The effectiveness of activated carbon as adsorbent in the oil purification process fish by-product of the fish canning industry

A Nadia1,4, S Subekti2, A Manan3 dan P Wahyudin2
1 Aquaculture, Faculty of Fisheries and Marine Airlangga University, Surabaya 60115
2 Department of Aquaculture, Faculty of Fisheries and Marine Airlangga University, Surabaya 60115
3 Departemen Management of Fish and Aquaculture Health Management, Faculty of Fisheries and Marine Airlangga University, Surabaya

4 Corresponding author: aininnadia111@gmail.com

Abstract. Fish oil waste from the canning of low quality but can be recovered through purification processes correctly. Bleaching is a process to improve the color of the oil. The purpose of this study is to determine the effect of the use activated carbon to the effective characteristics and concentration on the fish oil purification byproduct of fish canning industry. This research method used is an experimental method using a completely randomized design (CRD) with five treatments with four replications. The concentrations used in this study is the treatment A (0 %), treatment B (2 %), treatment C (4 %), treatment D (6 %) and treatment E (8 %). The results showed that the addition of activated carbon adsorbent in the process of bleaching fish oil showed a highly significant (p <0.01) on levels of free fatty acids and significantly different (p <0.05) on the peroxide value. The highest level of free fatty acids is the treatment A (5.53 %). The lowest level of free fatty acids is the treatment of B (1.68 %). The highest value is peroxide of treatment E (110.35 meq / kg). The lowest level value is peroxide of treatment A (58.38 meq / kg).

1. Introduction

As the demand for canned fish in Indonesia increased; the amount of canning factory in Indonesia increased by 1.28% in 2006-2010 [1]. With the development of canning industry in Indonesia, the wastes it produced weren’t utilized effectively as it still contains fish oil. Oil acquired from the canning process possesses a low quality because of the peroxide and free fatty acid within it, produced from the pressing process [2], however it could be repurposed through appropriate purification process.

The oil purification process is beneficial for removing impurities, lowering free fatty acid content, and clears the oil color. Bleaching is a process to refine the oil color, because fish oil derived from waste tend to not look appealing, therefore it needs to be refined by bleaching, one of which is by utilizing adsorbent [3]. Active charcoal is one of the examples. The benefit of utilizing active charcoal is that it
doesn’t affect the color of the oil itself, unlike many other adsorbents [3]. Other than adsorbent, active charcoal is being used in food, feed, culture, industry, and many other fields [4].

2. Material and methods
Research was done from August until September 2016 at the Educational Laboratory of Fisheries and Marine Faculty, Airlangga University Surabaya. The pre-treated crude fish oil were obtained from Limited Company X (PT. X) in Bali. Active charcoal was obtained from LC. Brataco Surabaya, East Java. Active charcoal particle size test was carried out using Scanning Electron Microscope (SEM) at the LPPM Energy Laboratory Institut Teknologi Sepuluh November Surabaya.

2.1. Tools and material
Tools used were column, gas canister, heater-stirrer, burette, desiccator, furnace, thermometer, beaker glass, volumetric flask, Erlenmeyer, funnel, volumetric glass, dropper, digital scale, porcelain cup, glass stirrer, oven, spectrophotometer, micropipette, pH meter, Scanning Electron Microscope (SEM).

Testing material utilizes pre-treated fish oil waste from fish canning industry and active charcoal. Chemical used were cotton, distilled water, 95% alcohol, 0.1 N KOH, potassium iodide (KI), chloroform, 0.1 N sodium thiosulfate (Na₂S₂O₃), pp (phenolphthalein) indicator, amilum indicator, acetic acid solution, and NaCl.

2.2. Research procedure
Sample used in this research were fish oil by-product acquired from fish canning industry in Bali from March 2016. Fish oil sample were put into container, covered with aluminum foil, and were kept in freezer. Charcoal were chemically activated by soaking in 30% NaCl solution for 24 hours, then strained and washed with water to be neutralized and then were strained once more. The obtained active charcoals were then dried in a furnace on 110°C for 5-6 hours to evaporate the water within [5].

The purification of fish oil from sardine (Sardinella lemuru) fish canning by-product were based on research by [5] that has been through modification. Next was the purification process: Fish oil sample were measured 100 grams for each treatment. Purification by bleaching were carried out with active charcoal as its adsorbent with concentration variation of 0%, 2%, 4%, 6%, and 8%. Active charcoal was put into the prepared column and the fish oil was added in. Samples were put to rest for a day so that the charcoal and oil become homogenous, after that the tap was opened to let the oil drip out. Samples acquired were then characterized.

2.3. Testing procedure
The purified fish oil were characterized to the following aspects:

a. Free Fatty Acids [6]
Into 2 grams of sample were added 25 ml of 95% alcohol, then the solution was heated in a water bath for 10 minutes, 2 drops of PP indicator was then added after heating. Solution was shaken and titrated with 0.1 N KOH until a pink tint appears and doesn’t dissolve after 10 seconds.

Free Fatty Acid (%) = \( \frac{A \times N \times M}{10G} \)

In which:
A : Titrated KOH amount (mL),
N : KOH Normality,
G : example gram
M : Dominant fatty acid molecular weight (oleic acid 282,5 g/mol)
b. Peroxide number analysis [7]
Two grams of sample were added into 100 ml erlenmeyer and was then added 30 ml of acetic acid and chloroform solution of 3:2 ratio, mixture was then added 0.5 ml of potassium iodide solution, mixture was shaken carefully until homogenous and was then added 30 ml of distilled water. Mixture was then titrated with 0.01 N sodium thiosulfate (Na$_2$S$_2$O$_3$) until it turns yellow, after that 0.5 ml of 1% amilum indicator solution were added, turning the solution blue, titration was continued until solution turns light blue, indicating the release of iodine from chloroform, titration was continued until the light blue tint disappears. Peroxide value was calculated using the following formula:

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\text{Peroxide value (meq/kg)} = \frac{S \times M \times 1000}{\text{Sample mass (g)}}
\]

Keterangan:
S = Sodium thiosulfate amount (ml)
M= Sodium thiosulfate concentration (0,01)

Clarity analysis was carried out using spectrophotometer, wave length was determined beforehand. In this research, wave lengths used were 450, 550, 620, 665, and 700 nm. Cuvette was then cleaned and filled with standard solution. Standard was measured until the scale needle shows 100%. The cuvette filled with standard was then swapped with cuvette filled with sample oil and the clarity was measured in the form of transmission percentage. Measurements were done with 10 fold dilution; dilution was done by mixing 1 part (1 ml) of sample oil with 9 parts (9 ml) solvent. Solvent used was hexane.

2.4 Data analysis
Research was using experimental method of Complete Random Design (RAL). There were 5 treatments of 4 repetitions with active charcoal concentration as the discerning factor. Observed parameters were FFA, peroxide number, and clarity. Research data in the form of integers less than 10 were transformed with $\sqrt{y + 0.5}$ and data in the form of percentage were transformed with Arc Sin $\sqrt{y}$ [12]. Transformed research data were then analysis with Analysis of Variance (ANOVA) and continued with further test utilizing Duncan’s multiple range test to determine the difference between treatments. Statistical calculation was done using SPSS version 22.

3. Result and discussion
3.1. Pre-treatment data
Initial characterization data of fish oil sample showed that the concentration of FFA and the peroxide number were under the safe limits to be consumed, based on commercial fish oil standard by IFOS (Internasional Fish Oil Standards), that means that the cooking process carried out by the company was able to decrease the FFA concentration and the peroxide number, however the color of the oil was still dark brown.

| Table 1. Pretreatment Fish Oil Characterization |
| No | Description | IFOS | Value |
|----|-------------|------|-------|
| 1  | FFA Concentration (%) | < 7  | 6.93 ± 0.16 |
| 2  | Peroxide number (meq/kg) | < 5  | 3.8 ± 0.84 |

Measurement results were shown in graph in figure 1.
3.2. Free fatty acid

ANOVA statistical analysis result of active charcoal adsorbent utilization in bleaching of fish oil shows a significantly different result (p<0.01) towards FFA concentration. According to Duncan’s Multiple Range Test, treatment A was significantly different than treatment B, C, D, and E. Highest FFA concentration was on treatment A (5.53%) Lowest FFA concentration was on treatment B (1.68%). The produced fish oil was lower compared to pretreated fish oil 6.93% and the overall consumption fish oil still suffices the standard determined by IFOS with FFA under 7%.

Table 2. FFA Characterization Results of Post-treatment Fish Oil

| No. | Treatment | FFA ± SD  | $\sqrt{y + 0.5}$ transformation ± SD |
|-----|-----------|-----------|-------------------------------------|
| 1.  | A         | 5.53±0.87 | 2.45 ± 0.18                         |
| 2.  | B         | 1.68±0.86 | 1.45 ± 0.30                         |
| 3.  | C         | 2.08±0.94 | 1.58 ± 0.29                         |
| 4.  | D         | 2.33±0.72 | 1.67 ± 0.21                         |
| 5.  | E         | 1.94±0.75 | 1.54 ± 0.25                         |

Note: treatment A = 0 %, treatment B = 2 %, treatment C = 4 %, treatment D = 6 %, treatment E = 8 %. SD = standard of deviation

The increase of FFA on the oil could increase oxidation and oxidized product could result in rancidity of the aforementioned oil [3]. Concentration closest to the limit determined by IFOS and the initial fish oil from this research was found to be treatment A with concentration of 0%. This phenomenon could be the result of not giving the oil active charcoal adsorbent; therefore there was no reaction with the said adsorbent. [8] stated that adsorbents function as a substance to absorb components of FFA within the oil without hydrolyzing the oil itself. The lowest concentration of FFA was 1.68% from the 2% concentration treatment. This phenomenon went according to a statement by [9]; active charcoal is comprised of covalent-bonded free carbons, by which the greater the amount of active charcoal within, the more it decreases the selectivity of the charcoal itself because the constituent carbon will bind with each other.

3.3. Peroxide number

ANOVA statistical analysis results of active charcoal adsorbent treatment on fish oil bleaching process shows a significantly different result (p<0.05) towards peroxide number. According to Duncan’s Multiple Range Test, treatment A was significantly different than treatment B, C, D, and E. Highest peroxide number was on treatment E with the amount of 110.35 meq/kg. Lowest peroxide number was on treatment A with the amount of 58.38 meq/kg. The procured fish oil were higher compared to pre-
treated fish oil with the amount of 3.8 meq/kg and the overall fish oil quality were higher than the
determined standard with the peroxide number lower than 5 meq/kg.

Table 3. Peroxide Number Characterization Results of Post-treatment Fish Oil.

| No. | Treatment | Peroxide ± SD          |
|-----|-----------|------------------------|
| 1.  | A         | 58.38± 18.85            |
| 2.  | B         | 89.43± 12.54            |
| 3.  | C         | 91.33± 5.68             |
| 4.  | D         | 92.70± 6.90             |
| 5.  | E         | 110.35± 17.81           |

Note: treatment A = 0 %, treatment B = 2 %, treatment C = 4 %, treatment D = 6 %, treatment E = 8 %. SD = standard of deviation

The produced fish oil had higher peroxide number than what was determined by IFOS. Fish oil quality is determined by two main factors: temperature and extraction duration [10]. During the process, bleaching was not carried out with high heat, instead the duration was longer which in turn prolongs contact with oxygen, resulting in higher peroxide number. Fish oil contains unsaturated fatty acid with sufficient amount of double bonds which makes it easily oxidized if exposed to oxygen, creating peroxide. The increase of peroxide number indicates a rise in peroxide which causes damage to the oil and gives off foul odor from the oil [11].

3.4. Clarity
The clarity level of fish oil was presented in the form of light transmission percentage as shown on the spectrophotometer. The testing involves 5 different wave lengths: 450 nm, 550 nm, 620 nm, 665 nm, and 700 nm. The highest percentage got as close to 100% and was close to commercial fish oil transmission percentage, indicating high observed clarity of fish oil, compared to commercial fish oil. The best results were obtained from treatment B and treatment E, both are closest to 100% and both were the closest to commercial fish oil percentage.

Primary and secondary oxidation products tend to affect color and turbidity of fish oil, the higher the amount of primary and secondary oxidation products, the darker the color and in turn decreases the clarity [3]. The presence of impurities such as slime, sap, and gum in fish oil will result in lower transmission percentage.

Table 4. Transmission percentage value of pre-treated fish oil, commercial fish oil, and treatment A, B, C, D, and E utilizing spectrophotometer with wave length of 450 nm, 550 nm, 620 nm, 665 nm, and 700 nm.

|                | Crude Fish Oil | Commercial Oil | Treatment A | Treatment B | Treatment C | Treatment D | Treatment E |
|----------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------|
| Transmission   | 77 98.2        | 90 96.7        | 74.9 92.1   | 93.2 96.9   | 91 90.1     | 92.8 92.4   | 97.1 94.1   |
| percentage     | 98.8           | 97.8           | 93           | 96          | 90.1        | 91.4        | 93.6        |
|                | 98.8           | 98.1           | 92.4         | 96.3        | 92.1        | 91.5        | 93.2        |
|                | 99.4           | 98.9           | 92           | 96.5        | 89.7        | 91.9        | 93.2        |

3.5. Charcoal activation
Results from Scanning Electron Microscope testing of pre and post activated charcoal shows difference of pore size. The activation method used were chemical method by utilizing 30% NaCl solution for 24 hours and were then dried using furnace at 110°C for 2 hours to evaporate all the water within. The surface of active charcoal tends to have been separated from hydrocarbon deposits and it could adsorb because of its wide surface and it’s already opened pores [8].
Soaking using NaCl solution is a form of chemical activation; NaCl is classified as activating agent. According to [5], salt acts as a dehydrating agent, helps replace tar and hydrocarbon impurities sediment produced from carbonization process, and enlarges the cavity structure on the carbon, and so the adsorption area is larger. This large surface affects the results of adsorption.

4. Conclusion
It can be concluded that the utilization of active charcoal as adsorbent could affect the characteristics of fish oil. The effective concentration for bleaching is 2% because the FFA decreased 1.68% and clarity close to 100% transmission, although it was already highly oxidized when it was tested for peroxide. According to the research, it has come to attention that oil needs to be kept in a closed container because exposure towards oxygen increases the peroxide content; the same thing happens when bleaching with column method, high exposure to oxygen causes the adsorption process to be prolonged.

5. References
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