediction* | Verification** | Difference |
|-------------------|-------------|----------------|------------|
| Nitric Acid Conc. (M) | 0.75        | 0.75           |            |
| Heating temp. (°C)  | 430.77      | 430.77         |            |
| Colour Absorbent Efficiency (%) | 95.7601     | 94.68          | 1.128%     |
| Yield (%)          | 52.4881     | 51.43          | 2.016%     |

Note: * Design Expert calculation results; ** data from actual calculations

3.6. *Comparison of RSBE with Bleaching Earth*

The characteristics of RSBE were compared to the original Bleaching Earth (BE). The analysis carried out included absorption efficiency, water content, and pH. A comparison of the RSBE and BE as the control is illustrated in Table 3. The colour absorption efficiency of BE was 96.77%, higher than that of RSBE at 94.68%. The colour absorption efficiency using RSBE can compete with BE. The water content of RSBE was 1.01%, while that of BE was 13%. BE has a water content that is greater than RSBE probably because BE still had not undergone a heating process and had a long storage period. The duration of BE storage influences the percentage of water content due to the BE characteristic that quickly absorbs the surrounding water molecules. The pH of RSBE was 3.4, more acidic due to acid activation compared to that of 6.7 of BE.

**Table 3. Comparison of best treatment and controlled treatment**

| Characterization | (RSBE) | (BE) | SNI 13-6336-2000 |
|------------------|--------|------|------------------|
| Colour Absorption Efficiency (%) | 94.68 | 96.77 | Min. 40         |
| Water content (%) | 1.01  | 13   | Max. 15          |
| pH               | 3.4   | 6.7  | BE: 6.5 – 8.5   |
|                  |       |      | RSBE: 2 – 4     |

4. **Conclusions**

The optimum condition predicted by the Design Expert program is at the concentration of 0.75 M nitric acid and heating temperature of 430.82°C, resulting in a prediction of the response of colour absorption efficiency of 95.7% and yield of 52.5%. The optimum condition was then verified, and the results of the response to absorption and yield efficiency were close to the predicted at 94.68% and 51.43%, respectively. RSBE characteristics were comparable to that of BE.

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