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Characteristics of Pumice from Cicurug and Its Application as a Bleacher for Crude Palm Oil

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Abstract

Pumice is relatively abundant in Indonesia, especially in Cicurug District, Sukabumi. Pumice has unique characteristics, so it has the potential to be an alternative bleaching agent or a bleacher for crude palm oil. Bleaching is one of the stages in processing crude palm oil into palm cooking oil. In the cooking oil industry, the bleaching of crude palm oil generally uses bentonite as a bleacher. This research aims to determine the characteristics of pumice and the optimum conditions for the bleaching process of crude palm oil with pumice as a bleacher. The research method consists of pumice activation, activated pumice characterization, degumming of crude palm oil, bleaching of crude palm oil, and analysis of processed palm oil. The results show that the metal oxide composition in activated pumice is dominated by silica (62.99%) and alumina (14.79%) and has a non-uniform pore size distribution. Optimum bleaching conditions are achieved when using 30% pumice and a bleaching temperature of 105 °C for 30 minutes. Under optimal bleaching conditions, pumice can reduce the color brightness level of crude palm oil from 600 to 125 mg/L Pt, or a bleaching power of 79.2%.

Keywords: bleaching; crude palm oil; pumice.

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Introduction

Indonesia, according to the World Agricultural Production website, is, as of December 2022, the largest palm oil-producing country in the world with a production value of 45.5 million metric tons. Indonesia's palm oil production is above the production values of Malaysia, Thailand, and Colombia. From an economic perspective, palm oil exports have made a significant contribution to Indonesia's economic growth. In 2018, the value of Indonesian palm oil exports reached US$ 22,308 million and contributed 13.5% to the total value of national non-oil and gas exports (Adiarso *et al.*, 2019).

Crude palm oil from upstream processing of fresh palm fruit bunches still has poor physical and chemical properties as a food oil. The low quality of crude palm oil as food oil is caused by the presence of various types of impurities at levels above the permit threshold, such as gum and resin, pigments, free fatty acids, phospholipids and phosphatides, sediments, simple organic compounds that cause odor (aldehydes and ketones), and saturated fatty acids (Pahan, 2008). Therefore, further processing of crude palm oil is required through a refining process. The stages in the refining process of crude palm oil are degumming, bleaching, and deodorization. Bleaching, as one of the stages in the refining process of crude palm oil, aims to separate pigments and other unwanted components that negatively affect the taste, color, and aroma of palm oil. On an industrial scale, the bleaching process is generally carried out using the adsorption method using clay, carbon, and activated bleaching earth. However, the use of clay in bleaching crude palm oil has been postulated to be very costly, non-environmental friendly, non-renewable, and ineffective. Bleaching soils such as bentonite have adsorptive properties due to the presence of aluminum silicate (Usman *et al*., 2013). Studies on the bleaching of crude palm oil with adsorbents from local bleaching agents have been carried out by several researchers. Usman *et al*. (2013) have studied activated bentonite and kaolin clays from Afashio, Edo, Nigeria, as crude palm oil bleachers. Apart from that, activated charcoal (Haryono *et al*., 2012) and Lampung natural zeolite (Astuti *et al*., 2006) have also been used as bleaching agents for crude palm oil. Bleaching of crude palm oil has also been carried out with zeolite-Fe composites (Anis *et al*., 2022), activated groundnut hull (Ojewumi *et al*., 2021a), activated plantain peel ash (Raji *et al*., 2019), and activated snail shells and rice husk (Ojewumi *et al*., 2021b). Wood charcoal has also been used in refining waste cooking oil (Wahyuni *et al*., 2020), where a bleaching process can occur.

West Java Province is a large area and has geological potential; this includes a wealth of mining materials resulting from volcanic activity (Yuliadi *et al*., 2024), especially in the form of non-metallic minerals and rocks, which are very diverse. One type of non-metallic mineral and rock in West Java is pumice (Rosana *et al*., 2004). In West Java, pumice potential is found in Sukabumi District (Rosana *et al*., 2004) and is contained in tuff from Mount Tangkubanparahu, which spreads to Lembang, Dago, and North Bandung (Oktariadi *et al*., 2021). Pumice is an external igneous rock formed from volcanic activity. Indonesia is one of the countries with the most active volcanoes in the world, so pumice is relatively abundant. Pumice has several favorable physical and chemical properties, such as high silica and alumina content, neutral pH (7–7.3), high porosity (45–90%), and being non-toxic (Aldakshe *et al*., 2020; Meyyappan *et al*., 2019). Therefore, pumice has the potential to be used as an adsorbent. Pumice has been studied for its performance as an adsorbent for several contaminants in solution systems, such as the adsorption of lead (Hasanah *et al*., 2019) and phenol (Asgari & Rahmani, 2012). In adsorption, the adsorption rate is influenced by the type and characteristics of the adsorbent, the type and concentration of the adsorbate, and the adsorption conditions, such as temperature and adsorbent content (Radhi *et al*., 2019).

This research aims to determine the characteristics of pumice and the optimum conditions for the bleaching process of crude palm oil with pumice as a bleacher. The optimum conditions for the bleaching process of crude palm oil using activated pumice are based on the concentration of pumice as a bleaching agent, which reduces the color brightness of palm oil and bleaching power.

Method

The research was carried out using the following main laboratory equipment: a three-neck flask, a plate heater with a magnetic stirrer, a furnace, a centrifuge, a titration tool, a SEM-EDX (Scanning Electron Microscope-Elemental Diffraction X-ray) analysis instrument (Leo 1530 SEM, Georgia, USA), a color brightness analysis tool with a filter photometer (Nanocolor 25 Filter photometer, Macherey-Nagel GmbH & Co. KG, Germany), a UV-Vis spectrophotometer (Shimadzu 1800, Japan), Buchner filter, and oven. The main chemicals used in this research were crude palm oil obtained from PT Tunas Baru Lampung, pumice obtained from Cicurug District (Sukabumi Regency, West Java), 85% phosphoric acid solution (BrataChem, Bandung), 95% ethanol solution (Merck), 90% potassium hydroxide granular (Merck), 0.5 N hydrochloric acid solution (BrataChem, Bandung), and distilled water.

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The research stages include initial characterization of crude palm oil, preparation and activation of pumice, removal of gum (degumming) from crude palm oil, bleaching of crude palm oil, and characterization of the bleached oil. In the initial characterization of crude palm oil, the color brightness level was measured using standard procedures according to BPLG (2009). Before measuring the color brightness of the sample, the initial step is to calibrate the filter photometer instrument (Nanocolor 25) at a wavelength of 405 nm with a blank (distilled water) until the scale needle shows zero. The sample cuvette is rinsed with the oil sample and then filled to the mark. After that, measure the color of the oil sample by pressing the function button and reading the scale indicated by the scale clock hand to obtain the color brightness value. Meanwhile, other quality parameters (acid number, saponification, phosphorus content as a representative of gum, water content, and sediment content) are determined using procedures according to AOAC (1994).

The pumice is prepared by reducing its size to a measurement of 100 mesh. Activation of pumice was carried out by stirring a mixture of pumice and 0.2 N hydrochloric acid solution (ratio 3:5 w/v, the weight to volume ratio) for 3 hours. After filtering and washing with distilled water until neutral, the pumice was heated for 3 hours at a temperature of 600 □C. The activated pumice was then characterized for its surface morphology and oxide composition using SEM-EDX. SEM-EDX spectra were recorded with the Leo 1530 SEM (Georgia Tech., Georgia, USA) scanning electron microscope operating at an accelerating voltage of 20 kV with a magnification of up to 3000x, equipped with an energy-dispersive X-ray spectrometer detector.

The next stage is degumming by adding an 85% phosphoric acid solution for as much as 0.5% to crude palm oil. Degumming was carried out by centrifugation at 4000 rpm for 25 minutes. Crude palm oil from degumming was analyzed for phosphorus content using a UV-Vis spectrophotometer at a wavelength of 650 nm based on the phosphorus content in the oil analysis procedure according to AOCS Ca 12-55. Palm oil, after undergoing degumming, is then bleached with activated pumice. Optimization of bleaching conditions is carried out by varying the pumice content and bleaching temperature. The pumice content was varied at 1, 5, 10, 20, and 30% of palm oil, while the bleaching temperature was carried out at 90, 105, and 120 ^{o}C for 30 minutes (Pahan, 2008). Bleaching is assisted by stirring using a magnetic stirrer at a speed of 250 rpm. The bleached palm oil (RBPO: Refined and Bleached Palm Oil) is then separated from the pumice using a Buchner filter. The quality of RBPO is then analyzed based on color brightness parameters using a Nanocolor Filter photometer, acid number, saponification number, water content, and sediment content. The results of the quality analysis of RBPO are then compared with the SNI (Standar Nasional Indonesia, a standardization of industrial products in Indonesia) for pure palm oil.

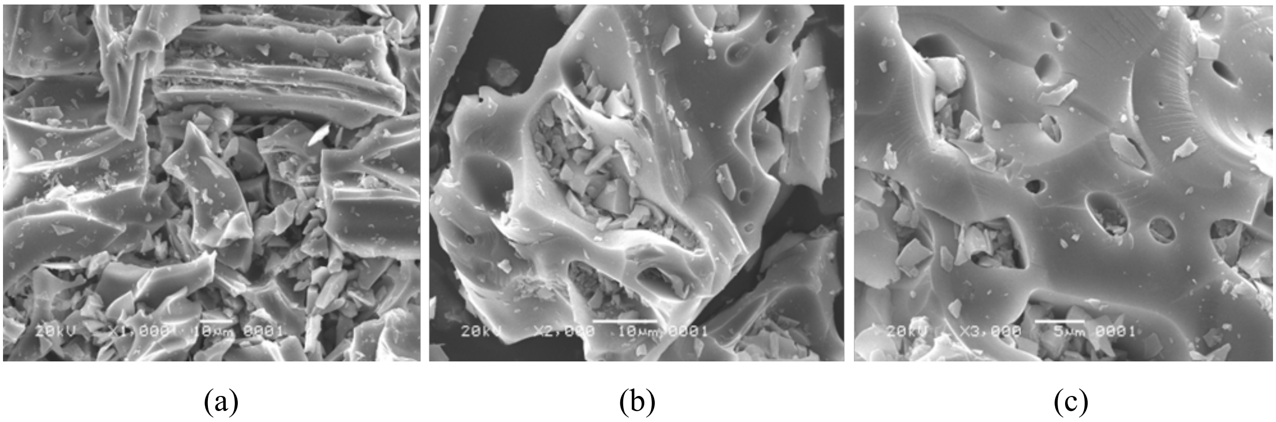
Results & Discussion

Characteristics of Pumice after Activation Stage

The purpose of activating minerals, including pumice, is to add, develop, and enlarge the diameter of the pores that have been formed and to create several new pores (Aleksandrova *et al*., 2023). The characterization of activated pumice was carried out to confirm that pumice, especially after activation, has a porous structure and is composed of various types of oxides, especially alumina and silica. The characterization results are shown in Figure 1, Figure 2, and Table 1. Figure 1 shows the surface structure of activated pumice from SEM results at various magnification scales. The results of characterizing the oxide composition using EDX are shown in Figure 2, while Table 1 shows the type and level of oxide in the pumice.

Figure 1 shows that activated pumice has a porous structure with irregular pore sizes and uneven pore distribution. In this study, the size and pore distribution of activated pumice were determined only visually and qualitatively based on imaging results from SEM analysis. The results of this characterization sufficiently confirm that pumice is a material with many pores, as reported by

Aldakshe *et al*. (2020), where pumice is amorphous and has a porosity of 45–90%. Pumice is reported to have a pore size of <125 μm–8 mm (Ersoy *et al*., 2010). Meanwhile, based on characterization using EDX (Figure 2 and Table 1), activated pumice is composed of various types of oxide compounds with the main composition of silica (62.99%) and alumina (14.79%). The composition of pumice is not much different from the research results of Muralitharan & Ramasamy (2015), where pumice is composed of 68.56% silica, 21.93% aluminum sulfate, and the rest are other metal oxides, especially magnesium oxide, sodium oxide, ferric oxide, and potassium oxide. The presence of dominant levels of silica in pumice makes pumice a potential adsorbent for purifying vegetable oils (Mourhly *et al*., 2015).



(a) (b) (c)

Figure 1. *Surface Morphology of Activated Pumice Using SEM: (a) 1000× magnification, (b) 2000× magnification, (c) 3000× magnification*

Determination of Optimum Conditions for Bleaching of Crude Palm Oil (CPO)

In this research, the optimum conditions at the bleaching stage for CPO were carried out based on operating parameters in the form of bleaching temperature and pumice content as a bleacher. The value of the variation in bleaching temperature for CPO after the degumming stage is based on the general conditions for bleaching palm oil in industry, namely at a temperature of 100–130 ºC for 30 minutes (Pahan, 2008). Since pumice is used as an alternative type of adsorbent, it is necessary to determine the optimum content of adsorbent or bleacher at the bleaching stage of CPO. The product of the degumming and bleaching of CPO is known as RBPO (Refined and Bleached Palm Oil). The term "Refined" refers to the results of refining palm oil from the degumming stage. In this study, initial-grade palm oil had a phosphorus content of 41.1 ppm. The phosphorus level decreased to 32.0 ppm after the crude palm oil underwent a degumming stage with 85% phosphoric acid under the conditions applied. A comparison of the appearance between CPO and palm oil after degumming is shown in Figure 3.

Palm oil, after the degumming stage with a phosphorus content of 32.0 ppm, is then bleached. The performance at the bleaching stage with activated pumice as a bleacher was measured based on the ability of the adsorbent to reduce pigments in palm oil. In this research, the pigment content of palm oil is represented by the color brightness level parameter. The results of measuring the color brightness level (in mg/L Pt) of RBPO (Refined and Bleached Palm Oil) after bleaching with activated pumice as a bleacher are shown in Figure 4. Meanwhile, the percentage of bleaching power of pumice is presented in Figure 5. Bleaching power is the percentage of the ratio between the color brightness levels of the RBPO and the CPO.

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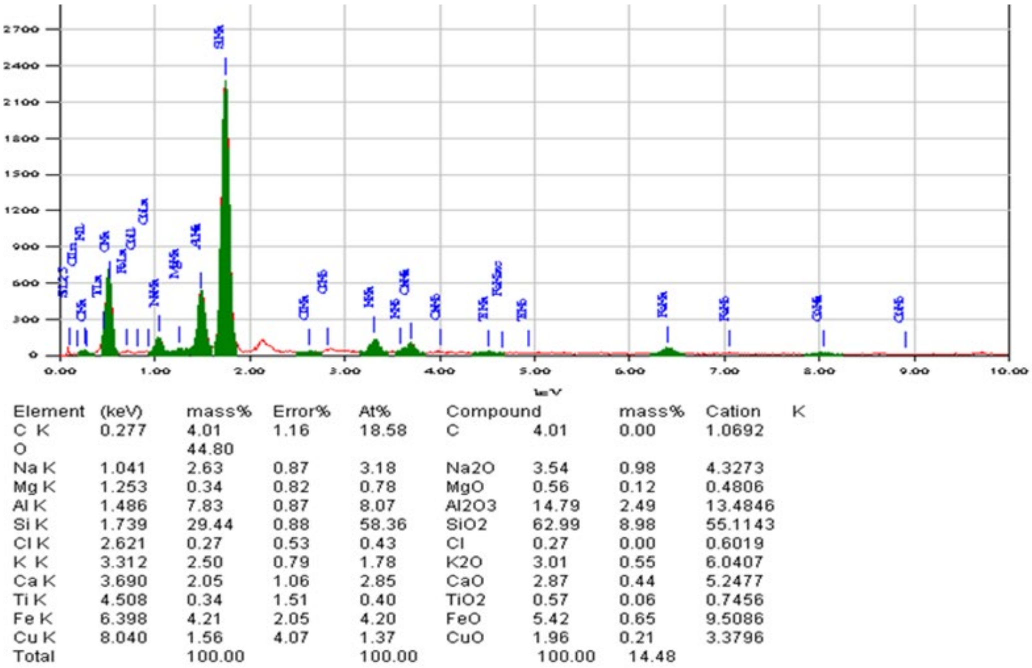

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Element  (keV)   mass%   Error%  At%     Compound        mass%   Cation    K
C  K     0.277   4.01    1.16    18.58   C       4.01    0.00    1.0692
O                44.80
Na K     1.041   2.63    0.87    3.18    Na2O    3.54    0.98    4.3273
Mg K     1.253   0.34    0.82    0.78    MgO     0.56    0.12    0.4806
Al K     1.486   7.83    0.87    8.07    Al2O3   14.79   2.49    13.4846
Si K     1.739   29.44   0.88    58.36   SiO2    62.99   8.98    55.1143
Cl K     2.621   0.27    0.53    0.43    Cl      0.27    0.00    0.6019
K  K     3.312   2.50    0.79    1.78    K2O     3.01    0.55    6.0407
Ca K     3.690   2.05    1.06    2.85    CaO     2.87    0.44    5.2477
Ti K     4.508   0.34    1.51    0.40    TiO2    0.57    0.06    0.7456
Fe K     6.398   4.21    2.05    4.20    FeO     5.42    0.65    9.5086
Cu K     8.040   1.56    4.07    1.37    CuO     1.96    0.21    3.3796
Total            100.00          100.00           100.00  14.48
```

Figure 2. *Composition of Elements and Oxide Compounds of Activated Pumice with EDX Analysis*

Table 1

Composition of Oxide Compounds of Pumice after Activation

Oxide Compound	Content (%)	Oxide Compound	Content (%)
Na_2O	3.54	CaO	2.87
MgO	0.56	TiO_2	0.57
Al_2O_3	**14.79**	FeO	5.42
SiO_2	**62.99**	CuO	1.96
K_2O	3.01		

Figure 3. *Crude Palm Oil: (a) Before Degumming and (b) After Degumming*

The color brightness level was measured with a filter photometer instrument (Nanocolor 25) at a wavelength of 405 nm. The brighter the color of a sample, the instrument will show that the measured value of the color brightness level is getting smaller, and vice versa. The research data in Figure 4 shows a consistent trend that the higher the adsorbent (bleacher) content and bleaching temperature (up to 105 °C), the color brightness level of RBPO decreases or the RBPO color becomes brighter. This has an impact on increasing the bleaching power of pumice in adsorbing pigments and other impurities in CPO, which contributes to the color level of the oil or makes the performance of activated pumice as an adsorbent in bleaching CPO more effective. The greater the adsorbent content, if facilitated by adequate contact methods between materials, the greater the total contact surface area of the adsorbent. Thus, the adsorbent's ability to bind or adsorb impurities from the oil phase will be more effective. Meanwhile, the temperature in the adsorption process plays a more important role in reducing the viscosity of oil as a medium in which impurities are dissolved and/or dispersed. In a liquid-phase medium, increasing temperature has the effect of decreasing the viscosity of the medium so that the viscous resistance or friction between the adsorbate molecules becomes smaller. As a result, the adsorbate can move from the medium phase to the adsorbent surface at an increasingly faster rate. In this study, increasing the CPO temperature from 105 to 120 °C no longer affected the decrease in color brightness and bleaching power of pumice. A bleaching temperature of 105 °C can be estimated as a condition for achieving the adsorption equilibrium of the adsorbate. The use of temperatures higher than 120 °C predicts that the performance of pumice as a bleach will be constant or will even cause damage to the chemical structure of the main oil components (triglycerides) and vitamins due to exposure to heat at high temperatures (thermal decomposition). Therefore, based on the research results on the limit value of the bleaching conditions studied, the optimum conditions for bleaching CPO with activated pumice adsorbent were determined to be the use of pumice with a content of 30% and a bleaching temperature of 105 °C. Under these optimum conditions, activated pumice can to reduce the brightness level of CPO from 600 to 125 mg/L Pt, or pumice has a bleaching power of 79.2%.

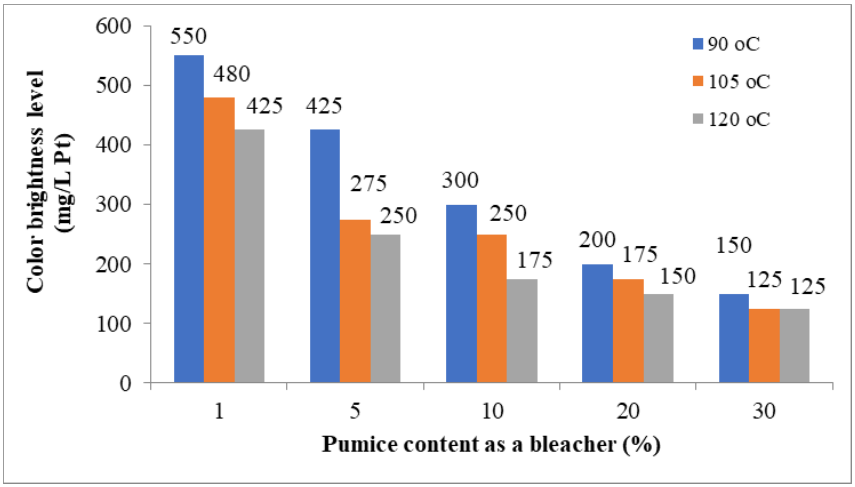

Figure 4. *The Effect of Bleacher (Pumice) Content and Bleaching Temperature on the Level of Color Brightness of RBPO*

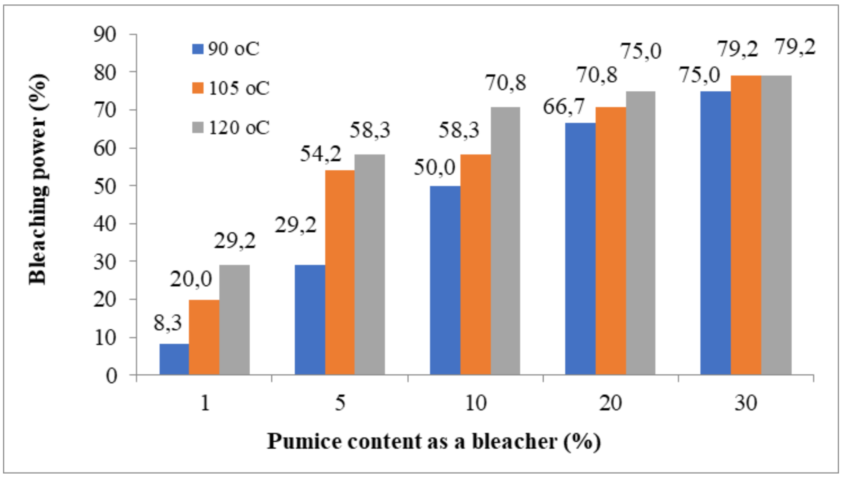

Figure 5. *Bleaching Power of Pumice at Various Bleacher Content and Bleaching Temperatures (Note: the color brightness level value of CPO is 600 mg/L Pt)*

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The ability of activated pumice as an adsorbent (bleacher) to bleach CPO, when compared with other types of adsorbents, is relatively less effective. Haryono *et al*. (2012) reported that commercial activated carbon had higher effectiveness as an adsorbent for bleaching CPO compared to activated pumice. The study reported that the use of activated carbon with much less content (5%), at a slightly higher temperature (120 °C) and the same bleaching time (30 minutes), was able to reduce the color brightness level of CPO from 600 to 40 mg/L Pt. Therefore, commercial activated carbon has a bleaching power of around 93.3%. Lampung natural zeolite as a CPO bleacher shows different performances. The use of Lampung natural zeolite with a content of 15% in bleaching CPO at a temperature of 60 °C for 1 hour showed optimum performance, with a bleaching power of 96.3% (Astuti *et al*., 2006).

Table 2

Comparison of Characteristics of Crude Palm Oil, Optimum RBPO (105°C, 30%), and SNI

Test Parameters	Values		
	CPO	RBPO	SNI*
Phosphor Content (ppm)	41.1	32.0	-
Color Brightness Level (mg/L Pt)	600	125	-
Acid Number (mg KOH/g)	15.49	7.18	Max. 0.6
Saponification Number (mg KOH/g)	162.22	161.08	-
Moisture Content (%)	0.18	0.07	Max. 0.1
Sediment Content (%)	6.08	5.58	0,22

*SNI 7709-2019: Palm Cooking Oil

RBPO from the bleaching stage at optimum conditions (30% pumice content and bleaching temperature of 105 °C) was then characterized more completely to be compared with the characteristics of CPO (before degumming and bleaching) and SNI (Indonesian National Standard) for Palm Cooking Oil (SNI 7709-2019). The characterization results are shown in Table 2, while a comparison of the physical appearance is shown in Figure 6. The comparison of the values of each test parameter in Table 2 shows that refining CPO, especially the bleaching stage, has been able to improve the quality of CPO. Impurities in the form of gum, resin, phosphatides, and phospholipids have been successfully reduced from 41.1 to 32.0 ppm (measured as phosphorus).

Figure 6. *Physical Appearance of Palm Oil: (a) CPO, (b) Resulting from Bleaching with Pumice at Optimum Condition (Temperature of 120℃ and Bleacher Content of 30%), (c) Bulk Cooking Oil, (d) Branded Cooking Oil*

Bleaching with activated pumice, apart from improving the physical appearance (brightness level) of CPO, was also able to improve the quality of CPO based on test parameters for acid number, water content, and sediment content. This shows that during adsorption at the bleaching stage, other impurities in the form of free fatty acids, water, and sediment are also adsorbed on the surface of the pumice stone together with the pigment. However, when compared with the requirements for palm cooking oil quality according to SNI, acid number, and sediment content, RBPO from this research still does not meet the requirements. This can be tolerated because the palm oil quality requirements according to SNI apply to CPOs that have undergone more complete processing stages. In the cooking oil industry, after undergoing the bleaching stage, the oil is further processed to reduce the levels of free fatty acids through a neutralization process and the levels of light organic compounds that cause odor and taste through a deodorization process. Then the oil must be separated between unsaturated oil (olein) and saturated oil (stearin) phases using a fractionation method or membrane process (Adiarso *et al*., 2019). Palm cooking oil products are products from the fractionation stage in the form of the olein phase. Meanwhile, the stearin phase is generally used as a raw material for the margarine industry.

Conclusions

Pumice from Cicurug District, Sukabumi Regency, West Java has a porous structure and is composed of various types of oxides, especially alumina (14.79%) and silica (62.99%). Apart from these two types of oxides, pumice also contains significant levels of other oxides, such as oxide compounds of iron, calcium, sodium, and potassium.

Pumice has the potential to be an adsorbent or bleacher for bleaching crude palm oil. Optimal conditions for bleaching crude palm oil with activated pumice were achieved at an adsorption temperature of 105°C and a bleacher content of 30%. Under optimal adsorption conditions, the color brightness of palm oil decreases from 600 to 125 mg/L Pt, so that pumice has a bleaching power of 79.2%.

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