BLEACHING OF CRUDE PALM OIL (CPO) USING ADSORBENT PREPARED FROM PYROLYZED COFEE RESIDUES

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ABSTRACT

The bleaching process in cooking oil production is very important. It helps cooking oil to have a better quality. During bleaching process, some impurities (such as : gums, dirt, Free Fatty Acid (FFA) and Oxidation products) are adsorbed by adsorbent. In this research, coffee residues were used as an adsorbent for the bleaching process of CPO. The objectives of this research were to study the effects of adsorbent concentration and adsorbent types in the bleaching process. Raw coffee residues were dried in an oven. The dried coffee residue were crushed and sieved to 1.0115 mm particle sizes. The coffee residue was prepared under two different treatments. In the first treatment, the residue were pyrolyzed then used as an adsorbent. In the second treatment, the residue was activated using phosphoric acid then pyrolyzed. In this bleaching process, 70 grams of CPO were agitated with adsorbent of different concentrations and heated for 150 minutes then analyzed. From the research, it can be recognized that the adsorbent made from coffee residues are able to reduce the FFA content, PV and colour of CPO. As the concentration of adsorbent increase, more colour, FFA and peroxides can be adsorbed. The highest percentage for removal was reached at 2,5 % adsorbent concentration. It was found that activated carbon has a better performance for reduction of colour in CPO, rather than char. Inversely, char was better for adsorption of FFA. Both type of adsorbents showed an almost equal performance for adsorption of PV.

Keywords : Adsorption, activated carbon, coffee residues, crude palm oil, bleaching

1. INTRODUCTION

Palm oil are consumed worldwide as cooking oil and as constituents of margarine and shortening The production of palm oil has been steadily increasing, particularly during the last two decades [1]. Indonesia is one of the main palm oil-producing countries.

Palm oil is a fruit flesh fat derived from the species Elaeis guineensis. Its distinctive orange red color is due to its high carotenoids content. Color is one of the important quality parameter of edible oil. Dark color may be an indication of poor quality oil. Dark color oils require bleaching processing for conversion to an acceptable light-colored product [1]. Bleaching edible oils by adsorption involve not only the removal of the color, but also removes the other minor constituents, such as soap, trace metals, phospholipids, oxidation products and polyaromatics. The removal of these impurities will improve the oil quality [2,3]

Different types of adsorbents such as activated clay [1,4,5,6], bentonite [7], activated carbon, activated earth, kiselguhr or diatomaceous earth [8] have been widely used as adsorbent in the bleaching process of edible oil. Due to economic constraints, there is a grown interest in the preparation of low cost adsorbent. In recent years, many of low cost or waste materials have been evaluated to be used as adsorbents for bleaching edible oil, such as rice hull, [5, 7, 9], sawdust [8] and various seed hulls [2].

. Coffee residues are solid wastes discarded from the extraction process of instant coffee manufacturing. These wastes are usually disposed of by burning as fuel or mixed with fertilizer. Since coffee residues hold several functional groups [10], they might be potential for further treated to be an adsorbent in the bleaching process. Hence, the use of coffee residues as adsorbent might be good opportunities for cost saving in the oil processing industry.

Based on the preparation process, there are two types of carbonaceous adsorbent, chars and activated carbon. Chars are the carbonization products from various carbon-containing materials, such as coals, fruit shells, seed hulls, and wood. Activated carbon is obtained through (1) partial gasification of the char with steam or carbon dioxide, or (2) by chemical activation of the precursor with chemical agent like zinc chloride or phosphoric acid [2]. When compared to zinc chloride, phosphoric acid is preferred. Carbons activated using zinc chloride can not be used in food and pharmaceutical industries as it may contaminate the product. Moreover, there is also environmental disadvantage associated with zinc chloride [11].

In this research, coffee residues were used as precursor of adsorbents for the bleaching process of crude palm oil (CPO). The coffee residues were carbonised and acid activated, and their performance in bleaching CPO were evaluated

2. EXPERIMENT

2.1. Materials

The coffee residues were provided by Aneka Coffee Industry, an instant coffee industry in Sidoarjo, Indonesia. The coffee residue dried in an oven at 100^oC, then ground and sieved to 1.0115 mm particle sizes. CPO was provided by PT Mega Surya Mas (Sidoarjo, Indonesia)

2.2. Adsorbents preparation

2.2.1. Carbonization

Dry ground coffee residues were subjected to carbonization by placing it in a tube furnace. The temperature was raised gradually to reach 500^oC and the carbonized coffee residue left for 30 min at this temperature. Nitrogen was flown through the furnace during carbonizing. Then the carbonization product was allowed to cool to room temperature. This treatment gives the product designated as char.

2.2.2. Acid activation

Dry ground coffee residues were impregnated in 50 wt % H_3PO_4 for 24 h, followed by heating up to 550 ^oC and kept for 2 h at this temperature, then cooled to room temperature. To remove the unreacted acid, the product was thoroughly washed with hot water until the washings attained pH>6.5, and then dried in an oven at 110 ^oC. This acid activation process gives activated carbon as the product.

2.2.3. Surface area determination

The surface areas of both adsorbents were determined by I_2 adsorption method and were calculated using an equation [12]:

$$\Sigma = 1{,}09 \times \left(\frac{N \times q_M}{M} \right) \times \left(\frac{M}{N \times \rho_L} \right)^{\frac{2}{3}} \quad \ldots\ldots(1)$$

Σ = surface area of adsorbent, m^2/g
N = Avogadro number (6.02 x 10^{23})
q_M = maximum adsorption capacity, mg/g
M = molecular weight of adsorbate, g/mole
ρ_L = density of solution, g/cm^3

2.3. BLEACHING OF CPO

Seventy grams of CPO and a certain amount of adsorbent were poured into a flask, stirred with a magnetic stirrer bar, and heated at 37 ^oC for 150 min. The contents of the flask were cooled and filtered through a Whatman no. 2 filter paper to remove the adsorbent. Filtered oil was then collected for the determination of free fatty acid content, peroxide value and color. This bleaching process was conducted with char and activated carbon as adsorbent at various adsorbent concentrations.

3. RESULTS AND DISCUSSION

Two series of experiments were performed to evaluate the performance of the adsorbents, char and activated carbon, in bleaching CPO in terms of free fatty acids content (FFA), peroxide value (PV) and color (measured by an UV-visible spectrophotometer as absorbance of the CPO/n-hexane solution). Five different concentrations (from 0.5 to 2.5 wt %) of char and activated carbon were used for bleaching. The FFA, PV and color of CPO before and after bleaching with various adsorbent concentrations are depicted in table 1 and can be seen on fig. 1, 2 and 3. In table 2, it can be seen the decomposition percentage of FFA, PV and color, whereas fig.4, 5 and 6 represents the second table.

It can be noted that char and activated carbon prepared from the coffee residues have the ability to reduce the FFA content, PV and color intensity of CPO during the bleaching process. Increasing the adsorbent concentration between 0,5-2,5% will increase the ability of the adsorbent in reducing the FFA content, PV and color intensity. It can be explained that the increase in the adsorbent ability was due to the increase of active sites for adsorption. Consequently, the FFA, peroxides, and colored pigments adsorbed increased when the adsorbent concentrations increased.

Table 1. FFA, PV and color of CPO before and after bleaching

Bleaching process	Adsorbent	Adsorbent concentration (%)	FFA (%)	PV (mek/100 g)	Color (absorbance)
Before bleaching	-	-	3.55	3.294	0.840
After bleaching	Char	0.5	3,53	3,172	0.792
		1.0	3,46	2,989	0,421
		1.5	1,47	2,135	0,364
		2.0	1,73	2,379	0,205
		2.5	0,56	1,281	0,143
	Activated carbon	0.5	3,44	2,928	0,541
		1.0	3,42	2,745	0,423
		1.5	2,25	2,257	0,286
		2.0	2,16	2,501	0,135
		2.5	0,91	1,525	0,104

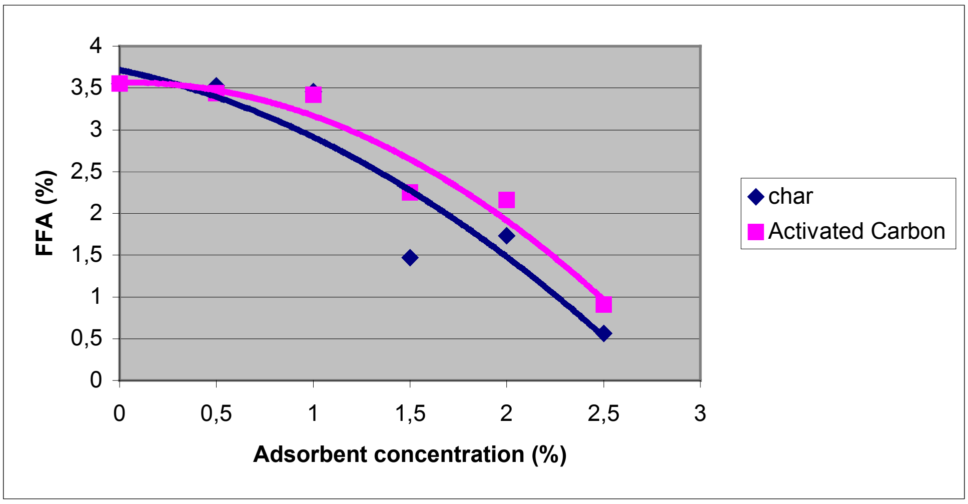

Figure 1. The effect of char and activated carbon concentrations on the FFA content of CPO

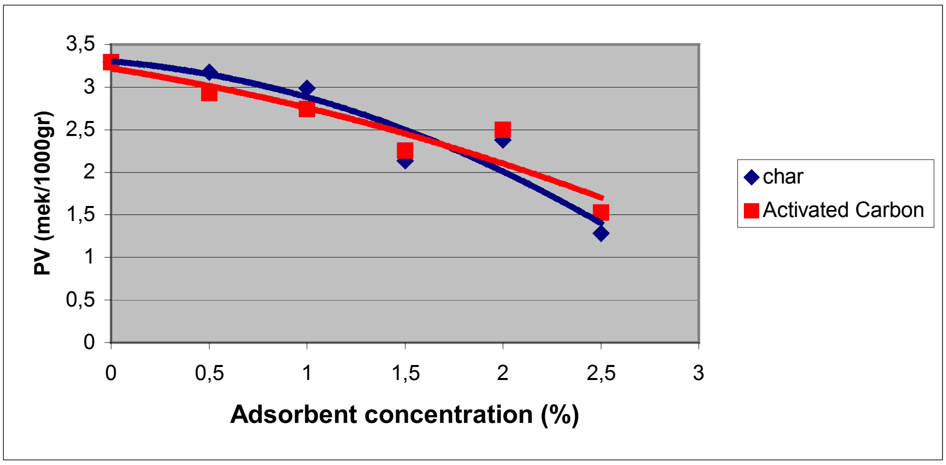

Figure 2. The effect of char and activated carbon concentrations on PV of CPO

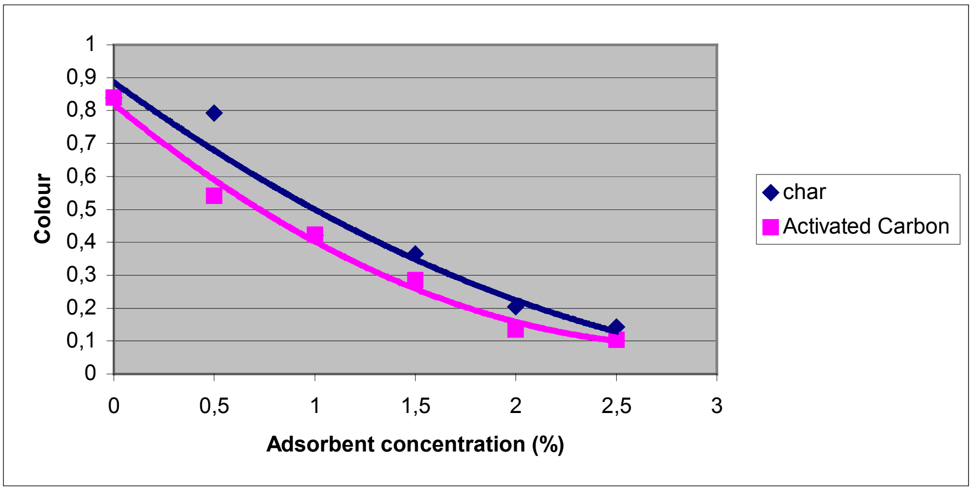

Figure 3. The effect of char and activated carbon concentrations on the color of CPO

Tabel 2. % Reduction of FFA, PV and color in CPO

Adsorbent	Adsorbent Concentration (%)	% Reduction in FFA (%)	% Reduction in PV (%)	% Reduction in Colour (%)
Char	0,5	0,56	3,70	5,71
	1	2,54	9,26	49,88
	1,5	58,59	35,19	56,67
	2	51,27	27,78	75,60
	2,5	84,23	61,11	82,98
Activated Carbon	0,5	3,10	11,11	35,60
	1	3,66	16,67	49,64
	1,5	36,62	31,48	65,95
	2	39,15	24,07	83,93
	2,5	74,37	53,70	87,62

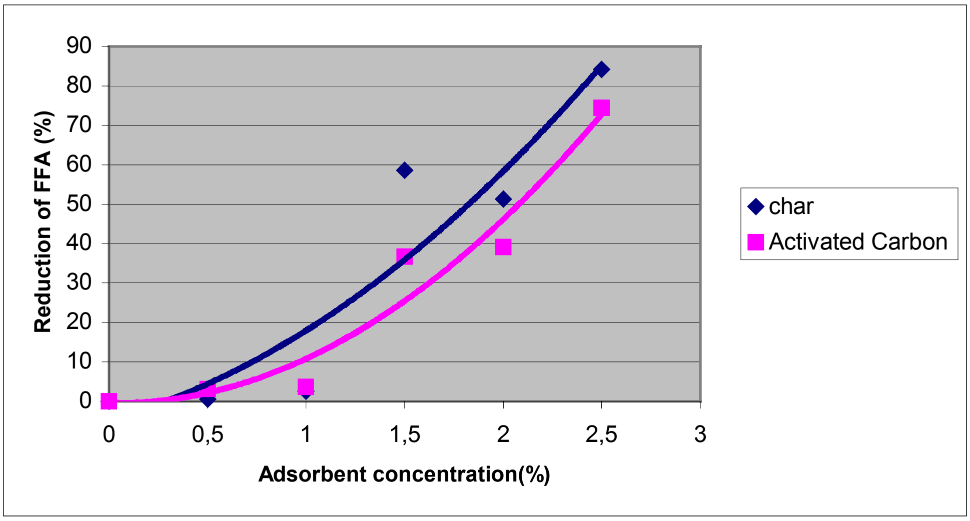

Figure 4. The effect of char and activated carbon concentration on the % reduction of FFA

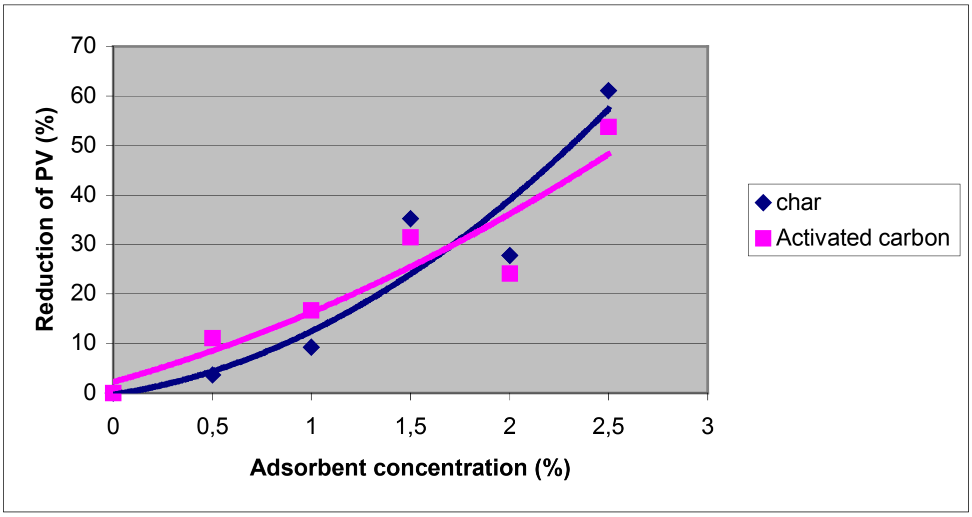

Figure 5. The effect of char and activated carbon concentration on the % reduction of PV

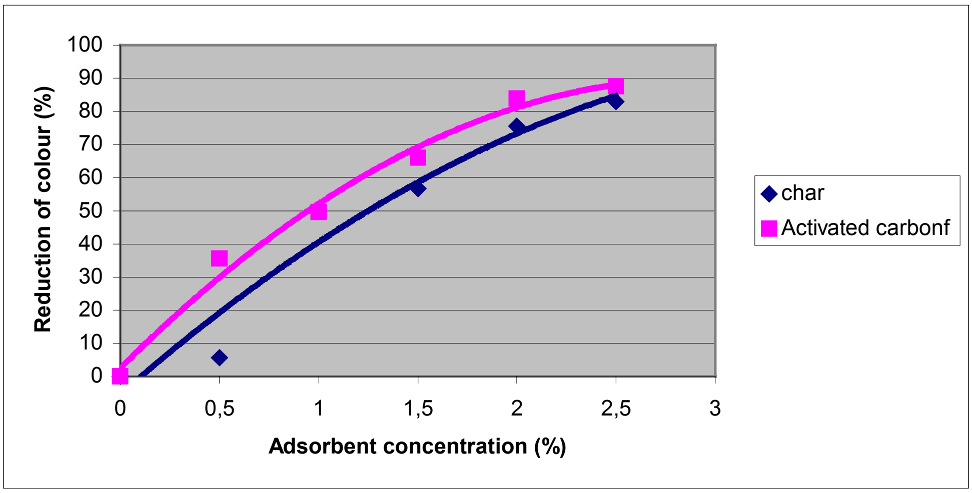

Figure 6. The effect of char and activated carbon concentration on the % reduction of colour

Omar (2003) reported that activation of seed hulls with phosphoric acid leads to produce highly porous activated carbon. During the preparation, activated carbon retains and develops considerable oxygen functional groups that determine their surface chemical properties. Chars as carbonized products develop the least amount such that they are mostly neutral with surface pH around 7 [2].

During bleaching, partial hydrolysis of the oil takes place, thus increasing FFA content. The extent of oil hydrolysis during bleaching depends on the acid properties of the adsorbent. Acid activation results in acidic surfaces that will more readily split the oil into FFA. Char possess neutral surfaces, hence resulted less hydrolysis of the oils during bleaching (Omar 2003). Therefore, the FFA content of the samples bleached with activated carbon are higher than the ones bleached with char. At adsorbent concentrations of 2,5 %, char can remove 84,2% of the FFA content, while activated carbon can remove only 74,4%.

It was also found that the colour removing capacity of activated carbon was better than char. Acid activation promotes pigment adsorption of activated carbon. They readily adsorb carotenoids [2]. Based on equation (1), it has been found that activated carbon has larger surface area than char (table 3).

Tabel 3. Surface area of char and activated carbon

Adsorbent	Surface area (m^2/g)
Char	123,3622
Activated carbon	384,4095

Since activated carbon has a larger surface area compare with char, it can be recognized that activated carbons are able to adsorb more amount of colour pigment compare with char. Rossi (2003) also found similar results from his experiments, i.e. acid activated clays were more efficient than natural clay in removing carotene pigments [3].

Figure 2 and 5 show the PV of the CPO after treatments with char and activated carbon. Char and activated carbon show an almost equal performance for the reduction of PV. During the bleaching process, acid activated adsorbent also oxidized the oil and hence increased the PV value. Adsorbent prepared without acid introduced less oil degradation [6]. At adsorbent concentrations < 1,5%, it seems that the activated carbon surface area has more influence on the adsorption of peroxides, hence samples bleached with activated carbon showed lower peroxide values. At higher adsorbent concentration (1,5-2,5%), the influence of the oxidation process is slightly dominant. Therefore, even the surface area of acid activated carbon is higher than char, they show about the same performance for the reduction of PV.

4. CONCLUSION

From the research, it can be recognized that the adsorbent made from coffee residues are able to reduce the FFA content, PV and colour of CPO. As the concentration of adsorbent increase, more colour, FFA and peroxides can be adsorbed. The highest percentage for removal was reached at 2,5 % adsorbent concentration. It was found that activated carbon has a better performance for reduction of colour in CPO, rather than char. Inversely, char was better for adsorption of FFA. Yet both of adsorbent showed an almost equal performance for adsorption of PV.

5. AKNOWLEDGEMENTS

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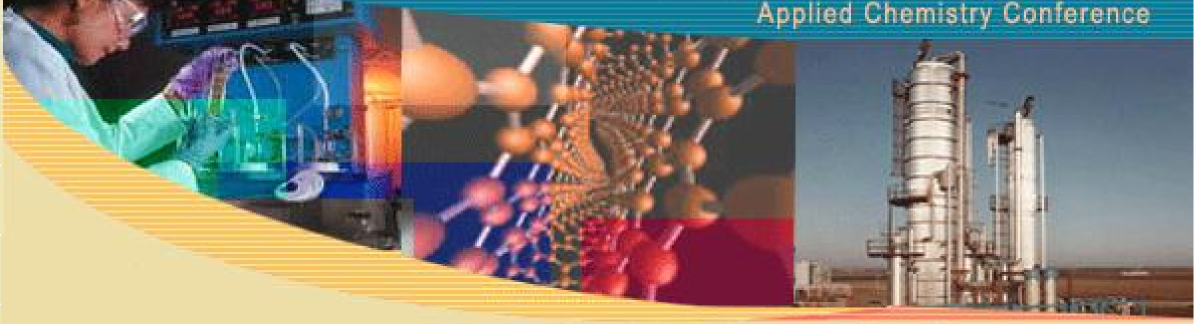

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